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DICTIONARY OF CHEMISTRY

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INTRODUCTION

TO THE ARTICLES RELATING TO ORGANIC CHEMISTRY.

The names used to denote ring formulæ are given below for convenience of reference.

Since the publication of the last volume I have been assisted in the work of reading and making abstracts of original memoirs by Drs. T. Cooksey, T. A. Lawson, Samuel Rideal, Messrs. J. Wilkie, G. N. Huntly, J. T. Norman, and D. A. Louis. I have also been assisted by Mr. Arthur G. Green and Mr. Cecil W. Cunnington in the work of revising the proof-sheets. I have great pleasure in thanking these gentlemen for the energetic and efficient manner in which they have carried out their share of the work.

H. Forster Morley.

Nomenclature of Ring Formulæ.

Hydrocarbons.

$CH_2<\substack{CH_2\\CH_2}$	*Trimethylene.*	$C_6H_4<\substack{CH_2\\CH}>CH$	*Indonaphthene.*
$CH_2<\substack{CH_2\\CH_2}>CH_2$	*Tetramethylene.*	$CH<\substack{CH\\CH}>CH$	*Tetramethenyl.*
$CH_2<\substack{CH_2.CH_2\\CH_2.CH_2}$	*Pentamethylene.*	$CH_2<\substack{CH:CH\\CH:CH}$	*Pentamethenyl hydride.*

Nitrogen compounds.

$NH<\substack{CH:CH\\CH:CH}$	*Pyrrole.*	$N<\substack{CH:CH\\CH.CH}>CH$	*Pyridine.*
$NH<\substack{N=CH\\CH:CH}$	*Pyrazole.*	$N<\substack{N=CH\\CH.CH}>CH$	*Pyridazine.*
$NH<\substack{CH:N\\CH:CH}$	*Glyoxaline.*	$N<\substack{CH:CH\\CH.CH}>N$	*Pyrazine.*
$N<\substack{CH:N\\CH.CH_2}$	*Metapyrazole.*	$N<\substack{CH:N\\CH.CH}>CH$	*Pyrimidine.*
$NH<\substack{CH:N\\CH:N}$ or $N<\substack{CH.NH\\CH:N}$	*Triazole.*	$N<\substack{CH.\ N\\CH:\ N}>CH$	*Triazoline.*
$NH<\substack{N:CH\\N:CH}$	*Osotriazole.*	$N<\substack{N\ .\ N\\N\ :CH}>CH$	*Osotetrazole.*
$NH<\substack{N=N\\CH:N}$	*Tetrazole.*	$C_6H_4<\substack{CH:CH\\N=CH}$	*Quinoline.*
$C_6H_4<\substack{CH\\NH}>CH$	*Indole.*	$C_6H_4<\substack{CH:CH\\CH:N}$	*Isoquinoline.*
$C_6H_4<\substack{CH\\N}>NH$	*Indazine.*	$C_6H_4<\substack{N\ :CH\\N\ :CH}$	*Quinoxaline.*
$C_6H_4<\substack{CH\\NH}>N$	*Pseudo-indazine.*	$C_6H_4<\substack{CH:N\\N=CH}$	*Quinazoline.*
$C_6H_4<\substack{CH\\N}>C_6H_4$	*Acridine.*	$C_6H_4<\substack{CH:CH\\N=N}$	*Cinnoline.*
$C_6H_4<\substack{N\\N}>C_6H_4$	*Phenazine.*		

Oxygen compounds.

$\mathrm{O}<\begin{matrix}\mathrm{CH:CH}\\ \mathrm{CH:CH}\end{matrix}$ *Furfurane.*

$\mathrm{O}<\begin{matrix}\mathrm{CH:N}\\ \mathrm{CH:CH}\end{matrix}$ *Oxazole.*

$\mathrm{O}<\begin{matrix}\mathrm{N{=}CH}\\ \mathrm{CH:CH}\end{matrix}$ *Iso-oxazole* or *Isoxazole.*

$\mathrm{C_6H_4}<\begin{matrix}\mathrm{CH}\\ \mathrm{O}\end{matrix}>\mathrm{CH}$ *Coumarone.*

$\mathrm{CO}<\begin{matrix}\mathrm{NH}\\ \mathrm{NH}\end{matrix}$ *Carbizine.*

$\mathrm{O}<\begin{matrix}\mathrm{CH:CH}\\ \mathrm{CH:CH}\end{matrix}>\mathrm{CH_2}$ *Furidane.*

$\mathrm{O}<\begin{matrix}\mathrm{CH:CH}\\ \mathrm{CH:CH}\end{matrix}>\mathrm{NH}$ *Pyroxazine.*

$\mathrm{C_6H_4}<\begin{matrix}\mathrm{O{=}CH}\\ \mathrm{NH:CH}\end{matrix}$ *Quinoxazine.*

$\mathrm{C_6H_4}<\begin{matrix}\mathrm{O}\\ \mathrm{NH}\end{matrix}>\mathrm{C_6H_4}$ *Phenoxazine* or *Phenazoxine.*

Sulphur compounds.

$\mathrm{S}<\begin{matrix}\mathrm{CH:CH}\\ \mathrm{CH:CH}\end{matrix}$ *Thiophene.*

$\begin{matrix}\mathrm{S}<\mathrm{CH:CH}\\ \mathrm{S}>\mathrm{C{=}C}\\ \mathrm{S}<\mathrm{CH:CH}\end{matrix}$ *Thiophthene.*

$\mathrm{C_6H_4}<\begin{matrix}\mathrm{N}\\ \mathrm{S}\end{matrix}>\mathrm{CH}$ *Methenyl-amido-phenyl-mercaptan.*

$\mathrm{S}<\begin{matrix}\mathrm{CH:N}\\ \mathrm{CH:CH}\end{matrix}$ *Thiazole.*

$\mathrm{S}<\begin{matrix}\mathrm{CH:N}\\ \mathrm{CH:N}\end{matrix}$ *Oiazthiole.*

$\mathrm{C_6H_4}<\begin{matrix}\mathrm{NH}\\ \mathrm{S}\end{matrix}>\mathrm{C_6H_4}$ *Imido-di-phenyl-sulphide.*

INITIALS OF SPECIAL CONTRIBUTORS.

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Articles by Mr. MUIR are initialed M. M. P. M.

UNSIGNED ARTICLES are by Dr. MORLEY.

ABBREVIATIONS

I. Journals and Books.

When an author has been mentioned in an article, he is usually referred to thereafter in that article by his initial only.

A.	Liebig's Annalen der Chemie.
A. A.	Annales de la Sociedad Cientifica Argentina.
A. Ch.	Annales de Chimie et de Physique.
P. Am. A.	Proceedings of the American Academy of Arts and Sciences.
Am.	American Chemical Journal.
Ann. M.	Annales des Mines.
Am. S.	American Journal of Science.
A. C. J.	Journal of the American Chemical Society.
Am. Ch.	American Chemist.
Am. J. Pharm.	American Journal of Pharmacy.
An.	The Analyst.
A. Ph. S.	Proceedings of the American Philosophical Society.
Ar. N.	Archives néerlandaises—The Hague.
Acad.	Mémoires de l'Académie des Sciences.
Ar. Ph.	Archiv der Pharmacie.
Ar. Sc.	Archives des Sciences phys. et nat.
B.	Berichte der deutschen chemischen Gesellschaft.
B. A.	Reports of the British Association.
Bl.	Bulletin de la Société chimique de Paris.
B. B.	Berliner Akademie-Berichte.
B. C.	Biedermann's Centralblatt für Agricultur-Chemie.
B. J.	Berzelius' Jahresberichte.
B. M.	Berliner Monatsberichte.
C.S. Mem.	Memoirs of the Chemical Society of London.
C. J.	Journal of the Chemical Society of London.
C.J. Proc.	Proceedings of the Chemical Society of London.
C. N.	Chemical News.
C. R.	Comptes-rendus hebdomadaires des Séances de l'Académie des Sciences—Paris.
C. C.	Chemisches Central-Blatt.
D. P. J.	Dingler's polytechnisches Journal.
Fr.	Fresenius' Zeitschrift für analytische Chemie.
G.	Gazzetta chimica italiana.
G. A.	Gilbert's Annalen der Physik und Chemie.
H.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
I.	Proceedings of the Royal Irish Academy.
J.	Jahresbericht über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften.
J. C. T.	Jahresbericht für Chemische Technologie.
J. M.	Jahrbuch für Mineralogie.
J. de Ph.	Journal de Physique et des Sciences accessoires.
J. Ph.	Journal de Pharmacie et de Chimie.
J. pr.	Journal für praktische Chemie.
J. Th.	Jahresbericht über Thierchemie.
J. R.	Journal of the Russian Chemical Society.
J. Z.	Jenaische Zeitschrift für Medicin und Naturwissenschaft.
L. V.	Landwirthschaftliche Versuchs-Stationen.
M.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
M. S.	Le Moniteur Scientifique.
Mém. S. d'A.	Mémoires de la Société d'Arcueil.
Mém. B.	Mémoires couronnés par l'Académie de Bruxelles.

N.	Nature.
N.Ed.P.J.	New Edinburgh Philosophical Journal.
N. J. P.	Neuer Jahresbericht der Pharmacie.
N. R. P.	Neues Repertorium für die Pharmacie.
N. J. T.	Neues Journal von Trommsdorff.
P. M.	Philosophical Magazine.
P.	Poggendorff's Annalen der Physik und Chemie.
P. B.	Beiblätter zu den Annalen der Physik und Chemie.
Pf.	Pflüger's Archiv für Physiologie.
Pr. E.	Proceedings of the Royal Society of Edinburgh.
Ph.	Pharmaceutical Journal and Transactions.
Ph. C.	Pharmaceutisches Central-Blatt.
Pr.	Proceedings of the Royal Society.
P. R. I.	Proceedings of the Royal Institution of Great Britain.
P. Z.	Pharmaceutische Zeitschrift für Russland.
R. T. C.	Recueil des travaux chimiques des Pays-Bas.
R. P.	Repertorium für die Pharmacie.
Q. J. S.	Quarterly Journal of Science.
S.	Schweigger's Journal der Physik.
Scher. J.	Scherer's Journal der Chemie.
S. C. I.	Journal of the Society of Chemical Industry.
Sitz.W.	Sitzungsberichte der K. Akademie zu Wien.
T. or *Tr.*	Transactions of the Royal Society.
T. E.	Transactions of the Royal Society of Edinburgh.
W.	Wiedemann's Annalen der Physik und Chemie.
W. J.	Wagner's Jahresbericht.
Z.	Zeitschrift für Chemie.
Z. B.	Zeitschrift für Biologie.
Z. f. d. g. Naturwiss.	Zeitschrift für die gesammten Naturwissenschaften.
Z. K.	Zeitschrift für Krystallographie und Mineralogie.
Z. P. C.	Zeitschrift für physikalische Chemie.
Bn.	Handbuch der organischen Chemie: von F. Beilstein, 2te Auflage.
E. P.	English Patent.
G. P.	German Patent.
Gm.	Gmelin's Handbook of Chemistry—English Edition.
Gm.-K.	Gmelin-Kraut: Handbuch der anorganischen Chemie.
Gerh.	Traité de Chimie organique: par Charles Gerhardt.
K.	Lehrbuch der organischen Chemie: von Aug. Kekulé.
G. O.	Graham-Otto: Lehrbuch der anorganischen Chemie [5th Ed.]
Stas, Rech.	Stas' Recherches, &c. } Aronstein's German translation is referred to as *Chem. Proport.*
Stas, Nouv. R.	Stas' Nouvelles Recherches, &c. } Aronstein's German translation is referred to as *Chem. Proport.*
Th.	Thomsen's Thermochemische Untersuchungen.

II. Terms and Quantities, &c., frequently used.

Aq	Water; *e.g.* NaOHAq means an aqueous solution of caustic soda.
aq	18 parts by weight of water.
A′, A″, A‴	Residues of mono-, di-, and tri-basic acids. Thus, in describing the salts of a monobasic acid NaA′, CaA'_2, AlA'_3 may be written, HA′ standing for the acid. For a dibasic acid we should write Na_2A'', CaA″, $Al_2A''_3$ &c.
B′ B″ &c.	Stand for bases of the ammonia type, in describing their salts. Thus the hydrochloride would be B′HCl or B″2HCl, according as the base is monacid or diacid, &c.
conc.	Concentrated.
dil.	Dilute.
g.	gram.
mgm.	milligram.
mm.	millimetre.
mol.	molecule.
oil.	liquid, nearly, or quite, insoluble in water.
pp.	precipitate.
to ppt.	to precipitate.
ppg.	precipitating.
ppd.	precipitated.

sol.	soluble in.
insol.	insoluble in.
v. e. sol.	very easily soluble in.
v. sol.	very soluble in.
m. sol.	moderately soluble in.
sl. sol.	slightly soluble in.
v. sl. sol.	very slightly soluble in.
v.	see.
cf.	compare.
c.	about.
[°]	a melting-point.
(°)	a boiling-point.
H.	Hardness (of minerals).
At. w.	Atomic weight.
Mol. w. or M. w.	Molecular weight.
D.	Density.
cor.	corrected.
uncor.	uncorrected.
i.V.	in vapour.
V.D.	vapour-density, *i.e.* density of a gas compared with hydrogen or air.
S.G.	Specific gravity compared with water.
S.G. $\frac{10}{0}$	,, ,, at 10° compared with water at 0°.
S.G. $\frac{15}{4}$	,, ,, ,, 15° ,, ,, ,, ,, 4°.
S.G. $\frac{12}{}$	,, ,, ,, 12°; compared with water of which the temperature is not given.
S.H.	Specific heat.
S.H.v.	,, ,, of a gas at constant volume.
S.H.p.	,, ,, ,, ,, ,, pressure.
H.C.	Quantity of heat, in gram-units, produced during the complete combustion of the mass of a solid or liquid body represented by its formula, taken in grams.
H.C.v.	Heat of combustion in gram-units of a gram-molecule of an element or compound, when gaseous, under constant volume.
H.C.p.	The same, under constant pressure.
H.F.	Quantity of heat, in gram-units, produced during the formation of the mass of a solid or liquid body represented by its formula, taken in grams, from the masses of its constituent elements expressed by their formulæ, taken in grams.
H.F.v.	Heat of formation of a gram-molecule of a gaseous compound from the gram-molecules of its elements under constant volume.
H.F.p.	The same, under constant pressure.
H.V.	Heat of vaporisation of a liquid, *i.e.* gram-units of heat required to change a gram-molecule of the liquid compound at B. P. into gas at same temperature and pressure.
T.C.	Thermal conductivity (unit to be stated).
S.V.	Specific volume; or the molecular weight of a gaseous compound divided by the S.G. of the liquid compound at its boiling-point compared with water at 4°.
S.V.S.	Specific volume of a solid; or the mass of the solid expressed by its formula, taken in grams, divided by its S.G.
E.C.	Electrical conductivity (the unit is stated in each case).
C.E. (10° to 20°)	Coefficient of expansion (between 10° and 20°).
S.	Solubility in water — of a gas = volume dissolved by 1 volume of water; of a liquid or solid = number of grms. dissolved by 100 grms. of water. In both cases the temperature is stated.
S. (alcohol)	,, ,, alcohol — of a gas = volume dissolved by 1 volume of water; of a liquid or solid = number of grms. dissolved by 100 grms. of water. In both cases the temperature is stated.
μ_β	Index of refraction for hydrogen line β.
μ_D, &c.	,, ,, ,, sodium ,, D, &c.
$R_D\ \frac{15}{0}$	Molecular refraction for sodium light, *i.e.* index of refraction for line D minus one, multiplied by molecular weight, and divided by S.G. at 15° compared with water at 0°.
R_D	The same; S.G. being determined at 15°–20° and referred to water at 4°.
R_∞	The same for line of infinite wave-length, index being determined by Cauchy's formula (Brühl's R_A).
$[\alpha]_D$	Specific rotation for sodium light.
$[\alpha]_j$	,, ,, ,, neutral tint. $[\alpha] = \frac{100}{p} \times \frac{a}{d}$. a = observed rotation for 100 mm. of liquid. d = S.G. of liquid. p = no. of grammes of active substance in 100 grammes of liquid.

M. M.	Molecular magnetic rotatory power $= \frac{m \times \alpha}{d \times \alpha' \times m'}$, where m = molecular weight of the body of S.G. $= d$, $\alpha =$ angle of rotation under magnetic influence, $\alpha' =$ angle of rotation of water under same influence, and $m' =$ molecular weight of water (18).
Ac . .	Acetyl C_2H_3O.
Bz . .	Benzoyl C_7H_5O.
Cy . .	Cyanogen CN.
Et . .	Ethyl C_2H_5. (in formulæ)
Me . .	Methyl CH_3. (in formulæ)
Ph . .	Phenyl C_6H_5. (in formulæ)
Pr . .	Normal Propyl $CH_2.CH_2.CH_3$. (in formulæ)
Pr . .	Isopropyl $CH(CH_3)_2$. (in formulæ)
R, R′ &c.	Alcohol radicles or alkyls.
prim . .	primary.
sec . .	secondary.
tert . .	tertiary.
n . . .	normal.
m, *o*, *p* .	meta—ortho—para.
c . . .	consecutive.
i . . .	irregular.
s . . .	symmetrical.
u . . .	unsymmetrical.
ψ . . .	pseudo.
ν . . .	attached to nitrogen.
α . . / β . . / γ . .	Employed to denote that the substituent is attached to a carbon atom which is next, next but one, or next but two, respectively, to the terminal carbon atom. The end to be reckoned from is determined by the nature of the compound. Thus $CH_3.CHBr.CO_2H$ is α-bromo-propionic acid.
ω . . .	denotes that the element or radicle which follows it is attached to a terminal carbon atom.
α, β, γ, &c.	indicate position in an open chain, only.
1,2,3, &c.	indicate position in a ring only.
(α), (β), &c.	Used when α, β, &c. are employed in a sense different from the above, *e.g.* (α)-di-bromo-camphor.
	Baeyer's Nomenclature:
(*B.*) . .	benzene ring.
(*Py.*) . .	pyridine ring. Thus (*B.* 1:3) dichloroquinoline, means a meta-dichloroquinoline in which the chlorine atoms are both in the benzene ring. While (*Py.* 1:3) dichloroquinoline, means a similar body, only the chlorine atoms are in the pyridine ring. The numbers are counted from two carbon atoms which are in different rings, but both united to the same carbon atom.
(*A.*) . .	denotes the central ring in the molecule of anthracene, acridines, and azines.
eso- . .	means that the element or radicle it precedes is in a closed ring.
exo- . .	,, ,, ,, ,, ,, not in a benzene ring.
allo- . .	denotes isomerism that is not indicated by ordinary formulæ; thus maleïc acid may be called *allo*-fumaric acid.
thio- . .	denotes displacement of oxygen by sulphur.
sulpho- .	,, the group SO_3H, except in the word sulphocyanide.
sulphydro-	,, the group SH.
	Tribromonitrobenzene sulphonic acid [1:2:3:4:5] means that the three bromines occupy positions 1, 2, and 3; the nitro- group the position 4, and the sulpho- group the position 5.

$^{\times}$ Denotes that the formula to which it is affixed has not been determined by analysis. But it by no means follows that formulæ without this mark are those of analysed compounds.

All temperatures are given in degrees Centigrade unless when specially stated otherwise.

Wave-lengths are given in 10^{-7} mm.

Formulæ, when used instead of names of substances, have a qualitative meaning only.

Thomsen's notation is used in thermochemical data.

DICTIONARY OF CHEMISTRY.

INDIGO-CARBOXYLIC ACID *v.* INDIGO.
INDIGO-CARMINE *v.* INDIGO.
INDIGO-SULPHONIC ACID *v.* INDIGO.
INDIGOTINE *v.* INDIGO.
INDIGO-WHITE *v.* INDIGO.
INDILEUCINE *v.* INDIGO.

INDIN $C_{16}H_{10}N_2O_2$. Formed by the action of potash upon isatyde, thio-isatyde, or di-thio-isatyde; formed also by heating isatan (Laurent, *A. Ch.* [3] 3, 471). Obtained also by boiling a solution of dioxindole in glycerin for a long time (Knop, *Z.* 1865, 273). Deep rose-coloured powder or minute needles. Insol. water, v. sl. sol. alcohol and ether. Dissolves in H_2SO_4, forming a red solution, whence it is ppd. unchanged by water. A solution in concentrated alcoholic KOH deposits black crystals, apparently either $C_{16}H_9KN_2O_2$ or, more probably, potassium indate $C_{16}H_{10}KN_2O_3$.

Di-bromo-indin $C_{16}H_8Br_2N_2O_2$. Formed by the action of bromine on indin or on di-thio-isatyde (Laurent). Formed also by heating di-bromo-isatyde at 220° (Erdmann, *J. pr.* 22, 265). Violet-black powder, sl. sol. alcohol.

Di-chloro-indin $C_{16}H_8Cl_2N_2O_2$. Obtained by heating di-chloro-isatyde either alone or with alcoholic potash (E.). Dirty-violet powder; insol. water, alcohol, and HClAq. Forms a yellowish solution in KOHAq, from which HCl ppts. yellow flakes.

Tetra-chloro-indin $C_{16}H_6Cl_4N_2O_2$. Formed by heating di-chloro-isatyde either with alcoholic potash or alone below 200° (E.). Dirty-violet powder.

Di-nitro-indin $C_{16}H_8(NO_2)_2N_2O_2$. Formed by boiling indin or hydrindin with HNO_3 (L.). Bright-violet powder, insol. water, v. sl. sol. alcohol and ether. Forms a dark-brown solution in KOHAq.

Indin di-sulphonic acid $C_{16}H_8(SO_3H)_2N_2O_2$? Formed by oxidising hydrindin di-sulphonic acid with HNO_3, with K_3FeCy_6, with NaOCl, or even by exposing it in alkaline solution to the air (G. a. A. Schlieper, *A.* 120, 24). Red deliquescent crystals, v. sol. water, sl. sol. alcohol, insol. ether. Its solution dyes silk and wool scarlet. Ammonium sulphide reduces it to hydrindin di-sulphonic acid. It forms a purple solution in KOHAq, and on warming the solution it becomes pale red, probably through assimilation of water. On adding HCl to the pale-red solution a yellow pp. is formed ($C_{16}H_{10}(SO_3H)_2N_2O_3$?), which, when heated, quickly changes to indin disulphonic acid. Salts.—K_2A'' 5aq: lustrous red needles. —Ag_2A'': bulky brown needles.—BaA'' 2aq: slender dark reddish-brown needles or crimson powder. M. sol. water, insol. $BaCl_2Aq$, alcohol and cold HClAq.

Hydrindin $C_{32}H_{22}N_4O_5$? Formed by the action of alcoholic potash upon indin, isatyde, thio-isatyde, or di-thio-isatyde (Laurent, *A. Ch.* [3] 3, 475). White, or pale-yellow powder or needles (from alcohol), insol. water, sl. sol. boiling alcohol. Boiling HNO_3 converts it into a violet powder. Hydrindin dissolves in warm aqueous KOH, and on cooling there separate pale-yellow needles of a salt $C_{32}H_{21}KN_4O_5$ 3aq, which is decomposed by washing with water, leaving hydrindin.

Hydrindin disulphonic acid, so called, $C_{16}H_{12}(SO_3H)_2N_2O_2$? Formed by the action of ammonium sulphide on indin sulphonic acid or on isatin sulphonic acid (G. a. A. Schlieper, *A.* 120, 20). Colourless radio-crystalline mass, which becomes reddish when exposed to air. V. e. sol. water, m. sol. alcohol, insol. ether. In alkaline solution it is oxidised by air to indin sulphonic acid.—BaA'' 4aq: white scales, v. sol. water, v. sl. sol. $BaCl_2Aq$.

Leucindin disulphonic acid $C_{16}H_{16}(SO_3H)_2N_2O_4$. Formed by boiling the preceding with baryta-water (G. a. A. Schlieper, *A.* 120, 33). White crystalline mass, v. sol. water, sl. sol. alcohol. Not reddened by the action of air on its alkaline solutions. On evaporating with HClAq there is formed indin disulphonic acid.—BaA'' 5aq: colourless crystals. Its solution is not ppd. by $AgNO_3$ till NH_3Aq is added.

INDIPURPURIN is identical with *Indirubin* *v.* INDIGO.

INDIRETIN *v.* INDIGO.

INDIRUBIN *v.* INDIGO.

INDIUM. In. At. w. 113·4. Mol. w. unknown, as V.D. of element has not yet been determined. [176°] (Winkler, *J. pr.* 102, 273). S.G. $^{20·4°}$ 7·11 to 7·147 (Reich a. Richter, *J. pr.* 93, 480); $\frac{15°}{}$ 7·362, $\frac{16·8°}{}$ 7·421 (Winkler, *J. pr.* 95 414; 102, 273). S.H. (0° to 100°) ·05695 (Bunsen, *P.* 141, 1). C.E. (0° to 100°) ·0000459 (Fizeau, *C. R.* 68, 1125). Characteristic lines in emission-spectrum 4510·2, 4101·3, 4071·6, 4032·7, 3852·8, 3834·7, 3257·8, 3255·5, 3038·7, 3008, 2982·3, 2940·8, 2889·8, 2559·5, 2527·1, 2351·3, 2306·9 (Hartley, *T.* 1884. 102).

The observation of two indigo-blue lines in the spark-spectrum of a specimen of the *zinc-blende* of Freiberg in 1863, led Reich a. Richter to the discovery of indium (*J. pr.* 89, 441; 90, 175; 92, 480).

Occurrence.—In some *zinc-blendes* from Freiberg (c. ·1 p.c.), also from Durham (Flight, *B.* 10,

2054), and from Bohemia (Kachler, *J. pr.* 96, 447); in some Italian *galenas* (Denegri, *B.* 11, 1249); in various zinc ores (Tanner, *J.* 1874. 1227); in the fumes from zinc-ovens (Böttger, *J. pr.* 98, 26); in some tungsten ores (Hoppe-Seyler, *A.* 140, 247).

Preparation.—Indium is more readily prepared from zinc which has been made from indium-containing blendes than from zinc-blende itself. The zinc is treated, for some days at the ordinary temperature, or for a shorter time at boiling temperature, with so much dilute H_2SO_4Aq or HClAq that a small quantity remains undissolved; the residue contains In, with some Zn, and Pb, Cu, Cd, As, and Fe. There are many methods for obtaining In from this residue; that of Bayer (*A.* 158, 372) is simple, and yields very pure In. The residue is washed, treated with a few drops of dilute H_2SO_4Aq (to remove any basic Zn salts), again washed thoroughly with hot water, dissolved in HNO_3Aq (any SnO_2 which may be present is allowed to remain), evaporated with excess of H_2SO_4 until all HNO_3 is removed, and treated with water; the solution now contains sulphates of In and the other metals which may be present, but the greater part of the $PbSO_4$ remains insoluble. Large excess of NH_3Aq is added, whereby hydroxides of In and Fe are ppd. with small quantities of hydroxides of Zn, Cd, Pb, and Cu; the pp. is well washed and dissolved in the smallest possible quantity of HClAq; the solution is boiled after addition of $NaHSO_3$ until the smell of SO_2 is almost gone; a basic sulphite of In, $2In_2O_3.3SO_2$, is thus ppd. as a fine crystalline powder. The pp. is free from salts of Cu, Zn, and Cd. If much Fe should have been present in the original Zn, small quantities of Fe salts may be ppd. by the action of the air during filtration; in this case ppn. should be conducted in CO_2, or the pp. should be dissolved in $NaHSO_3Aq$, and re-ppd. by boiling. The pp. may contain Pb salts and traces of alkali; it is dissolved in SO_2Aq, in which Pb sulphite is insoluble, after filtration In sulphite is ppd., free from Na salts, by boiling (*cf.* Winkler, *J. pr.* 102, 273; Böttger, *J. pr.* 98, 26; R. E. Meyer, *A.* 150, 137. For methods of preparing In from zinc-blendes *v.* Reich a. Richter, *J. pr.* 89, 441; 90, 175; 93, 480; Weselsky, *J. pr.* 94, 443; Richter, *J. pr.* 94, 414; Stolba, *D. P. J.* 198, 223). The ppd. basic In sulphite may be dissolved in H_2SO_4Aq; after boiling off SO_2, addition of NH_3Aq ppts. InO_3H_3, which when strongly heated yields In_2O_3. In is obtained from the oxide (1) by heating in a stream of pure H, (2) by mixing with pure C, and heating to a very high temperature, (3) by heating with an equal weight of Na cut in small slices, under a layer of fused NaCl in a porcelain crucible placed in a larger Hessian crucible, decomposing the alloy of Na and In so formed by water, and melting with Na_2CO_3 (Winkler, *J. pr.* 102, 275). Böttger (*J. pr.* 107, 39) recommends to ppt. In from solutions in H_2SO_4 by placing a stick of pure Zn in the liquid; he washes the ppd. metal with water, presses it with the finger, then between paper, and when quite dry fuses it under dry KCN.

Properties.—A silver-white, lustrous, ductile metal; softer than lead; leaves a mark when rubbed on paper. Non-crystalline. Electro-negative to Zn and Cd; much less volatile than these metals. Unchanged in air at ordinary temperatures; but burns to In_2O_3, with blue-violet flame and brownish fumes, when strongly heated in air. Combines directly with Cl, Br, I, and S when heated. Boiling water is not decomposed by In. Soluble in dilute acids with evolution of H and formation of salts In_2X_3 where X = SO_4, $2NO_3$, &c.

The at. w. of In has been determined (1) by synthesis of In_2O_3 from In (Reich a. Richter, *J. pr.* 92, 484; Winkler, *J. pr.* 94, 8; 102, 282; Bunsen, *P.* 141, 28); (2) by analyses of In_2S_3 (R. a. R., *l.c.*); (3) by decomposing $NaAuCl_4$ by In, and determining the Au (Winkler, *J. pr.* 102, 212); (4) by determining the V.D. of $InCl_3$, $InCl_2$, and InCl (Nilson a. Pettersson, *C. J.* 53, 814); (5) by determining the S.H. of In (Bunsen, *P.* 141, 1).

The atom of In appears to be monovalent (in InCl), divalent (in $InCl_2$), and trivalent (in $InCl_3$), in gaseous molecules; as the lower chlorides are decomposed by water with formation of In and $InCl_3$ it is probable that in solutions of its haloid compounds the atom of In is directly combined with at least three monovalent atoms.

In is distinctly metallic; with acids it evolves H and forms salts. A few basic, and some double, salts are known. In forms an ammonia alum. InO_3H_3 reacts towards acids as a salt-forming hydroxide. In is closely related to Al and Ga, less closely to Tl; it is also related to the other earth-metals Sc, Yt, La, and Yb (*v.* EARTHS, METALS OF THE, vol. ii. p. 424). The investigation of In compounds is as yet far from complete.

Detection and Estimation.—In salts colour the flame blue-violet. Hoppe-Seyler (*A.* 140, 247) boils c. 1 gram of an In ore with *aqua regia*, neutralises by soda, filters, adds Na acetate, and ppts. by H_2S; he dissolves the pp. in acid, and reppts.; the In_2S_3 is then tested in the flame after moistening with HClAq. The spectral-lines 4510·2 and 4101·3 are very characteristic. Boiling with $NaHSO_3$ causes ppn. of a fine crystalline pp. $2In_2O_3.3SO_2.8H_2O$; this salt is used for the estimation of In.

Indium bromide. $InBr_3$. White crystalline tablets, v. sol. water; formed by heating In in a stream of CO_2 charged with Br, and subliming (R. Meyer, *A.* 150, 429). V.D. not determined.

Indium chlorides. In combines with Cl in three proportions, forming InCl, $InCl_2$, and $InCl_3$.

INDIUM MONOCHLORIDE. InCl. Mol. w. 148·77. V.D. at c. 1100°–1400° = 78·16 (Nilson a. Pettersson, *C. J.* 53, 821). Obtained as a reddish black, vitreous, radiated, crystalline mass, by distilling $InCl_2$ (*q.v.*) on to In (rather more than the calculated quantity), heating for a little in a sealed tube, and distilling in a stream of CO_2 (N. a. P., *l.c.*). When melted InCl forms a dark-red liquid, in thick layers appearing almost black. Deliquescent; gradually decomposes in moist air, and quickly in water, to In and $InCl_3$.

INDIUM DICHLORIDE. $InCl_2$. Mol. w. 184·14. V.D. at 1000°–1400° = 99·62 (Nilson a. Pettersson, *C. J.* 53, 820). White radiated crystals, obtained by heating In to its melting-point in a current of dry HCl free from air until an amber-

coloured liquid is obtained, and removing any adhering HCl by heating in dry air-free CO_2. Unchanged in dry air, but deliquesces in ordinary air. Decomposed by water to In and $InCl_3Aq$ (N. a. P., *l.c.*).

INDIUM TRICHLORIDE. $InCl_3$. Mol. w. 219·51. V.D. at c. 850° = 106·9 (Nilson a. Pettersson, *C. J.* 53, 818); at bright-red heat V.D. = 113·88 (V. a. C. Meyer, *B.* 12, 611). $InCl_3$ does not appreciably volatilise at 440°; at c. 600° volatilisation is slow and V.D. is rather higher than that calculated for $InCl_3$; the normal V.D. is attained between 600° and 850°; at temperatures towards 1000° dissociation begins, probably into Cl and $InCl_2$ or InCl (N. a. P., *l.c.*). $InCl_3$ is prepared by heating In or a mixture of In_2O_3 with C, in a stream of dry Cl. Nilson a. Pettersson heated molten In in dry air-free HCl, and then gently heated the $InCl_2$ thus formed in air-free, dry, Cl, and finally distilled in a current of dry, air-free, CO_2. White, lustrous tablets, deliquescent; sol. in water with production of heat; the solution may be evaporated on a steam-bath almost unchanged, but at higher temperatures decomposition occurs, probably with production of oxychlorides.

$InCl_3$ combines with KCl, NaCl, LiCl, and $PtCl_4$ to form crystalline *double salts* (R. Meyer, *A.* 150, 144; Nilson, *B.* 9, 1059). The compound $2InCl_3.6KCl.3H_2O$ separates in quadratic crystals from a solution of the mixed salts in proper proportions on evaporation.

Indium cyanide *v.* vol. ii. p. 332.

Indium hydrosulphide. The white pp. produced by adding NH_4 sulphide, or KHS, to solution of an In salt, after addition of tartaric acid and NH_3Aq, is probably a hydrosulphide; when dried, H_2S is evolved and In_2S_3 remains (R. Meyer, *A.* 150, 429).

Indium hydroxide *v. Indium oxides and hydroxide.*

Indium iodide. InI_3. V.D. not determined. Yellow, crystalline; very hygroscopic; may be distilled in dry CO_2; easily melted to a dark-reddish-brown liquid. Prepared by heating In in I vapour (R. Meyer, *A.* 150, 144, 429).

Indium oxides and hydroxide. In forms two oxides, InO and In_2O_3; the V.D. of neither has been determined; the existence of intermediate oxides is probable. In_2O_3 forms at least one hydrate $In_2O_3.3H_2O$. The oxides are basic; only salts corresponding to In_2O_3 have been isolated, although the lower oxide is said to dissolve in dilute acids without decomposition into In and In_2O_3.

INDIUM MONOXIDE. InO. Mol. w. unknown, as the oxide has not been volatilised. Obtained by heating In_2O_3 in H at c. 300° until the oxide becomes almost black and water is no longer evolved. Forms a light, loose, powder, which quickly oxidises to yellow In_2O_3, if brought into air before it is quite cold. Very pyrophoric. InO is changed by conc. HNO_3Aq to $In3NO_3$ with evolution of NO; dilute acids dissolve it slowly without apparent formation of In_2O_3 or In (Winkler, *J. pr.* 94, 1; 95, 414; 98, 344; 102, 273).

INDIUM SESQUIOXIDE. In_2O_3. Mol. w. unknown as the oxide has not been volatilised. S.G. 7·179; S.H. (0°–100°) ·0807 (Nilson a. Pettersson, *B.* 13, 1459). Obtained by ppg. solution of an In salt by NH_3Aq, washing and heating the pp.; or by heating In to full redness in air; also by strongly heating In carbonate or nitrate. A yellow powder; becomes brown on heating but yellow again when cold. (It is doubtful whether pure In_2O_3 is yellowish or white.) Very infusible; reduced to metal by heating with C, or in H, or with Na; reduction in H begins at c. 190°–200°, and at c. 300° InO is formed (*v. supra*). Soluble in acids, quickly on heating, forming salts In_23X ($X = SO_4$, $2NO_3$, &c.).

Oxides intermediate between InO and In_2O_3 possibly exist. By heating In_2O_3 in H to c. 200°, a greyish-blue body is obtained probably In_7O_9; at c. 230° a green substance, probably In_4O_5 remains (Winkler, *l.c.*).

INDIUM HYDROXIDE. InO_3H_3 or $In_2O_3.3H_2O$. Formed by ppg. a solution of an In salt by NH_3Aq, washing the pp. and drying at 100°. The pp. by NH_3Aq is gelatinous and resembles AlO_3H_3; in air it dries to horny semitransparent lumps. Insol. in NH_3Aq, easily sol. in KOHAq or NaOHAq; dissolves in acids to form salts In_23X ($X = SO_4$, $2NO_3$, &c.). A series of very unstable hydrates of In_2O_3 probably exists (*cf.* Carnelley a. Walker, *C. J.* 53, 88).

Indium oxybromide. The white amorphous solid formed by heating In_2O_3 in Br vapour is probably an oxybromide; this substance is said not to be decomposed by heating with acids or alkalis (R. Meyer, *A.* 150, 137).

Indium oxychloride. When $InCl_3Aq$ is boiled down to dryness, the white residue is probably an oxychloride.

Indium salts. Not many salts of In have been isolated and examined. They are obtained by dissolving In or InO_3H_3 in acids, and evaporating; and in some cases by ppn. from other In salts in solution. The chief salts are the *carbonate*, *nitrate*, *sulphate*, and a *basic sulphite* (*v.* CARBONATES, NITRATES, &c.). The sulphate forms an ammonia alum, $In_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$; but with K_2SO_4 and Na_2SO_4 it forms double sulphates $In_2(SO_4)_3.K_2(Na_2)SO_4.8H_2O$.

Indium sulphide. In_2S_3. Mol. w. unknown as compound has not been gasified. Obtained by ppg. a neutral or feebly acid solution of an In salt by H_2S, and drying the pp.; also by heating together In and S, or In_2O_3 and S. A yellowish-grey solid. If In_2O_3 is heated with S and Na_2CO_3 and the fused mass is treated with water, In_2S_3 remains as lustrous tablets resembling mosaic gold (Winkler, *l.c.*). In_2S_3 is infusible; with acids it gives In salts and H_2S (Reich a. Richter, *l.c.*). Heated in air it is burnt to In_2O_3. According to Winssinger (*Bl.* (2) 49, 452) In_2S_3 is obtained in aqueous solution in a colloidal form, by passing H_2S into InO_3H_3 suspended in water; the dark-yellow liquid thus obtained can be freed from H_2S by boiling; it is coagulated by acetic acid and also by salts. For reactions of alkali sulphides with In salts *v.* R. Meyer, *l.c.*

Potassium, and *sodium*, *indium sulphides*. $K_2S.In_2S_3$; $Na_2S.In_2S_3$. Formed by fusing together 1 pt. In_2O_3, 6 pts. S, and 6 pts. K_2CO_3 or Na_2CO_3. The K salt remains as hyacinth-red quadratic tablets on lixiviating the fused mass with water; the Na salt goes into solution and separates on standing as $Na_2In_2S_4.H_2O$ which on drying gives $Na_2In_2S_4$ (R. Schneider, *J. pr.* [2] 9, 209).

M. M. P. M.

INDOGEN *v.* INDOXYL.

INDOGENIC ACID *v.* INDOXYLIC ACID.

INDOGENIDE OF BENZOIC ALDEHYDE $C_{15}H_{11}NO$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{CO}{NH}>C:CH.C_6H_5$. *Benzylidene ψ-indoxyl.* [176°]. Obtained by heating indoxylic acid with benzaldehyde (Baeyer, *B.* 16, 2197). Long flat orange needles. Sol. alcohol and chloroform to yellowish-red solutions, which have a yellowish-green fluorescence. In H_2SO_4 and strong HCl it dissolves with a deep-red colour; in alcoholic KOH with a greenish-blue, which gives the indigo spectrum.

(*α*)-**INDOGENIDE OF ψ-ISATIN** is INDIRUBIN.

(*β*)-Indogenide of ψ-isatin is INDIGO.

Indogenide of ethyl-ψ-isatin is *Ethyl-indirubin v.* INDIGO.

INDOGENIDE OF *p*-NITRO-BENZALDEHYDE $C_{15}H_{10}N_2O_3$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{CO}{NH}>C:CH.C_6H_4(NO_2)$. *p-Nitro-benzylidene-ψ-indoxyl.* [273°]. Formed by adding an acetic acid solution of *p*-nitro-benzaldehyde to an aqueous solution of indoxyl acidified with HCl. Red needles (Baeyer, *B.* 16, 2199).

INDOGENIDE OF PYRUVIC ACID $C_{11}H_9NO_3$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{CO}{NH}>C:CMe.CO_2H$. [197°]. Prepared by adding HCl to an aqueous solution of indoxyl and pyruvic acid (Baeyer, *B.* 16, 2199). Red needles. Easily soluble in alcohol and acetone. Dissolves with a red colour in alkalis, with a blue colour in conc. H_2SO_4.

INDOINE *v.* INDIGO.

INDOLE C_8H_7N *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{CH}{NH}>CH$. *Ketole.* Mol. w. 117. [52°]. (254°) (Ciamician a. Zatti, *B.* 22, 1980). V.D. 4·45 (calc. 4·05). Occurs in small quantity in human excrement (Brieger, *J. pr.* [2] 17, 133).

Formation.—1. By passing the vapour of oxindole over heated zinc-dust (Baeyer, *A.* 140, 295; *Suppl.* 7, 56; Engler a. Janecke, *B.* 9, 1411).—2. By distilling with zinc-dust the yellow product of the action of tin and HCl on indigo (B.).—3. By fusing o-nitro-cinnamic acid with KOH and iron filings (Baeyer a. Emmerling, *B.* 2, 679; *Z.* [2] 6, 213; Beilstein a. Kuhlberg, *A.* 163, 141).—4. Formed to the extent of 5 p.c. in the passage through a red-hot tube of di-ethyl-*o*-toluidine, in less quantity from di-methyl-*o*-toluidine, in small quantity from methyl-ethyl-aniline, ethyl-acetanilide, and di-ethyl-aniline, and in trace only from ethyl-aniline when subjected to like treatment (Baeyer a. Caro, *B.* 10, 692, 1262).—5. By digesting albumen with pancreas and water at 40° to 45° for several days (Nencki, *B.* 8, 336; Kühne, *B.* 8, 206). According to Harris and Tooth (*J. Physiol.* 9, 220) its formation is due to a special micro-organism.—6. By distilling albumen (1 pt.) with KOH (8 pts.), the yield being about ·25 p.c. (Engler a. Janecke, *B.* 9, 1411; Nencki, *J. pr.* [2] 17, 98).—7. By distilling (3,4,1)-nitro-propenyl-benzoic acid with lime (Widmann, *B.* 15, 2552). 8. By boiling aniline with di-chloro-acetic aldehyde or with di-chloro-di-ethyl oxide (Berlinerblau, *M.* 8, 180).—9. By heating *ω*-chloro-o-amido-styrene with NaOEt at 165° (Lipp, *B.* 17, 8067).—10. Together with ethane, ethylene, and propylene, by the distillation of *o*-cumidine $C_6H_4(NH_2)(C_3H_7)$ over red-hot PbO (Fileti, *G.* 13, 381).—11. By the dry distillation of *o*-tolyl-oxamic acid (Mauthner a. Suida, *M.* 7, 238).—12. From phenyl-ethylene diamines by successive oxidation with CrO_3 and distillation over zinc-dust (Prudhomme, *Bl.* [2] 28, 558).—13. By fusing carbostyril with potash (Morgan, *C. N.* 36, 239).—14. In small quantity, by heating the phenyl-hydrazide of pyruvic acid with $ZnCl_2$ at 200° (E. Fischer, *B.* 19, 1567).—15. By distilling calcium phenyl-amido-acetate with calcium formate (Mauthner a. Suida, *M.* 10, 253).

Preparation.—1. By heating aniline (50 g.) with an equal volume of water with inverted condenser and gradually adding di-chloro-ether (25 g.). After boiling for an hour the excess of aniline is distilled off, and the residue heated for 5 hours at 220° (Berlinerblau, *M.* 8, 180).—2. By distilling a mixture of calcium phenyl-amido-acetate with calcium formate, extracting the distillate with ether, shaking the ether with dilute acid to remove aniline, evaporating, and distilling with steam. The indole is purified by conversion into the picrate. The yield is 5 p. c. of the theoretical quantity (M. a. S.).

Properties.—Colourless laminæ; m. sol. hot water, v. sol. alcohol, ether, and ligroïn. Readily volatile with steam. An alcoholic solution, acidified by HCl, dyes pine-wood yellow. Has a peculiar, but not very powerful, odour. It is a very weak base; with conc. HClAq it forms a sparingly soluble salt, decomposed by boiling water.

Reactions.—1. Suspended in water and subjected to the action of ozonised oxygen indole is converted into indigo and resinous products (Nencki, *B.* 8, 727, 1517). Indigo appears in the urine after subcutaneous injection of indole. 2. Aqueous CrO_3 yields a bulky violet-brown pp., insol. ether, chloroform, and benzene, sl. sol. alcohol, forming a red solution, sol. conc. HClAq (E. a. J.).—3. Heated with MeI it gives di-methyl-quinoline dihydride (Ciamician a. Zatti, *B.* 22, 1980).—4. When to an aqueous solution of indole there is added a few c.c. of HClAq, and then a large quantity of fuming HNO_3 (previously partially freed from nitrous fumes by evaporation), a red pp. is formed which may be purified by solution in alcohol and precipitation by adding ether. This substance, so-called nitroso-indole nitrate $C_{16}H_{13}(NO)N_2HNO_3$, forms minute red needles, v. sl. sol. water and ether, v. sol. alcohol, nearly insol. dilute nitric acid. It detonates sharply when heated. Alcoholic ammonium sulphide reduces nitroso-indole nitrate to so-called hydrazo-indole $C_{16}H_{13}N_3$ (?), which forms yellow needles, sol. alcohol and ether, melting at 140° to a deep-blue mass. Acids and alkalis convert it into a dark-brown colouring-matter termed azo-indole by Nencki.

Picrate $C_8H_7NC_6H_2(NO_2)_3OH$. Long red glittering needles.

Acetyl derivative C_8H_6NAc. [183°]. From indole and Ac_2O at 190° (Baeyer, *B.* 12, 1314). Long needles (from water) or four-sided pyramids (by sublimation).

(*β*)-**Acetyl-indole** $C_6H_4<\genfrac{}{}{0pt}{}{C.CO.CH_3}{NH}>CH$. *Methyl indyl ketone.* [190° cor.]. Obtained by heating

indole (α)-carboxylic acid, prepared from methyl-ketole, with ten times its bulk of Ac_2O for 7 hours at 220° (Carlo Zatti, *Rend. Accad. Linc.* [4] 4, 184; *B.* 22, 662). White needles. Sublimes in colourless plates; sl. sol. cold, v. sol. warm water and benzene; may be extracted from its aqueous solution by ether. Gives indole when heated with conc. HClAq. It readily yields an oxim and an oily phenyl-hydrazide. Potash fusion converts it into indole (β)-carboxylic acid [214°] identical with that obtained by oxidising skatole.

Picrate. [183°]. Needles; sl. sol. cold benzene.

Oxim $C_8H_6C(NOH)Me$. [144°–147°]. White needles.

Di-acetyl-indole $C_6H_4\genfrac{}{}{0pt}{}{\diagup C.CO.CH_3}{\diagdown N.CO.CH_3}\!\!>\!CH$. [147°–150°]. Prepared by heating indole (α)-carboxylic acid with Ac_2O and separated from the preceding by its greater solubility in water containing Na_2CO_3 and in boiling benzene (Zatti). Needles (by sublimation); sl. sol. boiling water. When boiled with aqueous KOH or K_2CO_3 it yields (β)-acetyl-indole.

References. — Di-chloro-indole, Benzyl-indole, Methyl-indole, Methyl-ethyl-indole, Ethyl-indole.

Isoindole is Di-phenyl-pyrazine (*q.v.*).

Di-indole *v. Indoline* under Indigo.

Retin-indole C_8H_9NO? Obtained by treating di-chloro-indole (chloro-oxindole chloride) with HI dissolved in HOAc, passing in SO_2, and ppg. with NaOH (Baeyer, *B.* 12, 1313). Amorphous; insol. NaOHAq, v. sol. alcohol and ether. Not volatile with steam. Its solution in HOAc mixed with HCl colours pine-wood red. On dry distillation it yields indole.

INDOLE (α)-CARBOXYLIC ACID $C_9H_7NO_2$ *i.e.* $C_6H_4<^{CH}_{NH}>C.CO_2H$. [201°].

Formation.—1. By heating the phenyl-hydrazide of pyruvic ether with $ZnCl_2$ at 195° (E. Fischer, *B.* 19, 1567; *A.* 236, 140).—2. By fusing (α)-methyl-indole (methyl-ketole) (1 pt.) with KOH (15 pts.); the acid being ppd. by H_2SO_4 from the dissolved product; the yield is over 50 p.c. (Ciamician a. Zatti, *Rend. Accad. Linc.* [4] 4, 746).—3. From acetyl-(α)-methyl-indole $C_6H_4<^{CH}_{NAc}>CMe$ by potash fusion (Ciamician a. Magnanini, *B.* 21, 673).

Properties.—Needles (from water). M. sol. hot water and benzene, v. sol. alcohol and ether. May be sublimed in plates, but suffers partial decomposition thereby. At 230° it splits up into indole and CO_2. Pine wood acidified with HCl is not coloured yellow by it. With isatin and H_2SO_4 it gives a reddish-violet colouration. It forms a picric acid compound crystallising in slender golden needles. Its Ba salt is soluble. Ac_2O at 220° forms (β)-acetyl-indole and di-acetyl-indole.

Anhydride $C_{18}H_{10}N_2O_2$ *i.e.*

$$C_6H_4\left\langle\begin{array}{l}CH{:}C.CO.N\\ \quad\diagup\qquad\quad\diagup\\ N{-}CO.C{:}CH\end{array}\right\rangle C_6H_4.$$

[312°–315°]. Mol. w. Confirmed by Raoult's method (Magnanini, *B.* 22, 2503). Formed by boiling the acid with Ac_2O using an inverted condenser. Yellow needles.

Methyl-ether MeA'. [152°]. Needles.

Indole (β)-carboxylic acid

$C_6H_4<^{C(CO_2H)}_{NH}>CH$. [214°]. Formed by fusing (β)-methyl-indole (skatole) with KOH (Ciamician, Magnanini a. Zatti, *B.* 21, 673, 1929). Obtained also by fusing (β)-acetyl-indole with caustic potash (Zatti, *B.* 22, 664). Plates (from water), decomposed on fusion. Sl. sol. benzene and boiling water, m. sol. alcohol and ether, almost insol. ligroïn. Its aqueous solution evolves CO_2 on boiling. With isatin and H_2SO_4 it gives a brownish-violet colour. Its ammonium salt gives pps. with $CuSO_4$ and with $FeCl_3$. It does not yield a picric acid compound.

Indole di-carboxylic acid

$CO_2H.C_6H_4<^{CH}_{NH}>C.CO_2H$ [above 250°]. Obtained by saponifying its acid ether, which is formed when $CO_2Et.C_6H_4.N_2H{:}CMe.CO_2Et$, the product of the condensation of hydrazido-benzoic ether with pyruvic ether, is heated with zinc-dust (Roder, *A.* 236, 169). Slender needles, sol. hot alcohol and acetic acid, sl. sol. ether and water. Does not colour pine wood. Decomposed on fusion giving off CO_2 and yielding a product that behaves like indole towards pine wood.

Mono-ethyl ether EtHA''. [250°]. Yellow needles (from HOAc).

INDOLES. Alkylated derivatives of indole may be formed synthetically in the following ways: (*a*) By removal of NH_3 from the phenyl-hydrazides of ketones, aldehydes, or ketonic acids. Thus with the phenyl-hydrazide of acetone $C_6H_5N_2H{:}CMe_2 = NH_3 + C_6H_4<^{CH}_{NH}>CMe$, and in like manner from the phenyl-methyl-hydrazide of pyruvic acid $C_6H_5N_2Me{:}CMe.CO_2H = NH_3 + C_6H_4<^{CH}_{NMe}>C.CO_2H$ (E. Fischer, *A.* 236, 116). (*b*) By elimination of NH_3 from alkylated di-pyrroles:—

$$\begin{array}{cccccc}C(C_3H_7) & - & CH-CH & \text{———} & C(C_3H_7)\\ \| & & |\quad\;\; | & & \|\\ CH-NH & - & CH-CH & -NH- & CH\end{array}$$

$$= NH_3 + \begin{array}{l}C(C_3H_7){=}CH{-}C{-}C(C_3H_7)\diagdown\\ |\qquad\qquad\qquad\quad \|\qquad\qquad\quad CH\\ CH \;=\; CH{-}C{-}NH\;{-}\diagup\end{array}$$

(Dennstedt, *B.* 21, 3429). (*c*) By heating (β)-bromo-β-acetyl-propionic acid with aromatic amines (Wolff, *B.* 21, 3360). Thus *o*- or *p*-toluidine gives tri-methyl-indole; (β)-naphthyl-amino gives di-methyl-(β)-naphthindole; while ethyl-anilino forms di-methyl-ethyl-indole:

$$C_6H_5.NHEt + CH_3.CO.CHBr.CH_2.CO_2H$$
$$= HBr + H_2O + CO_2 + C_6H_4<^{CMe}_{NEt}>CMe.$$

Indoles may be converted by alkyl iodides into derivatives of quinoline dihydride:

$$C_6H_4<^{CH}_{NH}>CH + 3MeI = C_6H_4\left\langle\begin{array}{l}CH{:}CMe\\ \qquad\quad |\\ NMe.CH_2\end{array}\right. + 3HI.$$

INDOLINE *v.* Indigo.

INDONAPHTHENE. The hypothetical hydrocarbon C_9H_8 or $C_6H_4<^{CH}_{CH_2}>CH$ which stands in the same relation to indole that naphthalene stands to quinoline (Baeyer a. Perkin, jun., *B.* 17, 122). The name *indene* has also been proposed for

he same hydrocarbon (Roser, *A.* 247, 132); *v.* also METHYL-INDONAPHTHENE. Besides the methods mentioned below, indonaphthene derivatives may be formed by condensation of naphthalene derivatives. Thus $C_6H_4<\begin{smallmatrix}CO\,.\,CO\\ \quad|\\ CHCl.CCl_2\end{smallmatrix}$, a product of the chlorination of (β)-naphthoquinone is converted by cold aqueous NaOH into $C_6H_4<\begin{smallmatrix}C(OH).CO_2H\\ CHCl\end{smallmatrix}>CCl_2$ (Zincke, *B.* 20, 2894) which may be oxidised by chromic acid to $C_6H_4<\begin{smallmatrix}CO\\ CHCl\end{smallmatrix}>CCl_2$. [59°].

INDONAPHTHENE DIHYDRIDE CARBOXYLIC ACID $C_{10}H_{10}O_2$ *i.e.* $C_6H_4<\begin{smallmatrix}CH_2\\ CH_2\end{smallmatrix}>CH.CO_2H$. *Hydrindonaphthene carboxylic acid.* [130°]. S. ·833 at 100°.

Formation.—1. By heating the corresponding di-carboxylic acid until the evolution of CO_2 has ceased, and distilling the product (Baeyer a. Perkin, jun., *B.* 17, 122).—2. By the action of (1 mol. of) ω-di-bromo-xylene (*o*-xylylene bromide) upon aceto-acetic ether (1 mol.) and NaOEt (2 mols.) and saponification of the product with alcoholic KOH (Scherks, *B.* 18, 378).

Properties.—Colourless needles (from water); may be distilled when quickly heated. Sl. sol. cold water. On oxidation with $KMnO_4$ it yields phenyl-glyoxylic acid. It forms a bulky white silver salt, sl. sol. hot water.

Indonaphthene dihydride dicarboxylic acid $C_6H_4<\begin{smallmatrix}CH_2\\ CH_2\end{smallmatrix}>C(CO_2H)_2$. [199°]. Formed by the action of di-ω-bromo-o-xylene on malonic ether (1 mol.) and NaOEt (2 mols.) in ether (Baeyer a. Perkin, jun., *B.* 17, 122; Perkin, jun., *C. J.* 53, 7); the resulting ether being saponified. Trimetric plates; m. sol. hot water, alcohol, and ether, sl. sol. cold water. When heated above 200° it gives off CO_2 and leaves the mono-carboxylic acid.—Ag_2A'': white amorphous pp. becoming crystalline; sl. sol. water.

INDONAPHTHOQUINONE $C_9H_6O_2$ *i.e.* $C_6H_4<\begin{smallmatrix}CO\\ CO\end{smallmatrix}>CH_2$. [131°]. *Di-keto-indonaphthene. Di-keto-hydrindene.* Formed by warming its carboxylic ether $C_6H_4<\begin{smallmatrix}CO\\ CO\end{smallmatrix}>CH.CO_2Et$ with alkalis (Wislicenus, *A.* 246, 351). Best obtained by acidifying an aqueous solution of the sodium derivative $C_6H_4{:}C_2O_2{:}CNa.CO_2Et$, extracting with ether, and leaving the ethereal solution to stand, when CO_2 is given off.

Properties.—Small needles (from benzene-ligroïn); v. sol. hot alcohol and benzene, m. sol. ether and hot ligroïn, v. sl. sol. cold ligroïn and water. Dissolves in alkalis with intense yellow colour.

Reactions.—1. Gives a phenyl-hydrazide $C_6H_4<\begin{smallmatrix}C(N_2HPh)\\ CO\end{smallmatrix}>CH_2$ [163°] crystallising in yellow needles, insol. water and ligroïn, v. e. sol. ether and benzene. With phenyl hydrazine at 100° it gives rise to a di-phenyl-hydrazide $C_6H_4<\begin{smallmatrix}C(N_2HPh)\\ C(N_2HPh)\end{smallmatrix}>CH_2$, which forms flesh-coloured plates [171°], and when dissolved in H_2SO_4 is coloured deep bluish-green by $FeCl_3$ (W. Wislicenus a. Kötzle, *A.* 252, 73).—2. Forms a nitroso-derivative $C_6H_4<\begin{smallmatrix}CO\\ CO\end{smallmatrix}>C{:}NOH$ [198°] crystallising from HOAc in triangular plates.—3. *Benzoic aldehyde* at 120° forms $C_6H_4<\begin{smallmatrix}CO\\ CO\end{smallmatrix}>C{:}CHPh$ [150°].—4. Gives with *bromine* a compound $C_6H_4<\begin{smallmatrix}CO\\ CO\end{smallmatrix}>CBr_2$ [177°] crystallising in plates, m. sol. hot alcohol and HOAc, v. sol. ether and CS_2 (*cf.* Zincke, *B.* 20, 3216). This di-bromo-derivative, which is also formed by the action of bromine on $C_6H_4<\begin{smallmatrix}CO\text{———}C.NH_2\\ \qquad\qquad\|\\ C(NH)-CBr\end{smallmatrix}$ and on $C_6H_4<\begin{smallmatrix}CO\text{——}C.NH_2\\ \qquad\quad\|\\ C(NH).CH\end{smallmatrix}$, is converted by the action of alkali into bromoform, phthalic acid, and the compound $C_6H_4<\begin{smallmatrix}C(OH)\\ CO\end{smallmatrix}>CBr$ [118°], whence Br forms again the original $C_6H_4<\begin{smallmatrix}CO\\ CO\end{smallmatrix}>CBr_2$, while Cl forms $C_6H_4<\begin{smallmatrix}CO\\ CO\end{smallmatrix}>CClBr$ [147°] (Zincke, *B.* 21, 2394). The corresponding $C_6H_4<\begin{smallmatrix}CO\\ CO\end{smallmatrix}>CCl_2$ [125°] is formed by the action of chlorine on $C_6H_4<\begin{smallmatrix}CO\,.\,CO\\ \quad|\\ CCl_2.CCl_2\end{smallmatrix}$ dissolved in aqueous Na_2CO_3.

Indonaphthoquinone carboxylic ether $C_6H_4<\begin{smallmatrix}CO\\ CO\end{smallmatrix}>CH.CO_2Et$. [78°]. Formed by the action of NaOEt (2 mols.) on phthalic ether (1 mol.) and subsequent treatment with acetic ether, the product $C_6H_4<\begin{smallmatrix}CO\\ CO\end{smallmatrix}>CNa.CO_2Et$ being treated with dilute H_2SO_4 (Wislicenus, *A.* 246, 349). Slender yellow needles, insol. water, v. e. sol. alcohol, ether, benzene, and ligroïn. $FeCl_3$ colours its alcoholic solution deep red. Dissolves in aqueous Na_2CO_3, expelling CO_2. If its alkaline solution be boiled and then acidified CO_2 is evolved and indonaphthoquinone liberated. It forms a phenyl-hydrazide. If its acid solution is boiled with water there is formed $C_{18}H_{10}O_3$, which dyes wool violet-red and forms crystalline $C_{18}H_9BrO_3$ [196°] and $C_{18}H_8Br_2O_3$ [242°].

Salts.—$C_{12}H_9O_4Na$ aq: yellow needles (from water). Gives with MeI the compound $C_6H_4<\begin{smallmatrix}CO\\ CO\end{smallmatrix}>CMe.CO_2Et$, crystallising in prisms [74°]; v. e. sol. alcohol and ether, insol. water, sol. NaOHAq with rose colour.—$(C_{12}H_9O_4)_2Cu$: green crystals (from alcohol).

INDONE. The ketone $C_6H_4<\begin{smallmatrix}CO\\ CH\end{smallmatrix}>CH$, a number of the haloid derivatives of which have been described by Roser (*A.* 247, 132). Indone may also be viewed as the anhydride of DI-OXY-INDONAPHTHENE.

INDOPHANE $C_{22}H_{10}N_4O_4$. A blue substance, resembling indigo, produced, together with naphthyl-purpuric acid, by adding a hot concentrated solution of KCy (45 g.) to di-nitro-naphthol (30 g.) dissolved in boiling water (2 litres) to which just enough NH_3 has been added to effect

solution (Hlasiwetz; Sommaruga, *C. C.* 1871, 617). Violet mass with green lustre; insol. water, alcohol, ether, benzene, and CS_2; m. sol. H_2SO_4 and hot HOAc, forming purple solutions. May be sublimed. Nitric acid converts it into a brownish-red body, soluble in alkalis. Ferrous sulphate mixed with lime reduces it. Aqueous KOH forms $C_{22}H_9KN_4O_4$aq, a body greatly resembling indigo; NaOH acts in like manner.

INDOPHENIN $(C_{12}H_7NOS)_x$. Formed by shaking isatin (1 pt.) with H_2SO_4 and benzene that contains thiophene: $C_8H_5NO_2 + C_4H_4S = H_2O + C_{12}H_7NOS$ (Baeyer, *B.* 12, 1309; 16, 2188; 18, 2637; V. Meyer, *B.* 15, 2893; 16, 1465; P. Meyer, *B.* 16, 2269; Gumpert, *J. pr.* [2] 32, 278). Blue powder, which exhibits a coppery lustre when rubbed, or small needles (from alcohol-phenol). Insol. water, benzene, and ligroïn, v. sl. sol. alcohol, ether, and CS_2, sl. sol. HOAc. In H_2SO_4 it forms a blue solution, whence it is ppd. by water. Cannot be sublimed. May be reduced by zinc-dust and HOAc to a colourless body which is re-oxidised to indophenin on exposure to air. Bromo-, di-bromo-, and methyl-indophenins may be formed in like manner by using bromo-, di-bromo-, or methyl-isatin in place of isatin in the above preparation.

INDOPHENOLS. Quinonimides of the formula $C_6H_4<^{NH}_{NR'}>$, where R′ is an aromatic radicle containing hydroxyl (*cf.* INDAMINES). Thus when a mixture of di-methyl-*p*-phenylene-diamine and (α)-naphthol is oxidised with NaOCl or $K_2Cr_2O_7$ there is formed the dark-blue indophenol $C_6H_4<^{NMe_2Cl}_{N.C_{10}H_6.OH}$ (Pabst, *Bl.* [2] 38, 161); while *p*-amido-phenyl-piperidine mixed with phenol and oxidised by K_3FeCy_6 forms a similar body $C_6H_4<^{N.C_5H_{10}Cl}_{N.C_6H_4OH}$ (Lellmann a. Geller, *B.* 21, 2288).

INDOXANTHIC ETHER $C_{11}H_{11}NO_4$ *i.e.* $C_6H_4<^{CO}_{NH}>C(OH).CO_2Et$. [107°]. Prepared by the careful oxidation of indoxylic ether with Fe_2Cl_6 (Baeyer, *B.* 15, 775). Yellow needles or monoclinic prisms. Sol. water and ether. On further oxidation it gives $CO_2H.C_6H_4.NH.CO.CO_2Et$. On reduction it is reconverted into indoxylic ether. Decomposed by alkalis with formation of anthranilic acid.

Nitrosamine $C_{11}H_{10}(NO)NO_4$. [113°]. Light-yellow needles or tables. Sol. alcohol and ether, sl. sol. water.

INDOXYL C_8H_7NO *i.e.* $C_6H_4<^{C(OH)}_{NH}>CH$ (stable form) or $C_6H_4<^{CO}_{NH}>CH_2$ (transition form).

Formation.—1. By warming potassium indoxyl-sulphate with HCl or H_2SO_4.—2. By heating indoxylic acid alone or with H_2SO_4 (Baeyer, *B.* 14, 1744).—3. By boiling *o*-nitro-phenyl-acetylene with acid ammonium sulphite, and treating the product with zinc-dust and ammonia (Baeyer, *B.* 15, 56).—4. By reducing isatogen-sulphurous acid with zinc-dust and ammonia.

Properties.—Oil. Not volatile with steam. In the pseudo-form $C_6H_4<^{CO}_{NH}>CH_2$ it is not known in the free state, but di-substitution products of ψ-indoxyl are stable. Nevertheless indoxyl forms condensation products, called indogenides, with bodies containing a CO group, in which reactions it must be supposed first to change into the pseudo-form.

Reactions.—1. In alkaline solution it is rapidly *oxidised* in the air to indigo. $FeCl_3$ forms a white amorphous body, which is immediately converted by HCl into indigo (E. Baumann a. Tiemann, *B.* 13, 415).—2. Indoxyl is not affected by H_2SO_4 or conc. HClAq, but dilute HClAq converts it into an amorphous red substance.—3. A solution in H_2SO_4 treated with *o-nitro-phenyl-propiolic acid* gives indoïn.—4. On warming with a solution of Na_2CO_3 and *o*-nitro-phenyl-propiolic acid, indigo is produced.—5. By the action of Na_2CO_3 upon an alcoholic solution of *isatin* and indoxyl there is formed indirubin, while with bromo-isatin the product is bromo-indirubin (Baeyer).—6. *Bromine* gives tri-bromo-aniline (E. Baumann a. Tiemann, *B.* 12, 1192).—7. In alkaline solution $K_2S_2O_7$ forms indoxyl-sulphuric acid.—8. *Diazo-benzene chloride* forms $C_6H_4<^{C(OH)}_{N.N_2Ph}>CH$? [236°] (Baeyer, *B.* 16, 2190).

Nitrosamine $C_6H_4<^{C(OH)}_{N(NO)}>CH$. Formed by the action of nitrous acid on indoxyl (Baeyer, *B.* 16, 2188). Slender yellowish needles. When boiled with HCl it gives indigo.

Isonitroso- derivative of ψ-indoxyl $C_6H_4<^{CO}_{NH}>C{:}NOH$. See *oxim* of ψ-ISATIN.

Ethyl derivative $C_6H_4<^{C(OEt)}_{NH}>CH$. Formed by heating the ethyl derivative of indoxylic acid. Oil; volatile with steam. Smells like indole, and colours pine wood, acidified with HCl, brownish-red. Its picric acid compound $C_{10}H_{11}NOC_6H_2(NO_2)_3OH$ forms brown needles. Its nitroso- derivative $C_6H_4<^{C(OEt)}_{N(NO)}>CH$ forms yellow prisms [85°], sol. alcohol, insol. water, and converted into indigo by heating with HCl (Baeyer, *B.* 15, 781).

Indoxyl-sulphuric acid $C_8H_7NSO_4$. Occurs in the urine of herbivora and, in smaller quantity, in that of man (Schunck, *P. M.* [4] 14, 288; Hoppe-Seyler, *C. C.* 1864, 511; *H.* 8, 79; E. Baumann a. Tiemann, *B.* 13, 408). When indole is introduced into a dog by injection or in food large quantities of indoxyl-sulphuric acid appear in the urine (Jaffé, *Fr.* 11, 358; E. Baumann a. Brieger, *H.* 3, 254). Indoxyl-sulphuric acid is also formed by adding $K_2S_2O_7$ to a solution of indoxyl in aqueous KOH (Baeyer, *B.* 14, 1745).

Potassium salt. KA′. Plates (from hot alcohol). V. sol. water, v. sl. sol. cold alcohol. Not affected by KOH even at 170°. Decomposed by hot dilute HCl or H_2SO_4, or even by water at 120°, into indoxyl and $KHSO_4$. When warmed with $FeCl_3$ and a little HCl it is entirely converted into indigo. Indigo is also formed when the salt is heated alone.

INDOXYLIC ACID $C_9H_7NO_3$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{C(OH)}{NH}>C.CO_2H$ (stable form) or $C_6H_4<\genfrac{}{}{0pt}{}{CO}{NH}>CH.CO_2H$ (transition form). [123°]. Formed by saponifying its ether with fused NaOH at 180°. White crystalline pp., sl. sol. water. In dilute alkaline solutions it is converted into indigo by the action of air or oxidising agents. On heating it splits off CO_2 forming indoxyl.

Indoxylic ether $C_8H_5N(OH).CO_2Et$. Colourless prisms, [121°]; dissolves in alkalis and is reppd. by CO_2. Prepared by reduction of isatogenic ether or o-nitro-phenyl-propiolic ether. Heated with H_2SO_4 it gives indigo-sulphonic acid. On oxidation it gives successively indoxanthydic ether $C_{22}H_{20}N_2O_6$, indoxanthic ether $C_{11}H_{11}NO_4$, and hydrogen ethyl oxaloxyl-o-amido-benzoate $CO_2Et.CO.NH.C_6H_4.CO_2H$.

Acetyl-indoxylic ether $C_8H_5N(OAc).CO_2Et$: white needles, [138°].

Ethyl-indoxylic ether $C_8H_5N(OEt).CO_2Et$: large colourless crystals, [98°].

Ethyl-indoxylic acid $C_8H_5N(OEt).CO_2H$: plates, [160°]. Oxidised to indigo by Fe_2Cl_6, but not in alkaline solution.

Nitroso-ethyl-indoxylic acid $C_8H_4N(NO)(OEt).CO_2H$: flat golden needles. Decomposes at about 200°. Formed by the action of nitrous acid on ethyl-indoxylic acid (Baeyer, *B.* 14, 1742; 15, 775; 16, 2189; Forrer, *B.* 17, 976).

INDUCTION. When H and Cl are mixed in equal volumes and exposed to sunlight a measurable time elapses before chemical change begins. Bunsen a. Roscoe, who examined this phenomenon (*T.* 1857. 355), regarded the mixture as resisting chemical change, and they used the term *induction* to express the gradual overcoming of this resistance. The term has also been used by Wright, who noticed a similar phenomenon in the reduction of metallic oxides by CO and H (*C. J. Trans.* 1879. 475; 1880. 757); *v.* Chemical change, vol. i. p. 749.

M. M. P. M.

INDULINES (O. N. Witt a. Thomas, *C. J.* 43, 112). Coloured compounds formed by the action of such bodies as azo-, amido-azo-, nitro-, or nitroso- compounds on the hydrochlorides of certain aromatic amines with elimination of NH_3. Aniline hydrochloride gives a dark-blue colouration with amido-azo-benzene. Hofmann a. Geyger (*B.* 5, 474) supposed that only one dye-stuff was formed: $C_{12}H_{11}N_3 + C_6H_7N = C_{18}H_{15}N_3 + NH_3$. In reality a great number of dye-stuffs are got. If the mixture of diazo-benzene anilide (1 pt.), aniline (4 pts.), and aniline hydrochloride (1 pt.), which has been left until the diazo-benzene anilide has changed into amido-azo-benzene, be heated at 100° for 24 hours, crystals of azophenine $C_{30}H_{24}N_4$ separate. This forms garnet-coloured leaflets (from aniline) [237°] (*v.* Azophenine). If the mixture of aniline, aniline hydrochloride, and amido-azo-benzene, after heating at 100° till azophenine is formed, be further heated at 125°-130° for 12 hours, the azophenine disappears, and the mass turns blue. If it be slowly cooled crystals are formed. These may be separated from the mother-liquor (which contains 'induline B'), washed with spirit and with boiling water, and recrystallised from aniline mixed with aniline hydrochloride. So obtained, induline 3 B forms glistening brown leaflets, $C_{30}H_{23}N_5HCl$. It is insol. cold, sol. hot, spirit, and v. sol. aniline. Alcoholic NaOH liberates the free base, which forms purple solutions with alcohol and with aniline. Induline 3 B is sky-blue. Its sulphonic acid resembles that of induline B.

Induline 6 B—$C_{36}H_{27}N_5$. Is formed by heating a mixture of amido-azo-benzene (100 pts.), aniline hydrochloride (130 pts.), and aniline (300 pts.), for 5 hours at 110°, then adding more aniline hydrochloride (65 pts.), and heating to 165°–170°. The hydrochloride, B'HCl, separates as green crystals. The free base separates from aniline as brilliant green needles. The solution of this base is of a dark bluish-purple colour. The hydrochloride is insoluble in the usual solvents, and is hardly soluble in aniline. It dissolves in phenol and in H_2SO_4, forming a greenish-blue solution.

Induline B hydrochloride is v. sol. spirit, sl. sol. water, v. sol. a conc. aqueous solution of aniline hydrochloride. The base forms a brown-red spirit solution. The sulphonic acid is insol. water, but its neutral alkaline salts form reddish-blue aqueous solutions.

Formation of indulines is due to the dehydrogenating action of amido-azo-benzene, which itself becomes aniline and *p*-phenylene diamine, the latter then entering into the reaction. Azo-benzene, phenyl-amido-azo-benzene, chrysoïdine, nitroso-di-methyl-aniline, and even amido-azo-naphthalene, may be substituted for amido-azo-benzene, but if instead of aniline o-toluidine or naphthylamine be used, red dyes are got (azotoline, &c.). This would indicate that azophenine was an oxidation product of aniline, and not derived from the amido-azo-benzene. In the preparation of azophenine by heating aniline (4 pts.) with aniline hydrochloride (1 pt.) and amido-azo-benzene (2 pts.) at 85°, ammonium chloride and *p*-phenylene-diamine are constant by-products, indicating that phenylation and reduction of the amido-azo-benzene has taken place (Witt, *B.* 20, 1538). When azophenine (400 g.) is boiled with alcohol (40 litres) and strong H_2SO_4 (2 kilos.) for 10 hours quinone dianilide (195 g.) is formed. The compound $C_6H_4<\genfrac{}{}{0pt}{}{NPh}{NPh}>$ is converted by heating with aniline at 100° into azophenine (Baudrowski, *M.* 9, 414). These reactions confirm the formula $C_6H_2(NPhH)_2<\genfrac{}{}{0pt}{}{NPh}{NPh}$ (with the two NPh joined) proposed by Kimich and by Fischer a. Hepp for azophenine, which is also consistent with its formation from nitroso-di-phenylamine $C_6H_4<\genfrac{}{}{0pt}{}{N—HPh}{N}>O$ (O. Fischer a. Hepp, *B.* 20, 2479; 21, 676, 2617). By the action of aniline on azophenine, induline (6 *B*) of the formula $NPh.C_6H(NHPh)_2<\genfrac{}{}{0pt}{}{NPh}{N}>C_6H_4$ might be formed. A mixture of 3 B and 6 B induline is formed by heating *p*-nitroso-di-phenyl-amine with aniline and aniline hydrochloride in alcoholic solution at 130°. By heating *p*-nitroso-di-

phenyl-amine (1 pt.) with aniline hydrochloride (1 to 2 pts.) and aniline (4 pts.) at 135°-140°, a very rich yield of induline is obtained, which chiefly consists of 6 B. If pure azophenine is heated at 140° with equal parts of aniline and aniline hydrochloride 6 B induline is almost exclusively formed (Fischer a. Hepp, *B.* 20, 2484). By the action of azo-, nitro-, or nitroso- compounds on *m*- or *p*-diamines, indulines which are soluble in water are formed, *e.g. paraphenylene blue.*

Rosinduline $C_{28}H_{19}N_3$ *i.e.* $C_{10}H_5(NPh)\ll\genfrac{}{}{0pt}{}{N}{NPh}\gg C_6H_4$. [225°]. Formed by the action of nitroso-phenyl-(α)-naphthylamine hydrochloride on aniline and aniline hydrochloride at 120° (O. Fischer, *B.* 21, 2621). Formed also by oxidising tri-phenyl-tri-amido-naphthalene $C_{10}H_5(NHPh)_3$ [1:2:4]. Red plates, almost insol. water, m. sol. alcohol, v. sol. benzene. Reduced by HI and P at 150° to a yellowish-red base and aniline. Zinc and HCl give naphthalene and aniline.

Salts.—$B'HCl\,1\frac{1}{2}aq$: reddish-brown prisms. —$B'_2H_2PtCl_6$.—$B'H_2SO_4$ aq.—$B'HNO_3$. [231°].—Picrate: plates, insol. water.

INDYL PHENYL KETONE CARBOXYLIC ACID $C_6H_5.CO.C_6H_3<\genfrac{}{}{0pt}{}{CH}{NH}>C.CO_2H$. *Benzo-indole carboxylic acid.* [285°]. From the *eso*-benzoyl-phenyl-hydrazide of pyruvic acid by heating with $ZnCl_2$ at 220° (Ruhemann a. Blackman, *C. J.* 55, 617). White needles, sl. sol. boiling water. Decomposes on fusion.

INOGEN *v.* MUSCLE.

INOSIC ACID $C_{10}H_{14}N_4O_{11}$? Occurs in the mother-liquor in the preparation of creatine from flesh (Liebig, *A.* 62, 317; *A. Ch.* [3] 33, 129). Occurs to the extent of $\frac{1}{10}$ p.c. in the flesh of hens. Pigeon's flesh and human flesh contains none (Gregory, *A.* 64, 106; Schlossberger, *A.* 66, 82). It is found in some fish (Limpricht, *A.* 133, 301).

Preparation.—The filtrate from which creatin has separated is concentrated, then mixed with alcohol till it acquires a milky consistence, and left to itself for a few days. It then deposits a crystalline mixture containing the inosates of Na and Ba. The crystals are dissolved in hot water and $BaCl_2$ added. The Ba salt crystallises on cooling.

Properties.—Uncrystallisable; v. sol. water, forming a solution with a flavour of broth, whence alcohol ppts. it as an amorphous powder. Insol. ether.

Salts.—K_2A'' 7 aq : long, four-sided prisms, v. sol. water, insol. alcohol.—BaA'' 6 aq : prisms. S. ·25 at 16°.

INOSITE $C_6H_{12}O_6$. *Phaseomannite.* [217°] (Maquenne); [225° cor.] (Fick). (319° *in vacuo*) (M.). S.G. (of $C_6H_{12}O_6$ 2aq) $\frac{15}{}$ 1·524. S.G. (of $C_6H_{12}O_6$) $\frac{15}{}$ 1·752. S. (of $C_6H_{12}O_6$ 2aq) 10 at 12° (T. a. V.); 13 at 19° (Fick). H. C. 666500. H. F. 311500 (Berthelot a. Recoura, *C. R.* 105, 143). Discovered by Scherer (*A.* 73, 322; 81, 375) in muscular substance (ἴς, ἰνός, muscle). It occurs especially in the heart, but also in the lungs, kidneys, liver, and spleen of oxen (Cloetta, *A.* 99, 289), in the brain of oxen (W. Müller, *A.* 103, 140), in human kidneys, and in the urine in a case of Bright's disease to the amount of ·1 p. c., and sometimes in healthy urine (Külz, *Fr.* 16, 135). Found also in birds, in cephalopoda (Krukenberg, *J. Th.* 1881, 343), and in the flesh of a young porpoise (O. Jacobsen, *A.* 157, 227). Inosite occurs in green kidney beans (*Phaseolus vulgaris*) (Vohl, *A.* 99, 125; 105, 330), in the green pods and unripe seeds of peas (*Pisum sativum*), in unripe lentils (*Ervum Lens*), in the unripe fruits of the common acacia (*Robinia Pseud-Acacia*), in the heads of the common cabbage (*Brassica oleracea*, var. *capitata*), in foxglove leaves, in extract of digitalis, in the leaves of the dandelion (*Taraxacum dens leonis*), in potato shoots, in green asparagus and in its berries, in *Lactaria piperatus*, in *Clavaria crocea* (Marmé, *A.* 129, 222), in the leaves of the common ash (*Fraxinus excelsior*) (Gintl, *J. pr.* 104, 491), in grape juice (Hilger, *A.* 160, 333), in young vine leaves (Neubauer, *Fr.* 12, 45), in walnut leaves (Tanret a. Villiers, *A. Ch.* [5] 23, 389; *C. R.* 86, 486; Maquenne, *C. R.* 104, 225).

Preparation.—1. Walnut leaves are extracted with water. The brown liquid is treated, at 100°, with excess of milk of lime, filtered, ppd. with lead acetate, again filtered and treated with ammonia and lead acetate. The crude lead compound of inosite is treated with dilute sulphuric acid, and the inosite is ppd. with alcohol and ether. It can be further purified by recrystallisation from hot dilute acetic acid (Hilger; Maquenne).—2. The fresh-chopped tissue is covered with water, and allowed to stand for 24 hours in a cool place, with frequent stirring; the liquid is then separated, and the residue pressed; the solution is heated with a little acetic acid to separate albumin and hæmatin, then strained, evaporated on the water-bath to one tenth, ppd. with neutral acetate of lead, and filtered; and the filtrate is mixed with basic acetate of lead, whereupon inosite is thrown down in combination with oxide of lead, accompanied by uric acid, cystine, and other substances. The pp., after washing, is decomposed under water by H_2S, and the liquid filtered from the sulphide of lead; it then sometimes deposits crystals of uric acid, and when evaporated to a small bulk on the water-bath, and mixed with alcohol till a turbidity is produced, it yields crystals of inosite (Cloetta).—3. Crystals of inosite may often be obtained by evaporating an aqueous liquid containing it, and adding three volumes of alcohol to one of the boiling liquid (Cooper Lane, *A.* 117, 118).

Properties.—Monoclinic crystals (containing 2aq) $a:b:c = 1·090 : 1 : 1·535$; $\beta = 111° 39'$. Effloresces in dry air. At 100° it gives off its water of crystallisation. It has a sweet taste and is optically inactive. Sl. sol. cold dilute alcohol, insol. absolute alcohol and ether. Does not combine with NaCl or KCl. With lead subacetate it forms a gelatinous pp. which may be $C_6H_{12}O_6 2PbO$. Inosite does not react with phenyl-hydrazine (E. Fischer, *B.* 17, 582). Inosite is not turned brown by boiling alkalis, or by boiling dilute H_2SO_4. It does not reduce Fehling's solution but forms a green pp. It will not undergo alcoholic fermentation. In presence of decaying cheese or of putrid meat and chalk it forms butyric and lactic acids. Sodium-amalgam does not affect inosite. Inosite does not form an acid solution with borax.

Reactions.—1. Evaporated with *nitric acid* it leaves a residue which gives with $CaCl_2$ in ammoniacal solution a rose-red colouration (colour test).—2. When a solution of inosite is evaporated nearly to dryness and a drop of mercuric nitrate solution is added there is formed a yellow pp. which turns red on warming (Gallois, *Fr.* 4, 264).—3. Heated with oxalic acid it gives CO_2 and formic acid. According to Lorin (*Bl.* [2] 48, 235), this indicates that it is a polyhydric alcohol.—4. HIAq at 170° gives a trace of benzene, phenol, and tri-iodo-phenol [153°].—5. It forms no addition products with chlorine and bromine.—6. It does not reduce boiling ammoniacal $AgNO_3$, but on adding KOH a mirror is formed.—7. *Chromic acid* oxidises it to CO_2 and formic acid in the cold.—8. $KMnO_4$ gives CO_2.—8. Conc. HNO_3 at 100° forms oxalic acid, but in an open dish on the water-bath it gives on evaporation a white substance which dissolves in water, and the solution, mixed with alcohol and evaporated, then deposits black crystals of tetra-oxy-quinone. HNO_3 also forms rhodozonic acid (Maquenne, *Bl.* [2] 47, 290). According to Maquenne this reaction, and *reaction* 4 indicate that inosite is hexa-oxy-benzene hexahydride.

Hexa-acetyl derivative $C_6H_6(OAc)_6$. [212°]. (234° *in vacuo*). From inosite and AcCl or Ac_2O. Sublimes at 200°. Insol. water, sol. hot alcohol and Ac_2O. Saponified by alkalis and strong acids (Maquenne, *C. R.* 104, 1719; *Bl.* [2] 48, 58). According to Fick (*C. C.* 1887, 452), the acetyl derivative is $C_6H_7Ac_5O_6$ and melts at 216° cor.

Hexa-benzoyl derivative $C_6H_6(OBz)_6$. [258°]. Minute needles. Insol. all usual solvents.

Hexa-nitroxyl derivative $C_6H_6(ONO_2)_3$. '*Nitro-inosite.*' [120°]. Formed by adding a solution of inosite in fuming HNO_3 to conc. H_2SO_4. May be crystallised from alcohol, a crystalline tri-nitroxyl derivative being left in the mother-liquor. Trimetric tables; insol. water, v. sol. alcohol. Detonates when struck. Cold alcoholic KOH decomposes it forming KNO_2, the inosite being completely broken up. When boiled with alcohol and a little H_2SO_4 the products are nitrous ether and inosite.

INULIN $(C_6H_{10}O_5)_x$, or $C_{72}H_{121}O_{62}$. *Helenin. Alantin. Menyanthin. Dahlin. Synanthrin. Sinistrin.* Mol. w. 1980 (by Raoult's method. Brown a. Morris, *C. J.* 55, 464). [160°]. S.G. 1·35 (Kiliani); 1·36 (Payen); 1·46 (Dubrunfaut); 1·47 (Dragendorff). $[\alpha]_D = -35°$ (Dubrunfaut, *C. R.* 42, 803); −36·5° (Lescœur a. Morelle, *C. R.* 87, 216); −40° (Lefranc, *J. Ph.* [5] 2, 216). H.C. 684900 (Berthelot a. Vieille, *Bl.* [2] 47, 868; *A. Ch.* [6] 10, 459). H.F. 230600 (B. a. V.); 197000 (Von Rechenberg). A starch-like substance occurring in the roots of elecampane (*Inula Helenium*) (Valentin Rose, *A. D.* 1804), dandelion (*Taraxacum dens leonis*), chicory (*Cichorium Intybus*), feverfew (*Pyrethrum Parthenium*), and meadow saffron (*Colchicum autumnale*); in the tubers of the potato, the dahlia, and the Jerusalem artichoke (*Helianthus tuberosus*); in Lerp manna (from *Eucalyptus dumosa*), and in certain lichens (*Lichen fraxineus* and *Lichen fastigiatus*). Sinistrin, from the sea-onion (*Urginea Scilla*), is perhaps identical with inulin.

Preparation.—The finely divided roots are boiled with water in presence of a small quantity of $CaCO_3$. The filtrate is cooled by a freezing-mixture, and, after thawing the ice, filtered again. The pp. is redissolved in hot water, and the filtered solution again subjected to the action of a freezing mixture, the process being repeated until the inulin is perfectly white. The inulin is then freed from traces of levulose by treatment with 97 p.c. alcohol, and is finally dried over sulphuric acid. It still, however, contains about ·6 p.c. proteid matter corresponding to ·1 p.c. nitrogen, and also minute traces of inorganic substances (Kiliani, *A.* 205, 147).

Properties. — White powder, resembling starch. Tasteless. Occurs also in a gum-like or horny modification, probably as a hydrate. Sl. sol. cold water, v. sol. hot water, insol. alcohol. The powder is composed of minute spheres (Sachsse). It melts at 160°, becoming changed to amorphous 'pyro-inulin' (Prantl, *N. R. P.* 19, 513, 577, 641). Inulin is very hygroscopic, and even when dried at 100° its composition appears to be $(C_6H_{10}O_5)_6H_2O$ (Kiliani). The aqueous solution of inulin does not form a jelly like that of starch. It is not coloured blue by iodine. It dissolves in cold aqueous KOH and the solution, when acidified, deposits after a while unaltered inulin. It dissolves in ammoniacal cupric oxide solution (Cramer, *J. pr.* 73, 16) the solution yielding after a few hours a copious blue pp. (Schlossberger, *J. pr.* 73, 373). It dissolves in an ammoniacal solution of nickel oxide. It does not ppt. lead acetate or sub-acetate, but with a solution of lead acetate containing ammonia it gives a white pp. Inulin is not ppd. by salts of Fe, Cu, Hg, Ag, or Au. Inulin forms with alkalis unstable compounds which are soluble in water and ppd. therefrom by alcohol. When carbonised it emits an odour of burnt sugar. It reduces ammoniacal gold and silver solutions, but not Fehling's solution. It is not fermentable, nor is its optic activity affected by diastase. It is not converted into levulose by invertin. A solution of inulin dissolves PbO. Baryta-water gives a pp. soluble in excess of a solution of inulin, and not decomposed by CO_2.

Reactions.—1. When heated with *water* at 100° it is slowly but completely converted into levulose.—2. Boiling dilute *acids* quickly convert it into levulose.—3. Dilute *nitric acid* oxidises it to racemic, oxalic, glycollic, and formic acids, but forms neither saccharic nor mucic acids (Tollens, *A.* 249, 220).—4. By long contact with *bromine* it yields bromoform, oxalic acid, and CO_2.—5. With *bromine* and *silver oxide* it yields glycollic acid (from the intermediate formation of levulose).—6. When heated with *baryta-water* small quantities of lactic acid are formed.—7. *Sodium-amalgam* has no action on inulin.—8. With *chloro-sulphuric acid* ($ClSO_3H$) at 0° it forms $C_6H_7(SO_4H)_4(O)Cl$ ($[\alpha]_D = +11\frac{1}{2}°$) whence warm water produces levulose (Claesson, *J. pr.* 128, 27).

Acetyl derivatives. These are best formulated as derivatives of $C_{12}H_{20}O_{10}$.

Tri-acetyl derivative $C_{12}H_{17}Ac_3O_{10}$. Formed by boiling inulin (1 pt.) with Ac_2O (1 pt.) and HOAc (2 pts.) for 15 minutes (Ferrouillat a. Savigny, *Z.* [2] 5, 509; Lescœur a. Morelle,

C.R. 87, 216). Amorphous yellowish mass, v. sol. water and alcohol, insol. ether. Lævorotatory.

Tetra-acetyl derivative $C_{12}H_{16}Ac_4O_{10}$. From inulin by heating with Ac_2O (F. a. S.; Schützenberger, *A.Ch.* [4] 21, 234). Amorphous. Lævorotatory.

Hexa-acetyl derivative $C_{12}H_{14}Ac_6O_{10}$. Amorphous. Lævorotatory.

Hepta-acetyl derivative $C_{12}H_{13}Ac_7O_{10}$. Dextrorotatory.

Metinulin. When inulin is heated with glycerin alone, or when it is heated with dilute acids, the product contains bodies resembling dextrin. They are not very soluble in water and on heating yield soluble metinulin and inuloid which are not so powerfully lævorotatory as the unaltered inulin. Optically inactive derivatives are also formed, but they are not identical with levulosan (Hönig a. Schubert, *M.* 8, 529). Metinulin was prepared by Dragendorff by heating inulin (1 pt.) with water (5 pts.) in a closed vessel, and ppg. with alcohol. Inuloid is a similar or identical substance, said by Popp (*A.* 156, 190) to occur in the Jerusalem artichoke. It is twice as soluble in water as inulin.

INVERTIN *v.* Fermentation, vol. ii. p. 541.

IOD- or IODO-. *Use of this prefix applied to inorganic compounds*; for *Iodo- compounds* and *Iodo- salts v.* the element the iodo- compound of which is sought for, or the salts to the name of which *iodo-* is prefixed. Thus *iodo-chloride of lead* will be found under Lead, and *iodo-chromate of potassium* under Chromates.

IODATES and PERIODATES. *Salts of iodic and periodic acids, v.* Iodine, *Oxyacids of*, pp. 21, 23.

IODATION *v.* Iodo- compounds.

IODHYDRIC ACID HI. (*Hydriodic acid. Hydrogen iodide.*) Mol. w. 127·53. Solidifies at $-55°$ (Faraday, *T.* 1845. 170). V.D. 63·22. S.H.p. (21°–100°; equal mass of water = 1) ·055 (Strecker, *W.* 17, 447). $\frac{\text{S.H.p.}}{\text{S.H.v.}}$ (20°) 1·397; (100°) 1·396 (Strecker, *l.c.*). E.C. of HIAq *v.* Kohlrausch, *P.* 159, 233. S.G. of HIAq saturated at 0° = 1·99 (De Luynes, *A. Ch.* [4] 2, 385), 2·0 (Vigier, *Bl.* [2] 11, 125). Vapour-pressure of liquid HI at $-17·8°$ = 2·9 atmos., at 0° = 4 atmos., at 15·5° = 5·8 atmos. (Faraday, *T.* 1845. 170; values approx. only). H.F. [H, I] = $-6036°$ gaseous H and solid I to form gaseous HI; [H, I] = -436 gaseous elements at 180°; [H, I, Aq] = 13,170 (*Th.* 2, 35). HI does not occur in nature.

Formation.—1. By direct union of H and I, by passing a stream of H over I at a full red heat (Courtois, *A. Ch.* 88, 305; Merz a. Holzmann, *B.* 22, 869). Corenwinder passes H and I vapour over Pt black heated to 300°–400° (*A. Ch.* [3] 30, 242; 34, 77; *v.* also Blundell, *P.* 2, 216; Lemoine, *C. R.* 85, 34).—2. HI is formed by decomposing a metallic iodide by another acid, but a portion of the HI is generally decomposed with separation of I, and in some cases the HI reacts with the other acid, *e.g.* when H_2SO_4 is added to KI, SO_2 and H_2S are produced as well as HI and I. To prepare a solution of HI in water, Glover adds an exactly equivalent quantity of H_2SO_4 to BaI_2Aq, and separates from ppd. $BaSO_4$ (*P. M.* [3] 19, 92).—3. By the reaction between Na_2SO_3 (Mène, *C. R.* 28, 478), or $Na_2S_2O_3$ (Gladstone, *P. M.* [3] 35, 345), I, and H_2O (*cf.* formation of HBr, vol. i. p. 532).—4. By decomposing PI_3 by water (Kolbe, *J. pr.* 15, 172; Vigier, *Bl.* [2] 11, 125; Pettenkofer, *A.* 138, 57). Rieckher (*C. C.* 1863. 207) recommends to make PI_3 by adding P to I in CS_2 and distilling off the CS_2.—5. Étard a. Moissan (*B.* 13, 1862) heat I with colophony.

Preparation.—1. Washed H_2S is passed into water in which a little finely-powdered I is suspended ($2H_2SAq + 2I_2Aq = 4HIAq + 2S$), more I is added little by little, and the passage of H_2S is continued. When all the I has been added, and no brown colour is produced on shaking the liquid, the separated S is agglomerated by briskly agitating the vessel, the liquid is filtered, H_2S is removed by gently warming, and the liquid is distilled; HIAq of S.G. c. 1·7 distils at 126°–128°. An inverted untubulated retort with wide neck is a suitable vessel; the H_2S is passed down the neck of the retort by a tube dipping into the water in which the I is suspended. The HIAq thus prepared may be used for making gaseous HI or a more conc. solution. About 2 pts. I are dissolved in the HIAq made as described, and the solution is dropped from a tap-funnel on to amorphous P (in a flask) moistened with HIAq of the same concentration; the HI produced is passed through a wide U-tube containing glass beads and some amorphous P moistened with HIAq (to convert any I vapour into HI) [$PI_3 + 3H_2O + Aq = H_3PO_3Aq + 3HI$]. If dry HI is wished for, the gas is passed through a $CaCl_2$ (or better CaI_2) tube and then over P_2O_5, and collected by downward displacement. If HIAq is to be prepared, the gas coming from the first U-tube is passed into the tubulus of a retort, the neck of which dips a very little way beneath the surface of water kept cold by ice; this arrangement prevents the water from rushing back into the U tube. The flask containing P in HIAq, into which the solution of I is dropped, should be only very gently warmed for some time, as H_3PO_3 is among the first products of the reaction, and when this is heated H_3PO_4 and PH_3 are formed, the latter of which combines with HI to form PH_4I (*cf.* Bannow, *B.* 6, 1498).—2. L. Meyer recommends the following method of preparing HIAq by the formation and decomposition by water of PI_3 (*B.* 20, 3381). 100 g. I in a retort, with the neck inclined upwards, are moistened with c. 10 g. water; a tap-funnel (or a funnel into the neck of which fits a glass rod) is fitted into the tubulus of the retort; 5 g. amorphous P and 10 g. water are placed in the funnel, and a single drop of this is allowed to flow into the retort; after a little a drop or two more is allowed to follow, and a little later the liquid is added in larger quantities. HI passes off, and may be collected in water as described under 1. No heating is required. If more than one drop of the P in water is added at first an explosion usually follows. The I carried over is nearly all deposited on the neck of the retort. 3. 14 pts. KI are warmed with 20 pts. I and 1 to $1\frac{1}{2}$ pts. P with a little water (Millon, *J. Ph.* 28, 99; Roscoe, *C. J.* 13, 146).—4. Na_2SO_3 (6 pts.) is rubbed up with water (1 pt.), and after warming, I (3 pts.) is slowly added (Mène, *C. R.*

28, 478; *cf.* Gladstone, *P. M.* [3] 35, 345).—5. 60 g. of copaiba oil are slightly warmed in a 500 c.c. retort connected with a reversed condenser; 20 g. of I are added little by little, and the temperature is allowed to rise; after a few minutes a regular and steady stream of HI comes off; when this slackens the retort is allowed to cool somewhat, more I added, and heating is recommenced; about 145 g. HI may be obtained from 150 g. I (Bruylants, *B.* 12, 2059).

S. Kemp (*P. M.* [3] 7, 444) says that liquid HI may be prepared by placing H persulphide in one limb of a sealed tube and a little I in the other, and gently warming the persulphide; H_2S is evolved and liquefied, and the I dissolves in the liquid H_2S; on then adding a drop of water (this is done by a special arrangement of the tube) HI is produced and liquefied; no details are given as to how the HI is separated from the H_2S.

Properties.—HI is a colourless, strongly acrid gas; it is incombustible and extinguishes flame. Dry HI is unchanged when kept in closed tubes in the dark (Lemoine, *J.* 1877. 138). HI is readily liquefied (*v. ante*); liquid HI is colourless (Kemp, *P. M.* [3] 7, 444, says it is yellowish); at $-55°$ it solidifies to a colourless, ice-like mass (Faraday, *T.* 1845. 170). Liquid HI is a very bad conductor of electricity (Bleekrode, *W.* 3, 161; Hittorf, *W.* 4, 374). HI is very soluble in water; the solution contains a strong acid; affinity of HIAq is about the same as that of HClAq (*v.* AFFINITY, vol. i. p. 82). HIAq is a colourless, strongly acid, fuming liquid; the solution saturated at 0° has S.G. 1·99 to 2·0; this solution gives off much HI when warmed to 40°–50°. When HIAq containing more than c. 57 p.c. HI is distilled, HI is evolved until the S.G. becomes c. 1·67–1·70 when the B.P. becomes approximately constant at 127° (at 774 mm.), and the liquid contains 57·0 p.c. HI; if the original liquid contains less than 57 p.c. HI water distils over until the acid of 57 p.c. is produced, which then distils at 127° almost unchanged (Roscoe, *C. J.* 13, 160). By passing dry H through HIAq at 15°–19°, an acid of constant concentration, 60·3 to 60·7 p.c. HI, is obtained; at 100° the constant acid contains 58·2 to 58·5 p.c. HI (Roscoe, *l.c.*). Topsöe gives the following S.G. and composition of HIAq (*B.* 3, 403; *cf.* Wright, *C. N.* 23, 242):—

Temp.	S.G. referred to H_2O at same temp.	P.c. HI	Temp.	S.G. referred to H_2O at same temp.	P.c. HI
°			°		
13·5	1·017	2·29	13	1·413	40·43
,,	1·052	7·02	,,	1·451	43·39
,,	1·077	10·15	,,	1·487	45·71
13	1·095	12·21	,,	1·528	48·22
13·5	1·102	13·09	13·5	1·542	49·13
,,	1·126	15·73	13	1·573	50·75
,,	1·164	19·97	12·5	1·603	52·43
13·8	1·191	22·63	14	1·630	53·93
,,	1·225	25·86	13·7	1·674	56·15
13·5	1·254	28·41	13	1·696	57·28
,,	1·274	30·20	12·5	1·703	57·42
13	1·309	33·07	13·7	1·706	57·64
,,	1·347	36·07	12	1·708	57·74
,,	1·382	38·68			

HI is absorbed by charcoal; according to Favre 22,000 gram thermal units are produced for every 128 grams HI absorbed (*A. Ch.* [5] 1, 209).

Reactions.—1. HIAq is decomposed by *electrolysis* to HIO_3Aq and H (Riche, *J.* 1858. 101). 2. HI is slowly decomposed in *sunlight*, the decomposition proceeds without limit (Lemoine, *J.* 1877. 139). When *mixed with oxygen* and exposed to sunlight, even when the gases are dry, decomposition occurs, and proceeds the more rapidly the greater the mass of O (dry HCl and HBr are not decomposed under the same conditious) (Richardson, *C. J.* 51, 801). HIAq is readily decomposed with separation of I by exposure to air.—3. HI is decomposed by *heat* to H and I, slowly at 180°, quickly at 440° (Hautefeuille, *Bl.* [2] 7, 198); the dissociation of HI has been exhaustively studied by Lemoine (*v.* DISSOCIATION, vol. ii. p. 400).—4. *Heated with oxygen* H_2O and I are formed.—5. *Chlorine* forms HCl and I; with excess of Cl, ICl_3 is produced; *bromine* reacts similarly.—6. *Sulphur* and *selenion* form H_2S, or H_2Se, and iodide of S or Se (Hautefeuille, *Bl.* [2] 7, 198); in presence of water I reacts with H_2S to form HIAq and S (*v. Preparation* No. 1).—7. HI is without actiou on *amorphous phosphorus* at 100°, but with *ordinary phosphorus*, even at the ordinary temperature, it forms P_2I_4. HIAq slowly reacts with excess of P to produce H_3PO_3 and PH_4I [$2P + HIAq + 3H_2O = PH_4IAq + H_3PO_3Aq$] (Damoiseau, *J.* 1880. 272).—8. Conc. *nitric acid* decomposes gaseous HI instantaneously.—9. Conc. *sulphuric acid* forms I, and also SO_2 and H_2S.—10. *Sulphur dioxide* forms S, I, and H_2O.—11. *Iodic acid* reacts with HIAq to form I and H_2O.—12. Very many *oxidisers* separate I with simultaneous formation of H_2O; *e.g.* H_2O_2Aq, HClOAq, $HClO_4$, chromates.—13. Many *metals* form iodides and evolve H, with HIAq.—14. *Metallic oxides* and *carbonates* generally form iodides and H_2O; *metallic peroxides* form the same products and also separate I.—15. HI produces pps. of iodides when added to solutious of *salts of metals* which form insoluble iodides, *e.g.* salts of Hg, Ag, Cu, Pd.—16. *Potassium permanganate* produces KIO_3.—17. HI reacts with *carbon compounds* generally, especially with such as contain the group OH, as au energetic reducing agent (*cf.* Berthelot, *Bl.* [2] 9, 8, 91, 178, 265).

Combinations.—1. HIAq dissolves several *metallic iodides*, *e.g.* BiI_3, HgI_2, PtI_2, and PtI_4; some of the solutions thus formed react with alkalis and alkaline hydroxides to form salts, which are probably derived from acids containing I and tho metal whose iodide was dissolved in HI; *e.g.* by dissolving AuI_3 in HIAq and adding KOH the salt $KAuI_4$ is obtained; by similar reactions the salts Na_2PtI_6, $MgPtI_6$, &c., are formed. Such reactions render it probablo that HI combines with many metallic iodides, and that the products frequently react as acids; one or two such acidic compounds have been isolated, *e.g.* $H_2PtI_6.9H_2O$ (*cf.* BROMHYDRIC ACID, *Reaction* 7, vol. i. p. 533; and CHLORHYDRIC ACID, *Reaction* 13, vol. ii. p. 8).—2. HI combines with *ammonia* to form NH_4I; [NH^3,HI] = 43,462 (*Th.* 2, 75).—3. With *phosphine* HI combines to form PH_4I; [PH^3,HI] = 24,100 (Ogier, *C. R.* 89, 705).

The solution of HI in water is attended with production of much heat [HI,Aq] = 19,207 (*Th.* 2,

34). Thomsen's measurements of the heat of solution of HIAq point to the existence of a hydrate $HI.H_2O$; the results are similar to those obtained for HClAq, but cannot be represented by so simple a formula (*cf.* CHLORHYDRIC ACID, vol. ii. p. 8).

The heat produced by diluting HI in nH_2O with quantities of water varying from 200 to 300 H_2O is given by Thomsen as follows (*Th.* 3, 76):—

n	$[HI.nH^2O,(300-n)H^2O]$
2	6670
3	4400
5	1830
10	630
20	220
50	70
100	30

The acids HI, HBr, and HCl are very similar in their properties and reactions. All dissolve very freely in water, forming solutions of monobasic acids, the affinities of which are great and approximately equal. All combine with certain metallic haloid compounds, especially with those of Hg, Au, Pt, and Pd, to form compounds which are best regarded as distinct acids. The thermal reactions attending the syntheses of the three acids show a gradation. Thomsen (*Th.* 2, 39) gives the following data:—

X [H,X] gaseous, at 180°, from gaseous elements.
Cl 22,153
Br 12,413
I −436

X [H,X,Aq]
Cl 39,315 gaseous Cl at 19°.
Br 32,197 } calculated on assumption that Br
I 18,619 } and I are gaseous at 19°.

Of the three acids HI is the most easily decomposed by heat and by oxidisers (*cf.* HALOGEN ELEMENTS, vol. ii. p. 665, where HF is compared and contrasted with the other haloid acids HX).

M. M. P. M.

IODHYDRIN *v.* GLYCERIN.

Di-iodhydrin *v.* DI-IODO-PROPYL ALCOHOL.

IODIC ACID *v.* IODINE, *Oxyacids of*, p. 19.

IODIDES. Binary compounds of I with more positive elements, *i.e.* with any element except O, F, Cl, or Br. Iodides of almost all metals, and binary compounds of I with all non-metals except B, have been isolated. Most metallic iodides may be obtained by direct combination of the elements; many are obtained by heating I with metallic oxides, or by dissolving metals or their oxides in HIAq; I reacts with alkalis and alkaline hydroxides to form iodides and iodates. Some non-metallic iodides are formed by direct union of the elements, *e.g.* iodides of H, Br, Cl, Se, S, and P; NI_3 is obtained by the reaction between I and NH_3Aq; CI_4 by the reaction of Al_2I_6 on a mixture of CCl_4 and CS_2. O and I combine indirectly; oxides of I are obtained by the action of oxidisers on I. The non-metallic iodides as a class are more easily decomposed by heat than the chlorides or bromides; oxide of I is much more stable than oxide of Cl, and no oxide of either Br or F has yet been isolated. If two chlorides or bromides of a specified metal are known, the more stable iodide of that metal as a general rule corresponds to the lower chloride or bromide, *e.g.* $SbCl_3$ and $SbCl_5$ exist, but only SbI_3; $FeCl_2$ and $FeCl_3$ are stable, but if FeI_3 exists it very easily goes to FeI_2 and I; similarly with CuI_2, which exists only in solution, and very readily parts with I becoming CuI, whereas $CuCl_2$ is more stable than CuCl. In their reactions with water metallic iodides are usually less easily decomposed than the corresponding bromides and chlorides. Metallic iodides as a class dissolve in water without change; some, however, form oxyiodides, *e.g.* SbI_3 and BiI_3; and some form oxides and HIAq, *e.g.* SnI_2. Metallic iodides, generally speaking, are not so readily volatilised as chlorides or bromides; most of them are unchanged by heat, but some are decomposed to metal and I, *e.g.* iodides of Au, Pt, and Pd. As a whole, then, the metallic iodides are not so numerous or so varied in composition as the chlorides or bromides, and they are more stable towards heat and the action of water than the chlorides and bromides; they are also less easily reduced, *e.g.* by H or CO, than the chlorides or bromides.

The heat of formation of a metallic iodide is usually considerably less than that of the bromide or chloride of the same metal. The following data are taken from Thomsen:—

X	[Na, X, Aq]
Cl	193,020
Br	171,160
I	140,600
X	$[Ca, X^2, Aq]$
Cl	187,230
Br	165,360
I	134,940
X	$[Al^2, X^6, Aq]$
Cl	475,650
Br	410,040
I	318,780

The difference between the heat of formation in aqueous solution of a chloride and the analogous bromide of the same metal is approximately $n21,850$, and the difference in the case of a chloride and analogous iodide is approximately $n52,250$. Some metallic iodides exhibit differences in crystalline form and S.G.; for instance SbI_3 forms hexagonal crystals, and also exists in trimetric and in monoclinic forms; CdI_2 probably exists as a white salt S.G. 5·644 unchanged at 250°, and also as a brownish compound S.G. 4·626, which begins to change at 40° (*v.* vol. i. p. 656); there are also differences between BiI_3 according as it is prepared by sublimation or by ppn.

Iodides are usually decomposed when heated in Cl or Br with production of chlorides or bromides and I; heated in HCl they generally form chlorides and HI. Heated with conc. H_2SO_4, or conc. HNO_3, I is separated, and SO_2 (also sometimes H_2S), or NO_2, is evolved. I is separated from iodides by the action of many oxidising agents, such as CrO_3, ferric salts, MnO_2, &c.

Many metallic iodides dissolve freely in solutions of the alkali iodides, frequently with formation of double iodides. An aqueous solution of KI dissolves much I, with formation of KI_3, but the greater part of the I thus dissolved is ppd. on largely diluting the liquid. Some other periodides analogous to KI_3 are known; part of the I in such compounds is more loosely combined than the rest, and can generally be removed very easily; CuI_2 in solution, for instance,

is reduced to CuI by shaking with CS_2. Some iodides, *e.g.* PtI_4, HgI_2, combine with HI to form compounds which are best regarded as metallic acids (H_2PtI_6, H_2HgI_4, &c.). Some of the resemblances and differences between the three allied classes, chlorides, bromides, and iodides, are considered in the article HALOGENS, BINARY COMPOUNDS OF THE (vol. ii. p. 666).

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IODINE. I. At. w. 126·53. Mol. w. 253·06 (*v. infra*). [113°–115°] (Stas); [114·15°] (Ramsay a. Young, *C. J.* 49, 460): solidifies at 113·6° (Regnault, *J.* 1856. 41); (200°) (Stas); (184·35°) at 760 mm. (R. a. Y., *l.c.*). Sublimes *in vacuo* without melting (L. Meyer, *B.* 8, 1627). S.G. 4·917 at 40·3°, 4·886 at 60°, 4·857 at 79·6°, 4·841 at 89·8°, 4·825 at 107°, 4·004 liquid at 107°, 3·866 liquid at 151°, 3·796 liquid at 170°; vol. increases for 1° by ·000235 (Billet, *J.* 1855. 46). V.D. c. 250°–1000° 125-127; c. 1500° 68 (*v. Properties*, p. 10). S.H. (solid 9°–98°) ·05412 (Regnault, *A. Ch.* [2] 73, 1). S.H.p. for I vapour at 206°-377° (equal wt. of water = 1) ·03369 (Strecker, *W.* 17, 85); $\frac{\text{S.H.p.}}{\text{S.H.v.}}$ 1·294 at 220°–375° (Strecker, *W.* 13, 20). Heat of fusion = 11,710; heat of vaporisation = 23,950 (Favre a. Silbermann, *A. Ch.* [3] 37, 461). For vapour pressures of solid I from 58° to 114°, and of liquid I from 114° to 185°, *v.* Ramsay a. Young, *C. J.* 49, 458. S.V.S. 25·9. S. ·018 at 10°–12° (Wittstein, *J.* 1857. 123); ·015 at 6·3° (Dossios a. Weith, *Z.* 1869. 379); S. in glycerin = 1. (Regarding solubility *v.* further under *Properties*.) The absorption-spectrum of I vapour shows numerous fine lines extending from the red to the violet. As the thickness of the layer increases absorption becomes very marked in the red; but even when the whole of the red part is obscured, the violet portion remains without bands (Plücker, *J.* 1863. 109; Thalen, *P.* 139, 503; *cf.* Conroy, *J.* 1876. 146; and Salet, *A. Ch.* [4] 28, 29). The emission-spectrum shows many bright lines in the yellow-green and yellow. By using an induction-current of low tension lines are seen coincident with the dark absorption-lines (Salet, *l.c.*; Wüllner, *P.* 120, 158); at red heat a continuous spectrum is observed. I crystallises very easily from alcohol or HIAq, or by sublimation; the crystals are trimetric, $a:b:c$ = ·4866:1: ·7324 (Mitscherlich, *B. B.* 1855. 416).

Iodine was discovered by Courtois in 1811 in the mother-liquor of kelp after preparation of Na_2CO_3. Davy (*T.* 1814. 74) and Gay-Lussac (*A. Ch.* 88, 311, 319; 91, 5) showed I to be an element, and established its relationship to chlorine.

Occurrence.—Certain mineral waters contain small quantities of free I. According to Wanklyn (*C. N.* 54, 300), the water of Woodhall Spa, near Lincoln, is coloured slightly brown by free I. Iodides of Na and Mg, and iodate of Mg according to Sonstadt (*C. N.* 25, 196, 231, 241), occur in small quantities in sea-water; alkaline iodides are found in very many mineral waters; in the ashes obtained by burning sea-plants, and some sea-animals; and in certain specimens of Chili saltpetre, dolomite, phosphates, and some other minerals. Iodides of Hg, Ag, and Pb occur in small quantities in Mexico.

Formation.—1. By decomposing alkaline iodides by MnO_2 and H_2SO_4, or by Cl, or by $K_2Cr_2O_7$ and H_2SO_4, or by NO_2.—2. By heating an acidified solution of an iodide with $FeCl_3Aq$. 3. By reducing $NaIO_3$ by SO_2

$$(2NaIO_3Aq + 5SO_2 + 4H_2O = 2NaHSO_4Aq + 3H_2SO_4Aq + I_2).$$

Preparation.—The greater part of the I of commerce is prepared from *kelp*, which is the product of burning sea-plants; the kelp is lixiviated with hot water, and the liquid is evaporated in successive stages until most of the salts except NaI, Na_2S, and $Na_2S_2O_3$ have been removed. Enough H_2SO_4 is added to decompose the S compounds. After exposure to the air for some time S separates, and SH_2 and SO_2 escape. The liquid is then run off and distilled with addition of more H_2SO_4 and MnO_2, and the I is collected in a series of tubulated receivers luted one into the other. For details of manufacture *v.* DICTIONARY OF APPLIED CHEMISTRY. The I obtained as described is dried and sublimed. By slow resublimation fairly pure I is obtained, but ICy cannot thus be removed.

The chief impurities in commercial I are chlorides, water, traces of various salts, and sometimes ICy.

Stas (*Chem. Proport.* 137) gives two methods for preparing pure I:—1. KI is dissolved in its own weight of water, the solution is saturated with I (about 4 parts I are required to 1 part KI), water is added until formation of a permanent pp. begins. After settling, the liquid is poured off and shaken with $\frac{3}{4}$ of the quantity of water required to bring down all the I which can be ppd. by this method (the amount of water is determined by a preliminary experiment on a small quantity of the liquid). The separated I is washed by decantation until the washings are free from K, distilled with water from a large retort, allowed to drain, placed over dry $Ca2NO_3$, which is frequently changed (all other drying materials bring impurities into the I), and finally twice distilled after mixing with 5 p.c. finely-powdered pure BaO. The last traces of H_2O and traces of HI are thus removed.—2. N iodide is prepared by adding powdered I to cold conc. NH_3Aq until the dark-brown liquid is nearly colourless; the compound is washed by decantation with cold conc. NH_3Aq until NH_4I is removed, placed on a funnel, the neck of which is drawn to a fine point, and covered with cold water. When the black colour of the compound changes to brownish, and the wash-water is coloured yellowish brown, the moist iodide is placed in ten times its weight of water contained in a large glass balloon, and slowly heated on a water-bath to 60°–65°, when decomposition occurs with formation of crystals of I, solution of I in NH_4IAq, and a white salt, which is probably NH_4IO_3. When the change seems completed the liquid is warmed to 100° for a few minutes; if the temperature is at once raised above 65° decomposition occurs very rapidly, at 100° it proceeds with explosive violence, at the ordinary temperature the change is very slow. After cooling, the solid which separates is thrown on to a funnel with drawn-out neck and washed with water; it is then distilled with water from a retort (NH_4IO_3 is not

volatilised), and the I is dried over $Ca2NO_3$, and finally by distilling with pure BaO as in 1.

Recovery of iodine from laboratory residues. Beilstein (*Z.* 1870. 528) recommends to evaporate with excess of Na_2CO_3, to heat the residue until it is white, to add excess of H_2SO_4, and to pass in N oxides, obtained by heating starch with HNO_3, until all I has separated; to wash the I in cold water, dry over H_2SO_4, and sublime slowly. The stream of N oxides is best obtained by adding 15 grams starch to about 90 grams fairly conc. HNO_3Aq in a large flask (the acid must not be added to the starch, else the latter may cake on the bottom of the flask and cause it to break), heating till red fumes appear, and then removing the flame and cooling from time to time, if necessary, by cold water. If insoluble iodides, *e.g.* HgI_2, are present, Henry (*B.* 2, 599) heats with water and granulated Zn or Fe filings, whereby soluble ZnI_2 or FeI_2 is produced. The final sublimation of the recovered I may conveniently be conducted as described by Mohr. The rim of a flat porcelain basin is ground with sand, so that a glass plate placed on the basin touches the rim in every part; the I is placed in the basin, a little finely powdered KI is strewed on the surface, the glass plate is placed in position and bound to the rim by a strip of paper, and the basin is placed on a sand-tray and *very slowly* heated. The process of sublimation should occupy several days. If any ICl is present it reacts with the KI to give KCl and I.

Properties.—A greyish-black, soft, solid with metal-like lustre. Perfectly pure I is described by Stas as quite black, whether solid or liquid. Only the thinnest plates of I are transparent (*cf.* Schultz-Sellack, *P.* 140, 334). I is very easily vaporised; the vapour corrodes the skin and mucous membranes; unsaturated vapour has a violet colour, saturated vapour appears deep blue in thin layers (Stas); a layer 10 centims. thick is quite impervious to light (*cf.* Andrews, *C. N.* 24, 75). I vapour shows orange-yellow fluorescence (Lommel, *W.* 19, 356); solid I does not fluoresce (Stokes). Crystals of I polarise light (Conroy, *J.* 1876. 147). I is a non-conductor of electricity (Jolly, *P.* 37, 420). I dissolves freely in solutions of alkaline oxides and in HIAq; it is more soluble in solutions of NH_4 salts than in water. Dossios a. Weith (*Z.* 1869. 379) give the following numbers for the S..of I in KIAq:

S.G. at 7·9°	P.c. KI	P.c. I	S.G. at 7·9°	P.c. KI	P.c. I
1·0234	1·802	1·173	1·1382	8·663	7·368
1·0433	3·159	2·303	1·1637	10·036	8·877
1·0668	4·628	3·643	1·1893	11·034	9·949
1·0881	5·935	4·778	1·2110	11·893	11·182
1·1112	7·201	6·037	1·2293	12·643	12·060

I is more soluble in solution of tannic acid than in water; addition of ·015 parts of the acid increases S. to ·42 at c. 30°, and when 3·3 parts acid are present S. is ·24 at 12° (Koller, *Z.* 1866. 380). I is very sol. in CS_2, $CHCl_3$, ether and alcohol, C_6H_6 and various hydrocarbons; also sol. in SO_2 (Sestini, *Z.* 1868. 718), and in SO_3 (Weber, *J. pr.* 25, 224); solutions in ether or alcohol contain HI (*cf.* Carles, *Ph.* [3] 5, 88). Addition of CS_2 to an aqueous solution of I causes withdrawal of most of the I from the water; according to Berthelot a. Jungfleisch c. 400 parts of the I go into solution in the CS_2 for each part remaining in the water (*C. R.* 69, 338). Solutions of I in CS_2, $CHCl_3$, C_6H_6 and other liquid hydrocarbons are violet; solutions in ether, alcohol, and some other solvents are reddish-brown. The reddish solutions absorb light in the violet end of the spectrum up to midway between D and E; conc. violet solutions absorb the rays of mean refrangibility to the limits of the yellow and blue; very conc. solutions absorb all rays except the ultra-violet (*cf.* Vogel, *B.* 11, 919).

The at. w. of I has been determined:—1. By changing AgI into AgCl (Berzelius, *P.* 14, 558; Dumas, *J.* 1859. 3).—2. By synthesis of ZnI_2 (Gay-Lussac, *A. Ch.* 91, 5).—3. By synthesis of AgI (Marignac, *Bibl. Univ. Genève*, 46, 367; Stas, *Chem. Proport.*).—4. By determining the quantity of KI required to ppt. a known quantity of Ag dissolved in HNO_3 (Marignac, *l.c.*).—5. By analysis of $AgIO_3$ (Stas, *l.c.*).—6. By determining V.D. of many binary compounds.—7. By measuring S.H. of I.

Attempts have been made to determine the mol. w. of I in solution. Paterno a. Nasini (*B.* 21, 2153) measured the lowering of the freezing-point of benzene and acetic acid produced by dissolving I in these liquids; the results point to the existence of molecules of I_2 in very dilute benzene solutions, and more complex molecules in more conc. solutions; the numbers got with acetic acid lead to a mol. w. between I and I_2. Loeb (*C. J.* 53, 805) determined the vapour-pressure of I in solution in CS_2 and ether; ethereal solutions of I are reddish brown, solutions in CS_2 are violet; Loeb's results point to the mol. w. I_4 in red solutions, and a mol. w. between I_3 and I_2 in violet solutions.

Determinations of the S.G. of I vapour, by Gay-Lussac, Dumas, Bineau, Deville a. Troost, up to c. 1000° gave values from 8·78 to 8·62 (calc. for $I_2 = 8·75$). V. Meyer (*B.* 13, 401, 1723; 14, 1453) obtained the following results:—8·86 at 293°, 8·72 at c. 586°, 6·76 at c. 842°, 5·75 at c. 1027°, 5·7 at c. 1570°. Crafts a. Meier (*B.* 13, 870; *C. R.* 92, 39) obtained similar results; the S.G. remained constant (8·8) to c. 700°, even when pressure was diminished, but decreased above that temperature, and decreased the more rapidly the more the pressure was lowered; the S.G. decreased with rising temperature rapidly to a certain point and then more slowly; at a pressure of 230 mm. S.G. became constant at 1400°–1500° and was 4·6; at 152 mm. S.G. became constant at c. 1400°; at 76 mm. a constant value for S.G. was obtained at c. 1350°. At c. 1700° V. D. corresponds with molecular weight = I (Biltz a. Meyer, *B.* 22, 725). There can be little doubt that these results prove a gradual dissociation of I_2 into I (S.G. calc. for I = 4·375) (*cf.* DISSOCIATION, vol. ii. p. 394; *v.* also Naumann, *B.* 13, 1050). The molecule I_2 is more easily dissociated than either of the molecules Br_2 or Cl_2.

The atom of I is monovalent in gaseous molecules. I acts as a non-metallic element; it is negative to all elements except O, F, Cl, and Br. I combines directly with most of the metals, and with some of the non-metals, *e.g.* H, Br, Cl, Se, S, and P; binary compounds of I with all non-metals except B have been isolated. I is closely related to F, Cl, and Br; the relationship is con-

sidered in the article HALOGEN ELEMENTS, vol. ii. p. 664; *cf.* also IODIDES in this vol. p. 13.

Reactions.—1. I dissolves very slightly in *water*; the solution probably contains traces of HI. According to Cross a. Higgins (*C. J.* 35, 225) I dissolves slightly in water at 100° in a sealed glass tube with production of a little alkaline iodide and iodate. Electrolysis of IAq yields HIO_3Aq (Riche, *J.* 1858. 101).—2. I does not react directly with *oxygen*, even when I and O are heated to c. 300° in presence of spongy Pt (Wehsarg, *B.* 17, 2896). Ogier (*C. R.* 86, 722) says that if I vapour and O are subjected to the silent discharge, all the oxides of I are produced.—3. *Hydrogen peroxide* produces HIAq and O, but conc. HIAq is decomposed by H_2O_2 with separation of I.—4. *Hydrogen sulphide* is decomposed by I in presence of water forming HI and S; dry H_2S does not react with I.—5. With solutions of *caustic alkalis*, I forms alkaline iodide and iodate; according to Van Deventer a. Van't Hoff, KIO is also formed (the proof of this is indirect, *C. C.* 1888. 362).—6. *Ammonia gas* forms NH_4I and N (*v. Combinations*, No. 2); *ammonia solution* forms NH_4IAq and N iodide. 7. When I is shaken with *lime* suspended in water, a bleaching liquid is obtained which reacts as if it contained Ca hypoiodite $Ca(IO)_2$ and CaI_2 (Lunge a. Schock, *B.* 15, 1883).—8. I vapour heated with *oxides* or *carbonates of the alkaline earth metals*, in presence of oxygen yields periodates without formation of oxyiodides; with *lead oxides* various oxyiodides are produced (Cross a. Sigiura, *C. J.* 33, 405).—9. I is oxidised to I_2O_5 by *nitric acid*, *chromic anhydride*, *chlorates*, and some other oxidisers.—10. I in presence of water acts as an oxidiser towards some salts and other easily oxidised compounds; *arsenious oxide* and *arsenites* are oxidised to As_2O_5 and arsenates in alkaline solutions. *Sulphurous acid* is oxidised to H_2SO_4, *sodium thiosulphate* is oxidised to $Na_2S_4O_6$ and a little $NaHSO_4$ (Pickering, *C. J.* 37, 128).—11. With some *carbon compounds* I reacts to substitute I for H, but the HI formed tends to reproduce the original compound, so that the reactions of I with C compounds are much less marked than those of Cl and Br.—12. I dissolved in CS_2 reacts with ppd. *arsenious sulphide* (not with orpiment) to give AsI_3 and S; at a higher temp. As_2S_3 and I are re-formed; by distilling As_2S_3 and I in the ratio As_2S_3 : 6I and heating the distillate in a sealed tube to 72° $(AsI_3)_2SI_6$ was obtained (Schneider, *J. pr.* [2] 36, 498).

Combinations.—No combination of I with H_2O has been isolated.—1. With most *metals*, and with many *non-metals*, especially with H, Cl, Br, S, Se, P, As. According to Holzmann (*B.* 22, 869) Na is scarcely attacked by I when the pure elements are heated to 300°. Fe and I combine by shaking Fe filings with I in presence of water; FeI_2 is produced, and also Fe_2O_3 and HI probably by the formation and decomposition of FeI_3 (Fleury, *J. Ph.* [5] 16, 529).—2. *Ammonia* forms several compounds with I; the dry gas is absorbed forming a dark-blue liquid; the volume of NH_3 absorbed varies with temperature, at 20° it corresponds to $3NH_3.2I$, at 80° to NH_3I, at 0° to $(NH_3)_2I$, at −10° to $(NH_3)_5I_2$ (Raschig, *A.* 241, 253; *cf.* Bineau, *A. Ch.* [3] 15, 80; Millon, *A.* 62, 54).

Detection and Estimation.—Free I is detected in solution by the colour which it gives to CS_2 or $CHCl_3$; and by the formation of a deep-blue colour when a drop of starch-paste is added (*cf.* Béchamp, *Fr.* 14, 66; Mylius, *B.* 20, 688; Personne, *C. R.* 74, 617; Duclaux, *C. R.* 74, 533; Goppelsröder, *P.* 119, 57; Hlasiwetz, *W. A. B.* 1867. 131). I in soluble iodides is detected by adding a very little Cl water, or a drop of a solution of NO_2 in conc. H_2SO_4, and then a little starch-paste. Iodates are reduced to iodides by SO_2Aq; alkaline iodates mixed with alkaline iodides and a drop of a weak acid, *e.g.* tartaric, give free I. Many insoluble iodides may be converted into soluble ZnI_2 by treatment with Zn and dilute H_2SO_4Aq. Most non-metallic iodides are decomposed by water or caustic alkalis giving HI or alkaline iodide. I is estimated gravimetrically by ppn. as AgI; iodates are reduced by SO_2Aq and then ppd. by $AgNO_3Aq$. Volumetrically I is estimated by titration with standard $Na_2S_2O_3Aq$, or standard As_2O_3 dissolved in $NaHCO_3Aq$. The water in samples of ordinary I may be determined by mixing with a weighed quantity of Hg, rubbing up with a little alcohol, and carefully drying at 100°; loss of weight = water (Bolley, *D. P. J.* 126, 40). The quantity of I may be determined by dissolving in a conc. solution of an alkali sulphite, filtering, ppg. by $AgNO_3Aq$, washing pp. with NH_3Aq to remove AgCl and AgBr, boiling with H_2O containing a little $AgNO_3$ to remove Ag_2SO_4, washing the residual AgI, and weighing it, after drying, in the usual manner (Hesse, *A.* 122, 225).

Iodine, bromides of. Two bromides of I are known, IBr and IBr_5, but neither has been gasified; attempts to prepare IBr_3, analogous to ICl_3, have failed (Bornemann, *A.* 189, 183). The combination of I with Br has been studied by Balard (*A. Ch.* 32, 337), Lagermark (*B.* 7, 907), and Bornemann (*A.* 189, 201).

IODINE MONOBROMIDE IBr. Formula not necessarily molecular, but probably so, from analogy to ICl which has been gasified. Prepared by heating I with rather more than the calculated quantity of Br to 25°–50° in a retort, removing excess of Br by a stream of CO_2, and allowing to cool. Forms dark-greyish, iodine-like crystals, melting at 36°; probably sublimes with only partial decomposition; smells of Br, the vapour attacks the eyes and mucous membranes. The vapour appears red in thick strata (Gernez, *C. R.* 74, 1190). Soluble in alcohol, $CHCl_3$, CS_2, and ether; slowly decomposed by water with separation of I. Berthelot (*A. Ch.* [5] 21, 370) gives the H. F. of solid IBr from solid I and liquid Br as [I, Br] = 2470. A hydrate $IBr.5H_2O$ described by Löwig is merely a mixture of IBr and ice.

IODINE PENTABROMIDE IBr_5. A dark-brown liquid obtained by heating excess of Br with I; soluble in water; with alkali solutions forms bromide and iodate; solution in sunlight decomposes to HBr and HIO_3.

Iodine, carbide of, better called **Carbon iodide**; *v.* vol. i. p. 689.

Iodine, chlorides of. I combines rapidly with Cl even at −90° (Donny a. Mareska, *C.R.* 20, 817). Two chlorides of I have been isolated, ICl and ICl_3; ICl can be gasified without decomposition, ICl_3 decomposes when heated. Kämmerer (*J. pr.* 83, 83; *cf. B.* 8, 489, *note*) asserted

the probable existence of a tetrachloride ICl_4, but the non-existence of this compound has been proved (*cf.* Hannay, *C. J.* 35, 169); Brenken (*B.* 8, 487) failed to procure any higher chloride by passing Cl over strongly cooled ICl_3. By adding I to liquid Cl, Hannay (*C. J.* 35, 169) obtained a reddish liquid when the elements were present in the ratio I : 5Cl, but on removing pressure or raising temperature Cl was at once evolved.

Iodine monochloride. ICl. Mol. w. 161·9. [24·2°]; (101·3°); S.G. $\frac{0°}{4°}$ 3·18223 (Thorpe, *C. J.* 37, 174). H.F. [I, Cl] = 2,100 (solid ICl from gaseous Cl and solid I), 6,700 (solid ICl from gaseous constituents) (Berthelot, *A. Ch.* [5] 21, 370). V.D. 80·29 at 120°, 83·2 at 512° (Hannay, *C. J.* [2] 11, 819). Absorption-spectrum of vapour *v.* Gernez, *C. R.* 74, 660.

Preparation.—1. By passing dry Cl over carefully dried I till liquefaction occurs and purifying by distillation with a gram or two of I.—2. By heating an intimate mixture of I with 4 parts $KClO_3$ and distilling the product from powdered $KClO_3$ ($I_2 + 3KClO_3 = KClO_4 + KIO_3 + KCl + O_2 + ICl$).—3. By boiling I with excess of *aqua regia*, diluting with water, shaking with ether and evaporating the ethereal liquid (Bunsen, *A.* 84, 1).

Properties.—ICl seems to exist in two forms; a reddish-brown oily liquid (Gay-Lussac, *A. Ch.* 91, 5), and a hyacinth-red solid (Schützenberger, *Z.* 5, 1). Thorpe (*C. J.* 37, 175) says that ICl remains liquid in a closed vessel for weeks even in a freezing mixture but solidifies on addition of a minute fragment of ICl_3. If the liquid ICl is exposed to the air it solidifies after a time and is partially changed to ICl_3 and I (*cf.* Hannay, *C. J.* [2] 11, 815; Bornemann, *A.* 189, 183). According to Stortenbeker (*R. T. C.* 7, 152), two forms of solid ICl exist, one forming dark-red needles melting c. 27° obtained by cooling the liquid ICl to −25°, and another crystallising in dark-red plates melting at c. 14° obtained by crystallising the liquid between −10° and +5°. ICl smells of I and Cl, it attacks all mucous membranes rapidly and forms very bad sores if let fall on the skin; decolourises indigo, does not give blue colour with starch (*cf.* Christomanos, *B.* 9, 434). ICl dissolves in alcohol, also in HClAq. Can be distilled with only very slight decomposition (Schützenberger, *Z.* 5, 1; *cf.* Bornemann, *A.* 189, 183).

Reactions.—1. *Water* decomposes ICl forming HCl, HIO_3, and I (Hannay, *C. J.* [2] 11, 820). According to Schützenberger (*l.c.*) a compound ICl.HCl is formed (besides HIO_3 and I) by the reaction of water with ICl (*cf.* also Trapp, *J.* 1854. 310; and Bornemann, *A.* 189, 184).—2. *Potash solution* produces KIO_3 and KI with separation of I (H., *l.c.*).—3. *Ammonia solution* forms NH_4Cl, and N iodide which combines with a portion of the NH_3 (Bunsen, *A.* 84, 1).—4. Distilled repeatedly with *potassium iodide*, KCl and I are formed.—5. Dissolves in *carbon disulphide*; when a saturated solution is distilled CCl_4 and $CSCl_2$ are formed (H., *l.c.*).—6. With many *metals* ICl reacts to form chlorides and iodides (H., *l.c.*), *e.g.* with Hg, Sn, Sb, Bi, Al, Mg, Na.—7. With *mercuric oxide*, *cupric oxide*, and *lead peroxide*, forms chlorides and iodides with evolution of O and separation of I.—8. *Hypochlorites* and *chlorates* produce iodates with evolution of Cl (Henry, *B.* 3, 892).—9. *Mercuric chloride* forms a pp. of HgI_2 (Kane, *J. pr.* 11, 250).—10. Stannous chloride produces $SnCl_4$ and SnI_2.

Combination.—With *hydrogen chloride* to form HCl.ICl; a yellow, volatile, unstable compound; produced by dissolving ICl in water, extracting with ether, and evaporating (Schützenberger, *C. R.* 84, 389).

Iodine trichloride ICl_3 Mol. w. unknown; decomposed by heat to ICl and Cl. S.G. c. 3·1107 (Christomanos, *B.* 10, 789). [25°] (Trapp, *J.* 1854. 310); [33°] (Christomanos, *l.c.*). H.F. (Berthelot, *A. Ch.* [5] 21, 370) [I, Cl^3] = 21,700 solid ICl_3 from gaseous constituents; 16,300 solid product from solid I and gaseous Cl; [ICl, Cl^2] = 9,500 solid product from solid ICl and gaseous Cl. According to Brenken (*B.* 8, 487) ICl_3 is partially decomposed when it is melted. Stortenbeker (*R. T. C.* 7, 152) gives M.P. as varying from 20° to 60°, but says that at pressure of 16 atmos. the M.P. is definite and = 101°.

Preparation.—1. By leading excess of dry Cl over I or ICl until yellowish-red crystals are formed, and then subliming at as low a temperature as possible in a stream of Cl (Brenken, *B.* 8, 487).—2. By the action of HCl on warm powdered HIO_3; Cl is evolved (Ditte, *A.* 156, 335). 3. By the action of PCl_5 on I_2O_5.—4. Christomanos (*B.* 10, 434, 789) recommends to lead dry Cl and dry HI into a well-cooled glass receiver, keeping the Cl in excess ($HI + 4Cl = HCl + ICl_3$; if HI is in excess the reaction $HI + ICl_3 = HCl + 2ICl$ occurs). To prepare small quantities of ICl_3, say, in a bulb tube, Christomanos leads dry Cl through the tube, cools the place where the ICl_3 is to be deposited, then allows dry HI to stream through the tube, and finally leads dry Cl again, all parts of the apparatus being gently warmed except that where the ICl_3 is to be formed.

Properties.—A citron-yellow, crystalline, deliquescent solid. Very disagreeable smell; attacks the eyes and nose. Can be kept unchanged only in dry Cl (Hannay; Christomanos). In air sublimation with partial decomposition begins even at −12° (C.). Complete decomposition into ICl and Cl occurs at c. 70°–80°, even in an atmosphere of Cl at pressure of 760 mm. (Melikoff, *B.* 8, 490). According to Brenken (*B.* 8, 487) ICl_3 does not melt when heated, but decomposes even in an atmosphere of Cl into ICl and Cl at c. 25°, the temperature varying according to the pressure. ICl_3 is sol. water, with partial change to ICl, HCl, and HIO_3; at 100° this change occurs suddenly and completely (Bornemann, *B.* 10, 121; Christomanos, *l.c.*). Sol. benzene, sol. conc. H_2SO_4.

Reactions.—1. With *water* to form ICl, HCl, and HIO_3; in cold water a part of the ICl_3 remains unchanged; in hot water the change is complete; at 100° it occurs very rapidly.—2. With *caustic alkalis*, chloride and iodide, chlorate and iodate, of the alkali are produced (Christomanos, *l.c.*).—3. With excess of *ammonia*, NH_4Cl, NH_4I, and NI_3 are formed (C.).—4. *Nitric acid* produces Cl and I (C.).—5. *Hydrogen iodide* in excess forms ICl and HCl (C.).—6. *Carbon disulphide* produces some S chloride, the solution contains

$SI_2.xI$ (C.) (*cf.* Weber, *P.* 128, 459).—7. *Carbon dioxide* passed over ICl_3 forms a little $COCl_2$ (C.). 8. ICl_3Aq shaken with *silver oxide* forms AgCl and HIO_3, heated with excess of Ag_2O, Ag periodate (Philipp, *B.* 3, 4).—9. *Hydrogen* has no action at the ordinary temperature; when the ICl_3 is slightly warmed HCl + ICl are produced; at a higher temperature HCl, HI, and I are obtained (C.).—10. *Potassium* and *phosphorus* burn in ICl_3, forming chlorides and iodides (C.).—11. ICl_3 oxidises hot *sulphurous acid* solution to SO_3Aq, and hot *ferrous sulphate* solution to ferric sulphate (C.).—12. On *carbon compounds* the action of ICl_3 is to chlorinate; *e.g.* $C_2H_4O_2$ even in the dark forms $C_2H_3ClO_2$ with simultaneous production of HCl and ICl.

Iodine, cyanides of. Better called CYANOGEN IODIDE, *v.* vol. ii. p. 313; and CYANURIC IODIDE, *v.* vol. ii. p. 320.

Iodine, fluoride of. IF_5. A colourless, strongly smelling and fuming liquid; does not solidify at −20°; obtained by decomposing AgF by I. Attacks glass and Si at red heat; no action on Hg or Pt; decomposed by water to HIO_3 and HF (Gore, *C. N.* 24, 291; MacIvor, *C. N.* 32, 232).

Iodine, hydride of, *v.* IODHYDRIC ACID, p. 11.

Iodine, nitride of. Better called NITROGEN IODIDE (*q. v.* in this vol.).

Iodine, oxides of. The only oxide of I which has been certainly isolated is I_2O_5; the existence of IO_2 is probable. Other oxides have been described, but the proofs of their isolation are very meagre. I and O do not combine directly; Wehsarg (*B.* 17, 2896) passed I and O over spongy Pt heated to c. 300° without obtaining any compound. According to Ogier (*C. R.* 86, 722) when a mixture of I vapour and O is submitted to the silent electric discharge all the oxides of I are produced. I_2O_5 is the anhydride of HIO_3, which acid is known as a definite stable solid; IO_2 (if it exists) is not an anhydride, it is said to combine with H_2SO_4. The hypothetical anhydride of periodic acid, I_2O_7, has not been isolated. The heat of formation of I_2O_5 is a large positive quantity = c. 45,000. I_2O_5 is a much more stable body than any of the oxides of Cl; no oxide of Br or F has been isolated.

IODINE PENTOXIDE. I_2O_5. (*Iodic anhydride.*) Mol. w. unknown, as oxide has not been gasified. S.G. $\frac{0°}{}$ 4·487 (Ditte, *A. Ch.* [4] 21, 5); S.G. $\frac{9°}{}$ 4·7987 (Kämmerer, *J. pr.* 79, 94). C.E. 0°–51° = ·000066. H.F. from solid I $[I^2, O^5] = 45{,}029$; $[I^2, O^5, Aq] = 43{,}237$; $[I^2O^5, Aq] = -1{,}792$ (*Th.* 2, 164). S. = 187·4 at 13°; S.G. of this solution = 2·1269 (Kämmerer, *P.* 138, 390). A white crystalline solid; crystals belong to trimetric system (Schabus, *J.* 1854. 310). Produced by slowly heating dry HIO_3 to 170°. Melts when heated to c. 300°, with decomposition into I and O. When HIO_3 crystallises from solutions containing H_2SO_4, crystals of I_2O_5 are said to accompany the HIO_3 (Rammelsberg). Sol. water; insol. ether, alcohol, $CHCl_3$, CS_2, or C_6H_6 (Ditte, *C. R.* 70, 621). I_2O_5 dissolves in water to form HIO_3. The general reactions of I_2O_5 are those of an oxidiser: CO passed over warmed I_2O_5 forms CO_2 and I; SO_2 gives SO_3; H_2S produces HI, H_2O, S, and I; HCl forms ICl_3 and H_2O; NH_3 on heating gives H_2O, N, and I (Ditte, *l.c.*). NO does not react with I_2O_5 (Kämmerer, *J. pr.* 79, 94).

Combinations.—1. According to Kämmerer (*J. pr.* 83, 72) when dry SO_2 is passed over I_2O_5 heated to 100°, a part of the SO_2 is oxidised to SO_3, a little I being separated, and then a yellow crystalline compound $5I_2O_5.SO_3$ is formed. As soon as the compound is formed the SO_2 must be stopped. The compound is decomposed by moisture, even by exposure to ordinary air. Ditte (*C. R.* 70, 621) says that in this reaction only I and SO_3 are produced. According to Weber (*B.* 20, 87) the compound $I_2O_5.3SO_3$ is formed by heating the constituents in a sealed tube to c. 60°, and pouring off excess of SO_3; the compound is decomposed above 60°.—2. By heating HIO_3 slowly to 30°–40°, or more quickly to 130°, the hydrate $3I_2O_5.H_2O$ is said to be formed. Ditte, however, says this is only a mixture of I_2O_5 and HIO_3.

Nitroso-derivative (?). By treating perfectly dry finely-powdered I with c. 10 times its weight of the most conc. HNO_3Aq, or a mixture of equal parts of conc. HNO_3Aq and H_2SO_4, a loose flocculent yellow powder is obtained. This substance was regarded by Millon (*J. pr.* 34, 319) to be a compound of I, O, and HNO_3; according to Kämmerer (*J. pr.* 83, 65) it is $I_2O_4(NO)_2$, but no analyses are given. The substance is extremely unstable, it cannot be dried over CaO without decomposition; it is decomposed by water to HNO_3, HIO_3, and I. Heated in CO_2, NO_2 and I_2O_4 are formed.

IODINE DIOXIDE OR TETROXIDE. IO_2 or I_2O_4. This substance probably exists as a definite compound. One part of perfectly dry I is rubbed in a basin with 10–12 pts. conc. HNO_3Aq S.G. at least 1·486, until a loose flocculent yellow powder is produced (*v. supra*); excess of acid is poured off, the powder is placed in a funnel stopped with asbestos, and is then dried on a porous tile, and finally over lime; HIO_3 and I are then removed by washing with water and then with alcohol (Millon, *J. pr.* 34, 319, 337). IO_2 is described as a sulphur-yellow powder, unchanged in air, decomposed to I and HIO_3 by heating in air to 170°–180°, insol. cold water, but decomposed by boiling water giving I and HIO_3, not acted on by alcohol. Warm HNO_3 produces HIO_3 and I; but H_2SO_4 dissolves the substance, and on cooling crystals of $H_2SO_4.IO_2$ separate; HClAq forms ICl and Cl; aqueous alkali solutions produce iodates, but alcoholic solutions of alkalis are said to form red liquids containing very unstable compounds.

Other compounds of iodine and oxygen have been described, but it is very doubtful whether any definite compound except I_2O_5 and probably IO_2 has been isolated. By the action of ozone on I, Andrews a. Tait obtained a yellow powder; supposed by some chemists to be I_2O (A. a. T. *Pr.* 9, 608; no analyses given). Ogier (*C. R.* 85, 957) asserted the formation of I_2O_3 by the action of ozonised O on I; he described it as a yellow deliquescent powder, decomposing at 125°–130°, with evolution of I and O, giving HIO_3 and I with water. Millon (*J. pr.* 34, 336) supposed he had obtained $I_{10}O_{19}$ by exposing to moist air the product of boiling I_2O_5 with conc. H_2SO_4 until both I and O were coming off. Kämmerer, (*J. pr.* 83, 73) treated I_2O_5 with SO_2, and by

washing the product with alcohol and water obtained a brownish-yellow powder supposed to be I_6O_{13}. These substances were probably mixtures. Bengieser [in 1836] (*A.* 17, 254) says that by heating H_5IO_6 (*v. Periodic acid*) to 160° it loses water, and that at c. 180° O is evolved and I_2O_5 remains; possibly I_2O_7 may be formed at c. 160°; but Rammelsberg (*J. pr.* 103, 278) says that decomposition of H_5IO_6 begins at 133°, and Langlois (*J. pr.* 56, 36) puts the decomposition temperature at 130°.

Iodine, oxyacids of. The only oxyacids of I which are certainly known are HIO_3 and H_5IO_6; both are solids. There are indications of the existence of HIO in aqueous solution, but neither this acid nor any of its salts has been actually isolated. The periodic acid corresponding with $HClO_4$ has not been isolated, but many salts of the form M^IIO_4 are known; the periodates form several complex series of salts whereas all the perchlorates belong to the series M^IClO_4. HIO_3 is a product of the action of many oxidisers on I, *e.g.* HNO_3, Cl in presence of H_2O, KOHAq. This acid or an iodate is also formed by digesting MgO, HgO, or Ag_2O with I and H_2O, or by shaking up $AgNO_3$ with an alcoholic solution of I. Electrolysis of IAq or HIAq yields HIO_3. Iodides dissolved in water are oxidised by $KMnO_4Aq$, and by bleaching powder, to iodates. HIO_3 is produced by heating solutions of $HClO_3$, $HClO_2$, HClO, or $HBrO_3$ with I. If these reactions are compared with those whereby bromic and chloric acids are obtained (vol. i. p. 537, and vol. ii. p. 15) it is seen that it is more easy to pass from less oxidised, or non-oxidised, compounds of I to HIO_3 than from corresponding compounds of Cl or Br to $HClO_3$ or $HBrO_3$. The heat of formation of HIO_3 is much greater than that of HI, whereas the heats of formation of $HClO_3$ and $HBrO_3$ are considerably less than those of HCl and HBr:—[H, I, Aq] = 13,170; [H, I, O^3, Aq] = 55,800 (*cf.* vol. ii. p. 665). Periodic acid and its salts are stable compounds; they are more readily formed by oxidation processes than perchlorates, *e.g.* passing I vapour with O over heated BaO produces Ba periodate, and passing Cl into an alkaline iodate in presence of alkali produces an alkaline periodate. The anhydride of iodic acid, I_2O_5, is known as a stable solid; but the anhydride of periodic acid, I_2O_7, has not been isolated (*v. supra, Iodine, oxides of*).

Detection and estimation of iodates and periodates.—Iodates are detected by mixing with an alkaline iodide, adding a little starch paste, and a few drops of a weak acid, *e.g.* tartaric acid, when I is set free and colours the starch blue. Periodates give a brown pp. of $AgIO_4$ on addition of $AgNO_3$ in presence of HNO_3. Periodates may be separated from iodates by ppg. both as Ba salts and digesting pp. with NH_4 carbonate, when Ba periodate remains unchanged, but the iodate is converted into $BaCO_3$. Iodates may be estimated by reduction to iodides by means of SO_2 or SH_2, and ppn. with $AgNO_3$; or by digesting with KI and a little HCl, when Cl is set free and decomposes the KI, giving free I which is determined volumetrically. Periodates may be estimated by a similar method (*v.* Kimmins, *C. J.* 51, 361).

Hypo-iodous acid and Hypo-iodites. Neither the acid nor any of its salts has been isolated. According to Köne (*P.* 66, 302; Lippmann, *B.* 7, 1773) the solution obtained by shaking an alcoholic solution of I with ppd. HgO probably contains hypo-iodous acid, but this acid quickly decomposes to HIO_3 and I. When I is added to KOHAq or NaOHAq a yellowish liquid is obtained, which bleaches indigo, gives a blue colour with starch, and is decomposed by H_2O_2Aq with evolution of O; on heating, iodide and iodate are formed. This solution probably contains KIO or NaIO (Schönbein, *J. pr.* 84, 337; Berthelot, *B.* 10, 900; Van Deventer a. Van't Hoff, *C. C.* 1888. 362). Lunge a. Schock (*B.* 15, 1883), by the action of I on CaO suspended in water, obtained a colourless solution which bleached logwood, litmus, and cochineal; gave no colour with starch; addition of acids separated I; H_2O_2Aq caused evolution of O; the solution decomposed slowly in the dark, more rapidly in sunlight, but even on boiling for some hours it was only partially decomposed. L. a. S. suppose this solution to contain an I compound, analogous with bleaching powder, probably Ca.OI.I.

Iodic acid; and *Iodates.* HIO_3; MIO_3. The acid seems to have been first obtained by Connel by oxidising I by conc. nitric acid (*New Edin. Philos. Journ.* 10, 93, 337; 11, 72; 13, 284).

Occurrence.—Sometimes in commercial nitric acid (Pettenkofer, *J.* 1857. 581).

Formation.—1. By oxidising I by very conc. HNO_3Aq, or by $HBrO_3Aq$ (Kämmerer, *J. pr.* 79, 94), or $HClO_3Aq$ (Davy, *S.* 11, 68, 234; 16, 343).—2. By decomposing $Ba(IO_3)_2$ by the proper quantity of H_2SO_4Aq.—3. By suspending $AgIO_3$ in water, adding an equivalent quantity of I, filtering from AgI, and evaporating to dryness ($10AgIO_3 + 12I + 6H_2O + Aq = 12HIO_3Aq + 10AgI$; Kämmerer, *P.* 138, 390). The $AgIO_3$ is prepared by ppg. NH_4IO_3 by $AgNO_3$, and the NH_4IO_3 is made by digesting $Ba(IO_3)_2$ with solution of NH_4 carbonate.—4. By digesting an aqueous or alcoholic solution of $AgNO_3$ with I ($10AgNO_3Aq + 12I + 6H_2O = 10HNO_3Aq + 10AgI + 2HIO_3Aq$; Lassaigne, *J. Chim. méd.* 9, 508; Weltzien, *A.* 91, 43).—5. By decomposing KIO_3Aq by H_2SiF_6Aq, filtering, and evaporating to dryness; the product is impure.—6. By leading Cl into water containing I in suspension; the greater the dilution the greater the quantity of Cl required to change all the I into HIO_3 (*cf.* Bornemann, *A.* 189, 183; Sodini, *B.* 9, 1126).—7. By electrolysing solution of I or HI (Riche, *C. R.* 46, 348).—8. By the action of Au_2O_3 on I in presence of water

($6I + 5Au_2O_3 + 3H_2O + Aq = 6HIO_3Aq + 10Au$; Colin, *G. A.* 48, 280).—9. By moistening ICl_3 with a little water and then shaking with ether or alcohol (Liebig, *P.* 24, 363).—10. Alkaline iodates are obtained by acting on I with caustic alkalis, or by oxidising alkaline iodides by $KMnO_4Aq$ or solution of bleaching powder (Hempel, *A.* 107, 100; Reinige, *Fr.* 9, 39; Reichardt, *Ar. Ph.* [3] 5, 109: $KIAq + 2KMnO_4 + H_2O = KIO_3Aq + 2MnO_2 + 2KOHAq$;

$2KIAq + 6CaOCl_2Aq = Ca(IO_3)_2 + 5CaCl_2Aq + 2KClAq$).—11. $Hg(IO_3)_2$ is obtained, along with HgI_2, by shaking I with ppd. HgO suspended in water (Colin, *G. A.* 48, 280).

Preparation.—1. About 5-10 grams finely powdered I is placed in a large flask, twice its

weight of conc. nitric acid S.G. 1·5 (not fuming acid) is added, and the bottom of the flask is gently warmed; the I is gradually oxidised; by keeping the upper parts of the flask cool any I which volatilises is prevented from escaping. After a time the acid becomes diluted, it is then poured off, fresh acid is added, and the oxidation is continued until the whole of the I has been converted into white crystals of HIO_3. The greater part of the acid is poured off, the semi-liquid mass is evaporated to dryness in a basin, and the remaining acid is removed either by repeated evaporations with water or by heating to 100°–130° in an air-current. The crystalline mass may be dissolved in water and slowly evaporated to the crystallisation-point, and the crystals heated to 170°.—2. Two pts. conc. H_2SO_4 and c. 8 pts. water are added to 9 pts. finely powdered $Ba(IO_3)_2$, the whole is boiled for half-an-hour; after settling, $BaSO_4$ is removed by filtration, and the filtrate is evaporated until HIO_3 separates on cooling; the crystals are dissolved in water, a very little $Ba(IO_3)_2$ is added, and the liquid is evaporated and filtered. Stas says that pure HIO_3 cannot be obtained by this method; the crystals always contain either $Ba(IO_3)_2$ or H_2SO_4. The $Ba(IO_3)_2$ required may be prepared: (1) by adding $BaCl_2Aq$ to $NaIO_3Aq$ obtained by passing Cl into water containing I in suspension, till the I is all dissolved, then adding Na_2CO_3 till neutral, and again passing in Cl (Liebig, *P.* 24, 363); (2) by suspending I in hot saturated BaOAq and passing Cl into the liquid (Kämmerer, *J.* 1860. 94); (3) by adding rather more than the equivalent quantity of I to hot conc. $KClO_3Aq$, and then a few drops of nitric acid, Cl is freely evolved, and KIO_3 crystallises on cooling, the salt is recrystallised once and decomposed by $BaCl_2Aq$.—3. NH_4IO_3 is prepared by digesting $Ba(IO_3)_2$ with NH_4 carbonate solution, filtering, and crystallising; $AgNO_3Aq$ is added to a solution of the NH_4IO_3 and the $AgIO_3$ obtained is collected and washed; the $AgIO_3$ is suspended in water and I is added in the ratio of 1 gram to 1·857 grams of the $AgIO_3$; the reaction $10AgIO_3 + 12I + 6H_2O = 12HIO_3 + 10AgI$ proceeds when the liquid is warmed on the water-bath; AgI is removed by filtration and the liquid is evaporated to dryness and the residue heated to c. 170° (Kämmerer, *P.* 138, 390).

Properties.—HIO_3 forms colourless trimetric crystals; $a:b:c$ = ·589:1:1·1903 (Rammelsberg, *P.* 90, 12); $a:b:c$ = ·9388:1:1·3181 (Schabus, *J.* 1854. 310). It is doubtful whether HIO_3 shows dimorphism or not (*v.* Rammelsberg, *Handbuch der Krystall.-physikal. Chemie*, i. 41). Thomsen gives the following thermal data (*Th.* 2, 163):—$[H, I, O^3] = 57,963$; $[HIO^3, Aq] = -2,166$; $[I^2O^5, H^2O] = 2,540$. S.G. º 4·629 (Ditte, *C. R.* 70, 621). Very soluble in water; most conc. solution, according to Kämmerer, contains 68·51 p.c. HIO_3, boils at 100°, and has S.G. 2·1629. Kämmerer gives the following table:—

S.G. at 14°	P.c. HIO_3
1·0053	1·054
1·0263	5·27
1·0525	10·54
1·1223	15·51
1·2093	21·08
1·2773	26·35
1·3184	31·62
1·4428	36·89
1·5371	42·16
1·6315	46·93
1·7356	52·70
1·8689	57·97
1·9954	63·24
2·1269	68·51

Thomsen has determined the volume-change attending the dilution of HIO_3Aq. He expresses it by the formula $Va = 18a + 39\left(1 - \frac{a}{a+18}13{\cdot}1\right)$; the composition of the solution is represented by $HIO_3.aH_2O$; the volume of one molecular weight of water is taken as 18. For optical properties of HIO_3 crystals *v.* Lang, *W. A. B.* 31. S.H. of HIO_3 = ·1625 (Ditte, *A. Ch.* [4] 21, 52). Electrolysis of HIO_3 produces I and O (Magnus, *P.* 102, 1; Buff, *A.* 110, 257).

Reactions.—HIO_3 reacts as an energetic oxidiser. 1. Most *non-metals* are oxidised by HIO_3Aq; *e.g.* P to H_3PO_4, As to H_3AsO_4, B to HBO_2, Si at 250° to SiO_2 (Ditte, *Bl.* 1870. 318); S, Se, and C are oxidised by heating in sealed tubes with HIO_3Aq, S to H_2SO_4, Se to H_2SeO_3, gas coke at 180° and anthracite at 210° to CO_2; diamond is not acted on.—2. All *metals*, except the Pt metals and Au, are oxidised by HIO_3Aq.—3. *Sulphurous acid* is oxidised to H_2SO_4; *sulphuretted hydrogen* to S and HI; the lower *oxides of nitrogen* to HNO_3.—4. *Hydrochloric acid* forms ICl_3 and Cl.

Combinations.—1. With *water* to form $2HIO_3.9H_2O$; obtained by cooling saturated HIO_3Aq to −17°.—2. With *sulphuric acid*; by dissolving HIO_3 in hot conc. H_2SO_4 and cooling, crystals of $2HIO_3.3H_2SO_4$ are said to be obtained; the mother-liquor deposits other compounds of the two acids; if $H_2SO_4.2H_2O$ is used crystals of $3(H_2SO_4.2H_2O).2HIO_3.2H_2O$ are formed; these compounds are decomposed by water (Millon, *J. pr.* 34, 321). Crystalline bodies, supposed to be compounds (Davy), are obtained by mixing conc. HIO_3Aq with solutions of H_3PO_4 and HNO_3.

Basicity and formula of iodic acid.—HIO_3 is generally looked on as a monobasic acid, analogous to $HClO_3$ and $HBrO_3$. Besides the normal K salt there exist two acid salts, KHI_2O_6 and $KH_2I_3O_9$; there are no chlorates or bromates similar to these. Iodic acid is easily decomposed by heat to water and the anhydride I_2O_5; such a reaction does not usually occur with monobasic acids. Iodic acid is isomorphous with the dibasic acids, succinic and itaconic. The chlorates and bromates as a class are easily soluble in water; the iodates are very slightly soluble. The thermal phenomena attending the formation of the three acids, $HClO_3$, $HBrO_3$, and HIO_3, mark off HIO_3 from the two others, thus:—

[H,Cl,Aq] = 39,320	$[H,Cl,O^3,Aq]$ = 23,940
[H,Br,Aq] = 28,380	$[H,Br,O^3,Aq]$ = 12,420
[H,I,Aq] = 13,170	$[H,I,O^3,Aq]$ = 55,800

The heat of formation of the acid HX decreases as the atomic weight of X increases, whereas in the series of oxyacids the heat of formation decreases from Cl to Br, but then increases very largely from Br to I. A similar variation is shown in the K salts, thus:—

[K,Cl] = 105,610	$[K,Cl,O^3]$ = 95,840
[K,Br] = 95,310	$[K,Br,O^3]$ = 84,062
[K,I] = 80,130	$[K,I,O^3]$ = 124,489

The iodates are not generally isomorphous with the chlorates and bromates. Thomsen says the only case of isomorphism is presented by the Ba salts. There is no doubt that the constitution of periodic acid is very different

from that of perchloric acid; but iodic acid shows some fairly-marked analogies with periodic acid. Thus, if one molecular proportion of H_5IO_6 (228 grams) is dissolved in $80H_2O$ (1,440 grams), the volume of the solution is 1,440 + 60·2 = 1500·2 c.c.; if the molecular weight of iodic acid is taken as $H_2I_2O_6$, and this quantity in grams (352) is dissolved in $80H_2O$, the volume of the solution is 1440 + 59·9 = 1499·9 c.c. In other words, one molecular proportion of H_5IO_6, dissolved in 80 molecular proportions of water, produces the same expansion of the liquid as is produced by one molecular proportion of iodic acid, provided the formula of this acid is taken to be $H_2I_2O_6$. The foregoing are the chief arguments brought forward by Thomsen for establishing a difference between the constitutions of iodic acid on the one hand and chloric and bromic acids on the other hand, and for showing that iodic and periodic acids are closely related (*Th.* 2, 168, 423).

The heats of neutralisation of $HClO_3$, $HBrO_3$, and HIO_3 are practically identical (*Th.* 1, 242). When NaOHAq is added to $NaIO_3$ a very small quantity of heat is developed, about 4 p.c. of the total heat of neutralisation; but the reaction of NaOH with the monosodium salt of an undoubted dibasic acid is always accompanied by the production of as much, or nearly as much, heat as attends the addition of the first molecular weight of NaOH to the acid. If iodic acid is regarded as dibasic, then the salt $KH_2I_3O_9$ must be looked on as either a compound of the normal salt $K_2I_2O_6$ with $2H_2I_2O_6$ ($2KH_2I_3O_9 = K_2I_2O_6.2H_2I_2O_6$), or as the acid salt of a hypothetical acid $H_3I_3O_9$.

On the whole there appear to be marked differences between the oxyacids of I and those of Cl and Br. The oxyacids of I form more complex salts than those of the other halogens. The constitution of the iodates and periodates cannot be settled by defining the basicities of the acids HIO_3 and H_5IO_6. Several series of periodates certainly exist, and there is probably more than a single series of iodates.

The salts KHI_2O_6 and $KH_2I_3O_9$ may of course be formulated as $K_2O.2I_2O_5.H_2O$ and $K_2O.3I_2O_5.2H_2O$ respectively.

Iodates. These salts are formed by neutralising HIO_3 by bases, or in some cases by oxidising I in presence of a base (*v. Iodic acid, Formation*, Nos. 10 and 11), or by double decomposition from the alkali iodates. The iodates are generally insoluble or slightly sol. in water; the alkali iodates are readily soluble; KIO_3, however, is only slightly soluble (S. at 20° = c. 8). The iodates are decomposed by heat, generally giving a mixture of metallic iodide and oxide, sometimes iodide only. Solutions of iodates are more easily reduced than chlorates; reduction of KIO_3Aq is brought about by SO_2Aq or SH_2Aq; with HIAq iodates give I and metallic iodide; with HClAq they give ICl_3, Cl, H_2O, and metallic chloride; dilute H_2SO_4 produces HIO_3.

The following are the chief memoirs on iodates; they are referred to by numbers in the following descriptions:—(1) Bell, *J.* 1871. 298: (2) Berthelot, *C. R.* 84, 1408: (3) Cameron, *J.* 1876. 284: (4) Clarke, *J.* 1877. 43, 267: (5) Connel, *S.* 62, 493: (6) Ditte, *C. R.* 70, 621: (7) Flight, *J.* 1864. 147: (8) Gay-Lussac, *G. A.* 48, 24, 372; 49, 1, 211: (9) Gorlach, *Fr.* 1869. 290: (10) Grosourdy, *J. Chim. méd.* 9, 428: (11) Henry, *B.* 3, 893: (12) Kämmerer, *J. pr.* 79, 94: (13) Kremers, *P.* 84, 271; 97, 5; 99, 443: (14) Ladenburg, *A.* 135, 1: (15) Liebig, *P.* 24, 363: (16) Marignac, *J.* 1856. 296: (17) Melsens, *C. C.* 1872. 552: (18) Millon, *A. Ch.* [3] 9, 400; 12, 330; 13, 29: (19) Mitscherlich, *P.* 11, 162; 17, 481: (20) Naquet, *J.* 1860. 401: (21) Pellagri, *B.* 8, 1357: (22) Penny, *A.* 37, 202: (23) Pleischl, *S.* 45, 18: (24) Rammelsberg, *P.* 44, 545; 46, 159; 62, 416; 90, 12; 115, 584; 125, 147; 134, 368, 499; 137, 305: (25) Schönbein, *J.* 1857. 63: (26) Serullas, *P.* 19, 97, 112; 20, 515: (27) Sonnstadt, *J.* 1872. 187: (28) Stas, *J.* 1867. 162.

Ammonium iodate NH_4IO_3. Lustrous plates; decompose at 150°; S. 2·6 at 15°, 14·5 at 100°. S.G. 3·31–3·34. Formed by action of NH_3Aq on I, or of HIO_3Aq on NH_3Aq or $(NH_4)_2CO_3Aq$ (4, 24, 28).

Barium iodate $Ba(IO_3)_2.H_2O$. By dissolving I or ICl_3 in BaOAq; or by ppg. $NaIO_3Aq$ by $BaCl_2$ or $Ba(NO_3)_2$. Lustrous monoclinic crystals, which lose H_2O at 130°, and when strongly heated form Ba periodate $Ba_5I_2O_{12}$. S.G. 5·18–5·28. S. ·07 at 13·5°; ·15 at 100° (4, 8, 10, 12, 13, 16, 18, 24, 27).

Calcium iodate $Ca(IO_3)_2$. Occurs in sea-water. Formed by adding $CaCl_2Aq$ to KIO_3Aq, or HIO_3Aq to $Ca(NO_3)_2Aq$. By action of bleaching powder on KIAq crystallises with $6H_2O$, and from $KIO_3Aq + Ca(NO_3)_2Aq$ with $4H_2O$ (Flight). Efflorescent rhombic crystals; on heating gives mixture of CaO and Ca periodate; v. insol. water (6, 16, 18, 24, 27).

Copper iodates.—1. $Cu(IO_3)_2.2H_2O$; greenish-blue pp. by mixing conc. $NaIO_3Aq$ and $CuSO_4Aq$; salt with H_2O remains on warming. S. ·33 cold, ·65 at 100°.—2. $3Cu(IO_3)_2.3CuO.2H_2O$; by action of HIO_3Aq on strongly-heated CuO. By dissolving (1) in NH_3Aq the compound $Cu(IO_3)_2.4NH_3.3H_2O$ is formed (18).

Mercury iodate $Hg(IO_3)_2$. By warming freshly ppd. HgO with HIO_3Aq, or adding HIO_3Aq to $Hg(NO_3)_2Aq$ or $Hg(C_2H_3O_2)_2Aq$ (not by adding HIO_3 to $HgCl_2$). White powder; insol. water (3).

Potassium iodates.—Normal iodate KIO_3. Prepared by dissolving I in KOHAq, evaporating to dryness, and dissolving out KI by alcohol S.G. ·81; also by passing Cl into I suspended in water, neutralising by KOHAq and evaporating. Stas adds 1½ pts. $KClO_3$ to semi-fluid KI in a crucible, dissolves, on cooling, in hot water, and recrystallises the KIO_3 which separates (8, 16, 17, 28). Crystallises in cubical forms. S.G. $\frac{18}{}$ 3·975; KIO_3Aq S.G. 1·0741 at 19·5° contains 9·08 KIO_3 to 100 water (13). S. at ·5° 5·3, at 9·5° 6·7, at 14° 7·7, at 22·2° 9·2, at 45·8° 16·6, at 69·2° 27 (8). Insol. alcohol S.G. ·81. Poisonous. Decomposes, at higher temperature than $KClO_3$, to KI and O, without production of KIO_4; heated with MnO_2 forms I, O, and K_2O (8, 24, 25). KIO_3Aq shaken with finely-divided Fe gives KI (21). From solution in hot dilute H_2SO_4Aq rhombic crystals of $2KIO_3.H_2O$ separate, which lose H_2O at 190° (6). The *double salt* $KIO_3.KHSO_4$ is obtained by heating KIO_3 in large excess of dilute H_2SO_4Aq, evaporating at 25° until $KH_2I_3O_9$ crystallises out, and further

crystallising the mother-liquor (16).—2. Di-iodate or acid iodate KHI_2O_6 (or $K_2O.2I_2O_5.H_2O$). Obtained by half neutralising HIO_3Aq by KOHAq; also by acidifying KIO_3Aq by HCl and ppg. by alcohol; also by dissolving KIO_3 in hot dilute HNO_3Aq (6, 18, 26). Crystallises in three forms, one rhombic and two monoclinic (16). S. 1·33 at 15° (26°). Solution reacts acid. Insol. alcohol. Loses H_2O at 200° (6). Forms a *double salt* $KHI_2O_6.2KCl$; obtained by heating KIO_3 with dilute HClAq, or by adding to ICl_3Aq less than enough KOHAq to saturate it (c. ratio $KOH{:}2ICl_3$) and allowing to evaporate (16, 24, 26). 3. Tri-iodate $KH_2I_3O_9$ (or $K_2O.3I_2O_5.2H_2O$). Formed by adding a large excess of HIO_3Aq to KIO_3Aq and evaporating; also by heating KIO_3 with large excess of dilute H_2SO_4Aq and evaporating at 25°. Large transparent triclinic crystals; lose all H_2O at 200°. S. 4 at 15° (6, 16, 24, 26). Berthelot (2) describes a basic iodate $KIO_3.K_2O$ obtained by heating KI in O.

Silver iodate $AgIO_3$. Formed by ppg. $AgNO_3Aq$ by HIO_3Aq or $NaIO_3Aq$. Crystallises from NH_3Aq in monoclinic crystals. S.G. 5·4. Soluble without decomposition in dilute HNO_3Aq (4, 14, 16, 24, 28).

Sodium iodate $NaIO_3$. Prepared by saturating 10 pts. water holding 1 pt. I in suspension, with Cl, neutralising by Na_2CO_3, again passing Cl, again neutralising by Na_2CO_3 and passing Cl, and so on; finally the solution is evaporated to $\frac{1}{10}$th its bulk and mixed while warm with half its volume of alcohol; the crystals which separate are pressed and washed with alcohol till free from NaCl (15). Crystallises at under 5° with $2H_2O$, above 5° with H_2O; at 70° crystals of $NaIO_3$ form; hydrates with 8, 6, and 3 H_2O are also described (6, 18, 24). S. 2·52 at 0°, 33·9 at 100° (13). Loses O and I when heated (15). According to Rammelsberg (24), a compound of NaI with Na_2O_2 ($6NaI.Na_2O_2$) remains on heating $NaIO_3$. With conc. HClAq, Cl is evolved, and a compound of HIO_3 and NaCl remains (6). *Double salts* with NaI are obtained by evaporating mixtures of $NaIO_3Aq$ with NaIAq; $NaI.NaIO_3.8H_2O$, $NaI.NaIO_3.10H_2O$, and $3NaI.2NaIO_3.20H_2O$ are described (6, 16, 19, 24). The existence of acid iodates is denied (6, 32; *cf.* 18, 22, 26).

Besides the foregoing iodates, the following have been prepared:—$Cd(IO_3)_2$ (24); $Co(IO_3)_2.H_2O$ and $Co(IO_3)_2.6H_2O$ (4, 24); various Fe iodates (1, 5, 24); $Pb(IO_3)_2$ (23, 24); $Mg(IO_3)_2.4H_2O$ (6, 16, 18); $Ni(IO_3)_2.H_2O$ and $Ni(IO_3)_2.6H_2O$ (4, 24); $Sr(IO_3)_2$ (24); $Zn(IO_3)_2.2H_2O$. Iodates of Al, Bi, Ce, Cr, Di, Au, La, Li, Mn, Sr, Sn, U, Y, and Zn also seem to exist, but they have not been fully investigated.

Periodic acid and Periodates.—The only acid which has been isolated is H_5IO_6; but at least five distinct series of periodates are known. The anhydride of periodic acid has not been obtained; when the acid is heated it loses H_2O, O, and I, and iodic anhydride, I_2O_5, remains; Bengieser in 1836 (*A.* 17, 254) stated that by heating periodic acid to 160° it lost water of crystallisation, and that O comes off rapidly at 180°; but according to Rammelsberg (*J. pr.* 103, 278) and Langlois (*J. pr.* 56, 36) decomposition begins at c. 130°.

Periodic acid was first prepared by Magnus a. Ammermüller (*P.* 28, 514); they prepared it by reacting on $AgIO_4$ with cold water, whereby the acid went into solution and another Ag periodate, $Ag_4I_2O_9.3H_2O$, remained.

Formation.—By the action of I on conc. $HClO_4Aq$ (Kämmerer, *P.* 138, 406, 410).

Preparation.—1. $Na_2H_3IO_6$ is prepared by saturating a hot solution of equal parts NaOH and $NaIO_3$ with Cl, concentrating, and allowing to cool (Langlois, *A. Ch.* 34, 257). This process yields a mixture of $Na_2H_3IO_6$ and $Na_3H_2IO_6$; the latter salt is more soluble and may be removed by long-continued washing with cold water (Kimmins, *C. J.* 51, 357), but it is not necessary to do this in preparing H_5IO_6. The Na salt is dissolved in water with addition of just enough HNO_3 to form a clear solution, and $AgNO_3Aq$ is added; a brown pp. of Ag_2HIO_5 is thus obtained (Kimmins, *C. J.* 51, 358; former observers said that Ag_5IO_6 or $Ag_2H_3IO_6$ is produced). The brown Ag salt is suspended in water, and shaken with Br; AgBr ppts., and H_5IO_6 along with $HBrO_3$ goes into solution; the filtrate is evaporated to the crystallising point, whereby $HBrO_3$ is decomposed, and is then placed over H_2SO_4 *in vacuo* (Kämmerer, *P.* 138, 390).—2. Ag_2HIO_5 prepared as described in 1 is dissolved in conc. HNO_3Aq, and the solution is evaporated at 100°, orange-red crystals of $AgIO_4.H_2O$ separate; by treatment with cold water this salt decomposes to H_5IO_6Aq, and $Ag_4I_2O_9.3H_2O$ which may be again converted into $AgIO_4$ by solution in conc. HNO_3Aq and evaporation (Magnus a. Ammermüller, *P.* 28, 514).—3. $Na_2H_3IO_6$ prepared as described in 1, and mixed with $Na_3H_2IO_6$, is dissolved in as little dilute HNO_3Aq as possible, $Pb(NO_3)_2Aq$ is added, the pp. of Pb periodate ($Pb_3(IO_5)_2$, Kimmins) is digested with rather less dilute H_2SO_4Aq than suffices to decompose it all, and the liquid is filtered and evaporated (Bengieser, *A.* 17, 254).

Properties.—H_5IO_6 crystallises in transparent, colourless prisms, probably monoclinic (Rammelsberg). M.P. 133° (Rammelsberg, *J. pr.* 103, 278), 130° (Langlois, *J. pr.* 56, 36); melting is accompanied by partial decomposition (Bengieser, *A.* 17, 254, put the temperature of decomposition at 180°). H_5IO_6 does not lose weight at 100°, nor by keeping over H_2SO_4. Very deliquescent; fairly sol. in alcohol; slightly sol. in ether. Thomsen (*B.* 7, 71; *Th.* 2, 427) gives the following data for S.G. and expansion of H_5IO_6Aq:—

Ratio of $H_5IO_6{:}H_2O$	S.G. of solution	Expansion for each formula-weight of acid
$H_5IO_6.20H_2O$	1·4008	59·77
„ 40 „	1·2165	59·30
„ 80 „	1·1121	59·99
„ 160 „	1·0570	60·2
„ 320 „	1·0288	60·0

The volume when aH_2O is present is expressed by the formula $Va = 18a + 59{\cdot}6$. The following thermal data are taken from Thomsen (*Th.* 2, 166):—$[H^5,I,O^6] = 185{,}780$; $[H^5IO^6,Aq] = -1380$; $[I^2,O^7,Aq] = 27{,}000$. H_5IO_6Aq exposed to air becomes yellow, and smells strongly of ozone.

Reactions.—H_5IO_6Aq reacts as an energetic oxidiser; with HCl it gives Cl and HIO_3 (M. a. A., *l.c.*); with P and Bi it forms P_2O_5 and Bi_2O_5

(Kämmerer, *l.c.*); $C_2H_4O_2$, $C_2H_2O_4$, and many other C acids are oxidised to CO_2; SO_2Aq, SH_2, and HI are also oxidised; with Zn, Fe, Hg, and Cu it forms ZnO, Fe_3O_4, HgO, and $Cu(IO_3)_2$ respectively (Bengieser, *l.c.*).

Periodates. Most of the periodates are insoluble in water; they are generally prepared from the Na or K salts by double decomposition from solutions acidified with HNO_3. Many of them are decomposed by heat giving O and metallic iodides, *e.g.* KIO_4, $AgIO_4$; others evolve O and I, and leave either oxide, *e.g.* salts of Ni and Mg, or a mixture of oxide and iodide, *e.g.* salts of Pb, Cu, Cd; Hg salts give iodide and Hg; NH_4 salts decompose explosively to I, N, O, and H_2O. Very many periodates are known; they may be divided into several classes; the following scheme presents the chief classes and the chief salts in each class. The nomenclature is that adopted in Gmelin-Kraut's *Handbuch*. All the acids except H_5IO_6 are hypothetical; formulæ of salts are given here without water of crystallisation:—

$Ba_5(IO_6)_2$ is obtained, and $Ca(IO_3)_2$ undergoes a similar reaction. The salts obtained by double decomposition from alkali salts of the ortho-series, or of the dimeso- series, usually belong either to the ortho- or meso- series; thus the following salts are obtained:—

Starting from $Na_2H_3IO_6$		Starting from $K_4I_2O_9$
Cu_2HIO_6	ortho	Cu_2HIO_6
FeH_3IO_6		$Fe_5(IO_6)_2$
$Pb_3H_4(IO_6)_2$		$Pb_3H_4(IO_6)_2$
$Ag_2H_3IO_6$		$Ag_2H_3IO_6$
$CdHIO_5$	meso	$CdHIO_5$
Ag_2HIO_5		Ag_2HIO_5
$Ni_3(IO_5)_2$		

When a salt is obtained by ppn. from an acidified solution of an alkali salt, the series to which the ppd. salt belongs is conditioned by the relative quantity of acid present; thus when $AgNO_3$ is added to a solution of $Na_2H_3IO_6$, $K_4I_2O_9$ or KIO_4, acidified by a little HNO_3, Ag_2HIO_5 is obtained; when more HNO_3 is present the pp. is $Ag_2H_3IO_6$; and when conc. acid is present the salt $AgIO_4$ is obtained. Boiling salts of the ortho-, meso-, or dimeso- series with HNO_3Aq as a rule produces salts of the meta- series. Acid salts of the ortho- series are changed to normal salts of the meso- or dimeso- series by heating, and acid salts of the meso- series are changed to normal salts of the dimeso- series; thus $Pb_3H_4(IO_6)_2$ at 275° gives $Pb_3(IO_5)_2$ and H_2O, and Ag_2HIO_5 gives $Ag_4I_2O_9$ and H_2O at 300°. Some of the periodates show very distinctly the difference between so-called 'water of crystallisation' and 'water of constitution'; thus Ag_2HIO_5 (which might be written $Ag_4I_2H_2O_{10}$) and $Ag_4I_2O_9.H_2O$ (which also might be written $Ag_4I_2H_2O_{10}$) are quite different bodies; the change $2Ag_2HIO_5 = Ag_4I_2O_9 + H_2O$ occurs at 300°, but $Ag_4I_2O_9.H_2O$ loses H_2O at 130°; again $Ag_2H_3IO_6$ (which might be written $Ag_4I_2H_6O_{12}$) is a dark-red pp., obtained by adding $AgNO_3$ to $Na_2H_3IO_6$ in a slight excess of HNO_3Aq,

Periodates.

Ortho-periodates derived from H_5IO_6	*Meso-periodates* derived from H_3IO_5 ($H_5IO_6-H_2O=H_3IO_5$)	*Dimeso-periodates* derived from $H_4I_2O_9$ ($2H_5IO_6-3H_2O=H_4I_2O_9$)	*Meta-periodates* derived from HIO_4 ($H_5IO_6-2H_2O=HIO_4$)
$Ba_5(IO_6)_2$	$Ba_3(IO_5)_2$	$Ba_2I_2O_9$	$Ba(IO_4)_2$
BeH_2IO_6	$Cd_3(IO_5)_2$	$Cd_2I_2O_9$	$Cd(IO_4)_2$
$Ca_5(IO_6)_2$	$CdHIO_5$	$Ca_2I_2O_9$	$Ca(IO_4)_2$
Cu_2HIO_6	$Pb_3(IO_5)_2$	$Cu_2I_2O_9$	$Fe(IO_4)_2$
$Fe_5(IO_6)_2$	$Ni_3(IO_5)_2$	$FeHI_2O_9$	$Pb(IO_4)_2$
FeH_3IO_6	K_3IO_5	$Mg_2I_2O_9$	KIO_4
Hg_5IO_6	Ag_2HIO_5	$Ni_2I_2O_9$	$AgIO_4$
Ag_5IO_6	$Sr_3(IO_5)_2$	$K_4I_2O_9$	$NaIO_4$
$Ag_2H_3IO_6$		$K_3HI_2O_9$	$Sr(IO_4)_2$
$Ag_3H_2IO_6$		$Ag_4I_2O_9$	
$Na_2H_3IO_6$		$Na_4I_2O_9$	
$Na_3H_2IO_6$		$Sr_2I_2O_9$	
$Sr_5(IO_6)_2$		$Zn_2I_2O_9$	
$Zn_5(IO_6)_2$.			

Di-periodates derived from $H_8I_2O_{11}$ ($2H_5IO_6-H_2O=H_8I_2O_{11}$)		*Dimeso-diperiodates* derived from $H_{10}I_4O_{19}$ ($2H_8I_2O_{11}-3H_2O=H_{10}I_4O_{19}$)	*Trimeso-periodates* derived from $H_{10}I_6O_{26}$ ($6H_5IO_6-10H_2O=H_{10}I_6O_{26}$)
$Cd_4I_2O_{11}$		$Ba_5I_4O_{19}$	$Ba_5I_6O_{26}$
$Cu_4I_2O_{11}$		$Ag_{10}I_4O_{19}$	$Sr_5I_6O_{26}$
$Mg_4I_2O_{11}$			
$Hg_8I_2O_{11}$			
$Ag_8I_2O_{11}$			
$Zn_4I_2O_{11}$			

The series to which a periodate belongs seems to depend partly on the nature of the base, and to a large extent on the conditions of preparation. By neutralising H_5IO_6Aq by NaOHAq Rammelsberg (*P.* 134, 368, 499) obtained $NaIO_4$; by neutralising the same acid by various carbonates the following salts have been obtained:—

Ortho-series	*Dimeso-series*	*Meta-series*	*Di-series*
BeH_2IO_6	$Ca_2I_2O_9$	$Cd(IO_4)_2$	$Mg_4I_2O_{11}$
	$Cu_2I_2O_9$	$Mg(IO_4)_2$	$Zn_4I_2O_{11}$.
	$Mg_2I_2O_9$	$Sr(IO_4)_2$	
	$Zn_2I_2O_9$		

By passing Cl into a hot mixture of KIO_3 and KOH, KIO_4, $K_4I_2O_9$, and $K_3HI_2O_9$ are produced; but the Na salts formed under similar conditions are $Na_2H_3IO_6$, $Na_3H_2IO_6$, $Na_4I_2O_9$, and perhaps $NaIO_4$. By heating $Ba(IO_3)_2$ the salt

whereas $Ag_4I_2O_9.3H_2O$ (which also might be written $Ag_4I_2H_6O_{12}$) forms light yellow crystals, and is obtained by treating $AgIO_4.H_2O$ with water. As a rule water of crystallisation is removed at 100°, whereas the temperature of acid salts must be raised to 270°–300° before change begins with evolution of water. (For a comparison of the classes of periodates, *v.* Kimmins, *C. J.* 55, 152.) Thomsen (*Th.* 1, 244) has determined the heat of neutralisation by KOH of H_5IO_6, with the following results:—

n	$[H^5IO^6Aq, n\,KOHAq]$	*diff.*
1	5,150	
		21,440
2	26,590	
		3,150
3	29,740	
		2,300
5	32,040	

From these results Thomsen concludes that H_5IO_6 is dibasic, but that basic salts are produced when more than 2KOH reacts. To explain the existence of many of the periodates, Thomsen prefers to double the formula of the acid and to represent it as normally tetrabasic, thus $H_4I_2O_9.3H_2O$: he classifies the chief periodates as follows:—

Normal salts.

$R^I{}_4I_2O_9.3H_2O$

Basic salts.

(1) $R^{II}{}_3I_2O_{10}.2H_2O$ (2) $R^{II}{}_4I_2O_{11}.H_2O$ (3) $R^{II}{}_5I_2O_{12}$

The existence of undoubted acid salts, *i.e.* salts in which the H is not combined with O in the form of H_2O, militates against the classification of Thomsen. The reaction of KOHAq with H_5IO_6Aq is almost certainly a complex occurrence.

In the following description of periodates only one or two salts in each series are described in detail.

The following are the principal memoirs on periodates; they are referred to in the following paragraphs by numbers: (1) Atterberg, *J.* 1873. 257; (2) Bengieser, *A.* 17, 250; (3) Blomstrand, *B.* 3, 317; (4) Fernlund, *J.* 1867. 165; (5) Groth, *P.* 134, 536; (6) Kimmins, *C. J.* 51, 356; 55, 148; (7) Langlois, *J.* 1852. 345; (8) Lautsch, *J. pr.* 100, 65; (9) Magnus a. Ammermüller, *P.* 28, 514; (10) Philipp, *B.* 3, 4; (11) Rammelsberg, *P.* 44, 545; 46, 159; 62, 416; 90, 12; 115, 584; 125, 147; 134, 368, 499; 137, 305; (12) Ritter, *Gm.-K.* (6th ed.), 1 [2] 303.

Ortho-series; salts derived from H_5IO_6.

Barium orthoperiodate $Ba_5(IO_6)_2$. Prepared by heating $Ba(IO_3)_2$ in a current of dry air (Sigiura a. Cross, *C. J.* 35, 118); by passing I vapour and dry air over heated BaO (S. a. C.); by heating BaI_2 in a current of dry air so long as I is given off (S. a. C.). Insol. water; sol. HNO_3Aq; heated in H gives BaI_2 and BaO.

Silver orthoperiodates.—1. Ag_5IO_6: said to be ppd. as a brown salt by adding $AgNO_3Aq$ to a neutral solution of an alkaline periodate, also by shaking $Ag_4I_2O_9.3H_2O$ with cold $AgNO_3Aq$ (11); Kimmins (6) failed to obtain this salt; sol. in HNO_3Aq and in NH_3Aq.—2. $Ag_2H_3IO_6$: dark-red pp. by adding $AgNO_3Aq$ to $Na_2H_3IO_6Aq$ or $K_4I_2O_9Aq$ in slight excess of HNO_3 (6).—3. $Ag_3H_2IO_6$, slate-coloured pp. by adding $AgNO_3Aq$ to $Na_2H_3IO_6Aq$ or $K_4I_2O_9Aq$ in presence of a fair amount of HNO_3 (6).

Sodium orthoperiodates $Na_2H_3IO_6$ and $Na_3H_2IO_6$; white granular pps., formed by passing Cl into a boiling solution of equal weights of $NaIO_3$ and NaOH; the second salt is less soluble than the first, from which it may be separated by long-continued washing with small quantities of cold water (6).

For descriptions of the other salts of this series *v.* (1) for Be salt, (6) for Cu and Fe salts, (8) for Hg salt, (11) for Ca, Sr, and Zn salts (for formulæ of salts, *v.* p. 23).

Meso-series; salts derived from hypothetical H_3IO_5.

Barium mesoperiodate $Ba_3(IO_5)_2.6H_2O$. By ppg. the corresponding K salt by $Ba2NO_3Aq$ (11).

Potassium mesoperiodate $K_3IO_5.4H_2O$. KIO_4 is prepared by saturating with Cl a hot conc. solution of equal weights of KIO_3 and KOH, and repeatedly crystallising; the salt is dissolved in water and the solution is ppd. by alcohol (11).

Silver mesoperiodate (acid salt) Ag_2HIO_5. A dark-brown pp. by ppg. $Na_2H_3IO_6$ or $K_4I_2O_9$ in just enough dilute HNO_3Aq to form a solution (6).

For description of other salts of this series (formulæ given on p. 23), *v.* (6) for salts of Pb and Ni, and (11) for salts of Cd (crystallises with $5H_2O$) and Sr.

Dimeso-series; salts derived from hypothetical $H_4I_2O_9$.

Barium dimesoperiodate $Ba_2I_2O_9$. Obtained by ppn. from alkali periodates in presence of HNO_3. By neutralising H_5IO_6Aq by BaOAq, a salt with $7H_2O$ is obtained, which loses $4H_2O$ at 100°, and on strongly heating goes to Ba_5IO_6 (11, 7, 8).

Ferric dimesoperiodate (acid salt) $FeHI_2O_9$. By ppg. solution of $Na_2H_3IO_6$ or $K_4I_2O_9$ by $FeCl_3Aq$ and drying at 100°. Boiling with dilute HNO_3Aq does not change this salt (6).

Potassium dimesoperiodates $K_4I_2O_9$ and $K_3HI_2O_9$. Both salts are obtained by passing Cl into KIO_3 mixed with KOHAq (6). If equal weights of the KIO_3 and KOH are used, and the KIO_4 which separates is removed by filtration, the filtrate on concentration gives $K_4I_2O_9$; if this filtrate is exactly neutralised by HNO_3 the salt $K_4I_2O_9.3H_2O$ (*v.* also 11) crystallises out without concentration; if excess of HNO_3 is used, $K_3HI_2O_9$ is obtained. A solution of KIO_4 to which KOH is added is said to give triclinic crystals of $K_4I_2O_9.9H_2O$ on concentration (5, 9). $K_4I_2O_9$ is soluble in KOHAq; S. 10·3 cold water; solution has alkaline reaction; Cl led into boiling $K_4I_2O_9Aq$ produces KIO_4; with I, KI and KIO_3 are produced: strongly heated leaves $2KI.K_2O$ (11).

Silver dimesoperiodate $Ag_4I_2O_9.3H_2O$. Light-yellow crystals, obtained by treating $AgIO_4.H_2O$ with cold water (6, 9). Heated to 100° for 12 hours claret-coloured crystals of $Ag_4I_2O_9.H_2O$ are formed; and when the temperature is raised to 130° and kept there for many hours a chocolate-coloured powder, $Ag_4I_2O_9$, remains (6). When $Ag_4I_2O_9$ is treated with NH_3Aq, $Ag_8I_2O_{11}$ is produced (11).

For descriptions of other salts of this series

(formulæ given on p. 23) *v.* (2) for salt of Ca (crystallises with 7 and 9 H_2O), (6) for salts of Ni and Zn, (7) for Sr salt (crystallises with $3H_2O$), (8) and (9) for Na salt (crystallises with $3H_2O$), and (11) for salts of Cd (crystallises with $9H_2O$), Cu (with $6H_2O$), Mg (with 12 and 15 H_2O).

Meta- series; salts derived from hypothetical HIO_4.

Ferric metaperiodate $Fe(IO_4)_3$. Bright yellow, produced by boiling $FeHI_2O_9$ for some time with conc. HNO_3Aq (6).

Potassium metaperiodate KIO_4. Prepared by saturating with Cl a boiling conc. solution of equal parts KIO_3 and KOH, cooling, and crystallising repeatedly from water (6, 7, 9, 11). S. ·35 cold water; almost insol. KOHAq. KIO_4Aq shows acid reaction. At 300° forms KIO_3, decomposed by I at 160°. Reduced in solution by KI to KIO_3 and I, which is then oxidised to KIO_3 (8, 9, 10).

Silver metaperiodate $AgIO_4$. By dissolving $Na_2H_3IO_6$ or $Na_3H_2IO_6$ or $K_4I_2O_9$ in conc. HNO_3Aq and adding $AgNO_3$; also by treating $Ag_2H_3IO_6$, $Ag_3H_2IO_6$, or $Ag_4I_2O_9$ with conc. HNO_3Aq and evaporating on steam-bath. Orange-coloured crystals. Crystals are $AgIO_4.H_2O$; heated to 130° for 6 hours $AgIO_4$ remains as a bright-yellow powder (6). Decomposed by water giving $Ag_4I_2O_9.3H_2O$ (11).

For descriptions of other salts of this series (formulæ given on p. 23) *v.* (11) for salts of Ba, Cd, Ca, and Sr (crystallises with $6H_2O$), (5), (7), (8), (9), and (11) for salt of Na (crystallises with 2 and 3 H_2O).

Di-series; salts derived from hypothetical $H_8I_2O_{11}$.

Cadmium diperiodate $Cd_4I_2O_{11}.3H_2O$. By ppg. a slightly acidified solution of $NaIO_4$ by a soluble Cd salt (11).

Silver diperiodate $Ag_8I_2O_{11}$. By treating $Ag_4I_2O_9$ with NH_3Aq (8, 11).

For descriptions of the other salts of this series (formulæ given on p. 23) *v.* (11) for salt of Cu (crystallises with H_2O and $7H_2O$), (11) for salt of Mg (with 6 and 9 H_2O), (11) for salt of Hg (*cf.* 8), (7) for salt of Zn (*cf.* 11).

Dimeso-di and Tri-meso series; salts derived from hypothetical $H_{10}I_4O_{19}$, and $H_{10}I_6O_{26}$ respectively; *v.* (8) and (11).

Iodine, phosphides of, better called *Phosphorus iodides*; *v.* PHOSPHORUS.

Iodine, selenides of, better called *Selenion iodides*; *v.* SELENION.

Iodine, silicides of, better called *Silicon iodides*; *v.* SILICON.

Iodine, sulphides of, better called *Sulphur iodides*; *v.* SULPHUR.

Iodine, tellurides of, better called *Tellurium iodides*; *v.* TELLURIUM. M. M. P. M.

IODO-ACETIC ACID $C_2H_3IO_2$ *i.e.* $CH_2I.CO_2H$. Mol. w. 186. [82°].

Formation.—1. By digesting bromo-acetic ether with KI and alcohol, for about two hours in the dark, distilling off the resulting iodo-acetic ether and decomposing it with baryta-water (Perkin a. Duppa, *P. M.* [4] 18, 54).—2. By boiling Ac_2O with iodine and iodic acid (Schützenberger, *J. pr.* 107, 108).—3. By the oxidation of iodo-acetic aldehyde (Chautard, *A. Ch.* [6] 16, 152).

Properties.—Trimetric plates, decomposed by heat.

Reactions.—1. Moist *silver oxide* yields glycollic acid.—2. Resolved by HI, even in the cold, into acetic acid and free iodine (Kekulé, *C. J.* 17, 207).

Salts. The NH_4 and K salts are very soluble, crystalline, and non-deliquescent.—BaA'_2: crystalline, m. sol. water; ppd. from aqueous solution by alcohol.—PbA'_2: prisms. In solution it easily splits up into PbI_2 and glycollic acid.

Methyl ether MeA'. (170°). Pungent liquid (Aronstein a. Kramps, *B.* 14, 604).

Ethyl ether EtA'. (180°). From bromo-acetic ether, KI, and alcohol (P. a. D.). Also from chloro-acetic acid, KI, and alcohol (96 p.c.) by heating on the water-bath in the dark. Easily obtained by heating chloro-acetic ether with CaI_2 $3\frac{1}{2}$aq at 75° (Spindler, *A.* 231, 272). Pungent heavy oil. Decomposed by EtI at 230° giving acetic ether and ethylene iodide (Aronstein a. Kramps, *B.* 13, 489; 14, 604). With Me_2S it forms $MeS.CH_2.CO_2H$ and, finally, $S(CH_2.CO_2H)_2$.

Chloro-ethyl ether $Cl.CH_2.CH_2.O.CO.CH_2I$. S.G. $\frac{18}{}$ 1·954. From chloro-ethyl chloro-acetate by gently heating with an alcoholic solution of NaI (Henry, *C. R.* 97, 1308). Very pungent oil. Turns brown in daylight.

Propyl ether PrA'. (198°). S.G. $\frac{7}{}$ 1·679. From propyl chloro-acetate and alcoholic NaI (Henry, *C. R.* 100, 114). Pungent oil.

Amide $CH_2I.CO.NH_2$. [158°]. Formed from methyl iodo-acetate and alcoholic NH_3 (Henry). Also from chloro-acetamide and alcoholic KI, by standing a few days in the cold (Menschutkin a. Jermolajeff, *Z.* 1871, 5). Small needles or prisms.

Nitrile $CH_2I.CN$. *Iodo-acetonitrile.* (187°). S.G. $\frac{12}{}$ 2·307. From chloro-acetonitrile and alcoholic NaI (Henry, *C. R.* 103, 413). Colourless, very pungent oil, which becomes brown in daylight. V. sol. alcohol and ether. Slightly decomposed on distillation, with liberation of some iodine and HCy. AgOAc forms $CH_2(OAc).CN$.

Di-iodo-acetic acid $CHI_2.CO_2H$. Formed by heating di-bromo-acetic ether with KI, converting the resulting di-iodo-acetic ether into a Ca salt with milk of lime, and adding HCl (Perkin a. Duppa, *C. J.* 13, 1). Crystalline sulphur-yellow compound, volatile in the cold, sl. sol. water. Does not blister the skin. The K and Na salts are deliquescent.—BaA'_2: trimetric crystals, giving off iodine when heated.—CaA'_2: silky yellow needles.—PbA'_2: crystalline pp.—AgA': yellow crystalline powder.

Ethyl ether EtA'. Formed by treating di-chloro-acetic ether with $CaI_2 3\frac{1}{2}$aq at 75° (Spindler, *A.* 231, 273). Formed also by adding iodine to a solution of diazo-acetic ether in ether (Curtius, *J. pr.* [2] 38, 433). Oil, volatile with steam; reddens on exposure to air.

Amide $CHI_2.CONH_2$. [202°]. Formed by the action of iodine upon a cold alcoholic solution of diazo-acetamide (Curtius, *B.* 18, 1285). Formed also by the action of conc. NH_3Aq upon di-iodo-acetic ether. Greenish-white prisms (from hot water); v. sl. sol. water. Very stable towards acids and alkalis.

IODO-ACETIC ALDEHYDE $CH_2I.CHO$. S.G. $\frac{20}{}$ 2·14.

Formation.—1. By boiling an aqueous solution of chloro-acetic aldehyde with KI, allowing to stand for 12 hours, and then extracting with ether (Glinsky, *Z.* [2] 4, 618).—2. By the oxidation of a solution of iodine in alcohol.

Preparation.—By mixing iodine (50 g.), iodic acid (20 g.), aldehyde (30 c.c.) and water (60 c.c.) and leaving the closed flask to stand for about a week (in summer). Water (500 c.c.) is then added, when the iodo-acetic aldehyde separates as an oil (Chautard, *A. Ch.* [6] 16, 145; *C. R.* 102, 118; *C. N.* 54, 87; *cf.* W. P. Bloxam a. E. F. Herroun, *C. N.* 53, 301; 54, 133).

Properties.—Limpid colourless oil, uninflammable. Blackens rapidly when exposed to light. Its vapour is excessively irritating. Cannot be distilled even *in vacuo*. Decomposes at 80°. Miscible with alcohol, ether, chloroform, and CS_2. Sl. sol. water. Forms a crystalline hydrate. Forms a crystalline compound with $NaHSO_3$.

Reactions.—1. Dilute aqueous KOH forms iodoform. Conc. KOHAq resinifies it.—2. *Ammonia* either aqueous or alcoholic forms ammonium iodide and various bases, *e.g.* oxytrialdine $(C_2H_3)_2N.C_2H_4OH$.—3. *Chlorine* and *bromine* at ordinary temperatures displace iodine giving chloro- and bromo-acetic aldehydes and resins. 4. All *mineral acids* decompose iodo-acetic aldehyde.—5. *Reducing agents* (Na amalgam, Zn and HCl) remove the iodine.—6. *Oxidation* with HNO_3 yields $CH_2I.CO_2H$ [82°].—7. NaOEt and KOEt yield only resinous matters.—8. *Silver acetate* yields acetic ether (74°).—9. AgCN gives $CH_2(CN).CO.H$.—10. AgSCN similarly gives $CH_2(SCN).COH$.—11. The *amines* form crystalline bases with elimination of water. Thus aniline gives $CH_2I.CH(NH.C_6H_5)_2$, and *p*-toluidine gives $CH_2I.CH.(NH.C_6H_4.CH_3)_2$.

Tri-iodo-acetic aldehyde $CI_3.CHO$. *Iodal* (above 200°). From chloral or bromal and HI (Bertrand, *J.* 1881, 588).

IODO-ACETO-ACETIC ETHER $CH_3.CO.CHI.CO_2Et$. S.G. $\frac{14}{14}$ 1·7053. From cupric aceto-acetic ether and iodine in ether (Schönbrodt, *A.* 253, 178). Yellowish oil; v. sol. ether. Begins to decompose at 25°. AgCl gives chloro-aceto-acetic ether. AgCy gives dioxy-terephthalic ether dihydride. $AgNO_2$ forms nitro-aceto-acetic ether. Reduced silver gives di-acetyl-fumaric ether. Sodium aceto-acetic ether in benzene forms di-acetyl-succinic ether.

IODO-ACETONE C_3H_5IO *i.e.* $CH_3.CO.CH_2I$. S.G. $\frac{15}{}$ 2·17. Formed by the action of KI on chloro-acetone (Glutz a. E. Fischer, *J. pr.* [2] 4, 52). Prepared by mixing acetone (200 c.c.) with iodine (100 g.) and iodic acid (40 g.), and, after a week, boiling for three hours, adding water (500 c.c.), drying the separated oil over $CaCl_2$, and distilling *in vacuo* in the dark (De Clermont a. Chautard, *C. R.* 100, 745). Very pungent oil. Not inflammable. Decomposes slowly in sunlight, but more rapidly when heated. Reduces Fehling's solution. Mineral acids convert it into $CH_2I.CO.CH_2I$. Silver chloride forms chloro-acetone. KOAc gives $CH_3.CO.CH_2.OAc$.

Di-iodo-acetone $C_3H_4I_2O$ *i.e.* $CH_2I.CO.CH_2I$. [62°] (M. Simpson, *J. pr.* 102, 380; O. Völker, *A.* 192, 90).

Formation.—1. From acetone (48 g.), water (1000 g.), and ICl_3 (96 g.) at 68°. As soon as reaction begins the liquid is cooled. The oil that separates is exposed to the air till crystals separate (eight weeks); these are recrystallised from alcohol.—2. From $CH_2Cl.CO.CH_2Cl$ and aqueous KI.

Properties.—White needles. Violently attacks the mucous membrane. Decomposed when heated. Not very soluble in chloroform, CS_2, or alcohol. Sol. benzene, v. sol. ether and acetone. Cannot be distilled undecomposed.

Reactions.—1. *Silver chloride* gives solid $CH_2Cl.CO.CH_2Cl$ [43°].—2. Decomposed by cold KOH, and by boiling K_2CO_3.—3. Not converted into acroleïn or acrylic acid by Ag_2O, AgCy, or HgO.—4. Hg_2I_2 forms acetone, iodo-acetone, HI, and acetic acid, but no acroleïn.—5. *Zinc* and *acetic acid* reduce it to acetone.

p-**IODO-ACETOPHENONE** [1:4]$C_6H_4I.CO.CH_3$ [79°]. Obtained by diazotising *p*-amido-acetophenone, and heating the diazo-chloride with excess of HI (Klingel, *B.* 18, 2692). White flat needles or plates. Easily sol. alcohol and ether, and to a certain extent in hot water. By CrO_3 it is easily oxidised to *p*-iodo-benzoic acid [266°].

IODO-ACETOTHIENONE *v.* Iodo-thienyl methyl ketone.

IODO-ACETYLENE HC:CI. Formed by passing a current of steam through a solution of barium iodopropargylate $(C_2I.CO_2)_2Ba$ (Baeyer, *B.* 18, 2274). Crystalline solid. Sol. water. Volatile with steam. Very poisonous. It gives a purple-red pp. with ammoniacal Cu_2Cl_2, which is soon converted by an excess of the copper solution into copper-acetylene and cuprous iodide. It soon polymerises on keeping.

Di-iodo-acetylene IC:CI. [78°]. Formed by the action of iodine upon acetylene-silver. By treatment with an excess of ammoniacal Cu_2Cl_2 it is converted into copper-acetylene and cuprous iodide. It readily polymerises (Baeyer, *B.* 18, 2275).

Di-iodo-diacetylene IC:C.C:CI. [101°]. Colourless crystals. Odour resembling iodoform. Formed by the action of a solution of iodine in aqueous KI upon silver-diacetylene. By treatment with an excess of ammoniacal Cu_2Cl_2 it yields copper-diacetylene and cuprous iodide. It explodes violently on heating, with a brilliant red flash. It soon polymerises on keeping (Baeyer, *B.* 18, 2276).

IODO-ACETYLENE CARBOXYLIC ACID *v.* Iodo-propiolic acid.

IODO- ACIDS *v.* Iodo- compounds.

IODO-ACRYLIC ACID $C_2H_2I.CO_2H$. Large, colourless, four-sided prisms [65°]; or plates [140°]. Easily soluble in water, alcohol, and ether. Formed by the addition of HI to propiolic acid (Bandrowski, *B.* 15, 2703; Stolz, *B.* 19, 542). The Pb and Ag salts are white crystalline pps.

αβ-Di-iodo-acrylic acid $CHI:CI.CO_2H$. [106°]. Formed by treating propiolic acid with an ethereal solution of iodine (Homolka a. Stolz, *B.* 18, 2284). Colourless prisms, or long needles. Volatile with steam. Easily soluble in alcohol, ether, and hot water.

β-Di-iodo-acrylic acid $I_2C:CH.CO_2H$. [133°]. Formed by addition of HI to iodo-propiolic acid

$IC:C.CO_2H$ (Homolka a. Stolz, *B.* 18, 2284). Prisms. Easily soluble in alcohol and ether, tolerably in hot water, very sparingly in cold. Not volatile with steam.

Tri-iodo-acrylic acid $CI_2:CI.CO_2H$. [207°]. Formed by the action of an ethereal solution of iodine upon iodo-propiolic acid $CI:C.CO_2H$ (Homolka a. Stolz, *B.* 18, 2286). Large colourless prisms. Easily soluble in alcohol and ether, insoluble in cold water.

IODO-DI-ALLYL-ACETIC ACID $C_8H_{11}IO_2$ *i.e.* $CI(C_3H_5)_2.CO_2H$. *Iodo-octinoic acid.* From $C(OH)(C_3H_5)_2.CO_2H$ and fuming HIAq (Schatzky, *J. R.* 17, 78). Crystals; insol. water, v. sol. alcohol and ether. Easily decomposes.

IODO-ALLYL-ALCOHOL $C_3H_4I.OH$. [160°]. Produced by the action of aqueous Na_2CO_3 on di-iodo-propyl alcohol (Hübner a. Lellmann, *B.* 13, 460). Needles. Highly volatile with steam. Insol. water, sol. alcohol, chloroform, and HOAc. Not attacked by Ac_2O.

IODO-ALLYLENE C_3H_3I *i.e.* $CH_3.C:CI$ (?). (98°). S.G. 1·7. From silver-allylene and iodine in KIAq (Liebermann, *A.* 135, 270). Pungent oil. Almost insol. alcohol. With zinc and HCl it gives off allylene. Combines with iodine (1 mol.).

Iodo-allylene $CH_2I.C:CH$. *Propargyl iodide.* (115°). S.G. $\frac{0}{}$ 2·0177. From propargyl bromide and alcoholic NaI (Henry, *B.* 17, 1132). Liquid. V. e. sol. alcohol and ether, m. sol. boiling water. Readily combines with iodine, forming colourless needles of $CHI:CI.CH_2I$ [41°]. Combines with mercury.

IODO-ALLYLENE IODIDE *v.* TRI-IODO-PROPYLENE.

TRI-IODO-ALLYL ETHYL OXIDE $C_5H_7I_3O$ *i.e.* $CI_2:CI.CH_2.OEt$. From the silver derivative of propargyl ethyl oxide and iodine in ethereal solution (Liebermann, *A.* 135, 285). Oil.

DI-IODO-ALLYL-IODIDE *v.* TRI-IODO-PROPYLENE.

TETRA-IODO-DI-ALLYL PHOSPHITE $(CHI:CI.CH_2O)_2P(OH)$. [49°]. From propargyl alcohol, iodine, and red phosphorus (Henry, *B.* 8, 398; 17, 1133). Long slender needles (from alcohol). Very pungent.

IODO-AMIDO-BENZOIC ACID $C_7H_6INO_2$ *i.e.* $C_6H_3I(NH_2)CO_2H$ [3:2or6:1]. [137°]. Formed by reducing iodo-nitro-benzoic acid [235°] dissolved in glacial acetic acid (Grothe, *J. pr.* [2] 18, 326). Dark-brown crystals. V. sol. water. By further reduction it forms o-amido-benzoic acid [143°].—HA'HCl.—BaA'_2 aq.

Iodo-amido-benzoic acid $C_6H_3I(NH_2)CO_2H$ [3:6or2:1]. [209°]. From iodo-nitro-benzoic acid [174°]. Needles, sl. sol. water. May be reduced to o-amido-benzoic acid.—CaA'_2 2aq.—SrA'_2.—BaA'_2.

Di-iodo-*m*-amido-benzoic acid $C_6H_2I_2(NH_2)CO_2H$. Formed, together with $N_2(C_6H_2I_2CO_2H)_2$, by treating an alcoholic solution of *m*-amido-benzoic acid [173°] with iodine and mercuric oxide (Benedikt, *B.* 8, 384). The acids are separated by fractional ppn. of their alcoholic solution by lead acetate. Long needles. Decomposed by heat. Insol. water, v. sol. alcohol, ether, aqueous acids, alkalis, and Na_2CO_3.—KA': long silky needles, obtained by mixing alcoholic solutions of the acid and KOH.

Di-iodo-*p*-amido-benzoic acid $C_6H_2I_2(NH_2).CO_2H$. [above 300°]. Obtained by dissolving *p*-amido-benzoic acid in dilute HCl and passing in the vapour of ICl (2 mols.) (Michael a. Norton, *Am.* 1, 264). Tables. Insol. water, alcohol, and HOAc; sol. nitro-benzene. Does not combine with acids.—NaA' 5aq: long white needles, sol. hot water.—BaA'_2 4aq: needles, sol. hot water.—AgA'.

DI-IODO-*p*-AMIDO-PHENOL $C_6H_2I_2(NH_2)OH$. [222°]. Formed by reducing the corresponding nitro-phenol with $SnCl_2$ and HCl (R. Seifert, *J. pr.* [2] 28, 437). Needles (from alcohol) or plates (from MeOH). With HCl and bleaching powder it gives di-iodo-quinone chlorimide (*q. v.*). With H_2SO_4 and $K_2Cr_2O_7$ gives di-iodo-quinone (*q.v.*).—B'HCl. Decomposed by water.

IODO-AMIDO-THYMOL $C_6HIMePr(OH)(NH_2)$ [6:5:2:1:4]. From the oxim of iodo-thymoquinone by reduction with $SnCl_2$ (Kehrmann, *J. pr.* [2] 39, 392). Its stanno-chloride forms large colourless prisms.

IODO-AMIDO-TOLUENE SULPHONIC ACID $C_6H_2MeI(NH_2).SO_3H$ [1:4:2:5]. Formed from the corresponding nitro-toluidine sulphonic acid by diazotisation and treatment of the product with conc. HIAq at 135° (Foth, *A.* 230, 308). Slender silky needles (from water). V. sl. sol. cold water.

IODO-AMYL ALCOHOL $C_5H_{11}IO$? *Amylene glycol iodhydrin.* Formed by shaking up amylene with iodine, water, and HgO (Lippmann, *Z.* 1867, 17; *A. Suppl.* 5, 124). Heavy oil, decomposed by distillation.

IODO-AMYLIDENE-ANILINE $C_4H_8I.CH:NC_6H_5$. Formed by heating iodo-iso-valeric aldehyde with aniline (Chautard, *A. Ch.* [6] 16, 168). Yellow prismatic needles or rectangular tables. Decomposed by heat. V. sol. alcohol, sol. water and ether; v. sl. sol. benzene and chloroform. With HCl it forms an uncrystallisable salt.

o-IODO-ANILINE C_6H_6IN *i.e.* $C_6H_4I(NH_2)$ [1:2]. Mol. w. 219. [56·5°]. Formed by heating at 100° a mixture of o-iodo-nitro-benzene (25 pts.) with ferrous sulphate (250 pts.) and a moderate excess of dilute ammonia. The product is extracted with ether, the extract distilled with steam, the product dissolved in dilute H_2SO_4, freed from iodo-nitro-benzene by shaking with ether, ppd. by ammonia, and the iodo-aniline again distilled with steam (Körner a. Wender, *G.* 17, 486). Long silky needles, with an odour resembling pyridine. Sl. sol. hot water, v. sol. other solvents. Exhibits an alkaline reaction. Turns brown on exposure to air and light. Decomposes when heated, evolving iodine. Iodine converts it into di-iodo-aniline [96°].

S a l t s.—B'HCl aq: small prisms or cubes, turning opaque on exposure, with loss of water of crystallisation.—$B'_3(H_2SO_4)_2$: silky needles, m. sol. water.—N i t r a t e: small four-sided tables.

Acetyl derivative $C_6H_4I.NHAc$. [110°]. Prisms or hexagonal tables; m. sol. hot water, v. sol. alcohol.

m-Iodo-aniline $C_6H_4I(NH_2)$ [1:3]. [27°]. Formed by reducing *m*-iodo-nitro-benzene (Griess, *Z.* 1866, 218). Silvery plates.

Acetyl derivative $C_6H_4I(NHAc)$. [119·5°].

Glistening needles; more stable than the *o*-isomeride (Körner a. Wender, *G.* 17, 486).

p-**Iodo-aniline** $C_6H_4I(NH_2)$ [1:4]. [63°]. Formed by reducing *p*-iodo-nitro-benzene [172°] (Griess, *C. J.* 20, 85). Formed also by adding iodine (3 pts.) to aniline (2 pts.) and mixing the solution with aqueous HCl (S.G. 1·11) when *p*-iodo-aniline hydrochloride is ppd. (Hofmann, *A.* 67, 64). Prisms or needles; heavier than water. Has no action on litmus. Sl. sol. cold water; v. sol. other solvents. Bromine converts it into tri-bromo-aniline. — B′HCl: thin laminæ or needles (from hot water); sl. sol. cold water, almost insol. HClAq; sol. alcohol, insol. ether.—$B'_2H_2PtCl_6$: orange pp.—$B'_2H_2C_2O_4$: long needles, sl. sol. water and alcohol, insol. ether.—$B'_2H_2SO_4$: scales.

Acetyl derivative $C_6H_4I(NHAc)$. [183°]. S. (alcohol of 95 p.c.) 6·4 at 20·5°. Small glistening tables or trimetric prisms (K. a. W.). Formed by dissolving acetanilide in glacial acetic acid, and passing in vapour of iodine chloride, the yield being 85 p.c. (Michael a. Norton, *Am.* 1, 255).

Benzoyl derivative $C_6H_4I.NHBz$. [180°]. Long needles (Hübner, *B.* 10, 1717). An isomeride [210°] is formed from benzanilide and ICy.

Di-iodo-aniline $C_6H_3I_2NH_2$ [4:2:1]. [96°]. Formed by the action of iodine on phenylated 'white precipitate' NHPh.HgCl (Rudolph, *B.* 11, 78). Formed also by passing ICl (2 mols.) into a solution of aniline in HOAc (Michael a. Norton, *Am.* 1, 255; *B.* 11, 109). Needles. Sl. sol. boiling water and ligroïn, v. sol. ether, chloroform, CS_2, acetic ether, and hot alcohol. Volatile with steam. It is slightly basic, but its hydrochloride is decomposed by cold water.—B′HCl: long white needles, decomposed at 50°. — $B'_2H_2PtCl_6$.—$B'HNO_3$.—$B'_3(H_2SO_4)_2$.

Benzoyl derivative $C_6H_3I_2NHBz$. [181°]. Slender needles (Rudolph).

Tri-iodo-aniline $C_6H_2I_3(NH_2)$ [6:4:2:1]. [185·5°]. Prepared by the action of ICl (3 mols.) on a solution of aniline in HClAq (Michael a. Norton, *Am.* 1, 255). Long white needles; sol. CS_2 and acetic ether; insol. water.

IODO-ANISIC ACID *v. Methyl derivative* of Iodo-oxy-benzoic acid.

IODO-BENZENE C_6H_5I. *Phenyl iodide.* Mol. w. 204. (188°). S.G. $\frac{0}{0}$ 1·8606; $\frac{15·2}{0}$ 1·8380 (Young, *C. J.* 55, 486); $\frac{0}{4}$ 1·8578; $\frac{11}{4}$ 1·8403; $\frac{20}{4}$ 1·8321. S.V. 130·55 (R. Schiff, *B.* 19, 564). $\mu_D = 1·6189$ (Seubert, *B.* 22, 2520).

Formation. — 1. By treating phenol with iodine and phosphorus. The yield is bad (Williamson a. Scrugham, *C. J.* 13, 244).—2. By the action of ICl on sodium benzoate (Schützenberger, *C. R.* 52, 963).—3. By heating benzene for some time with iodic acid (Peltzer, *A.* 136, 194).—4. By the action of HI on diazobenzene salts (Griess, *J.* 1866, 447).—5. By heating benzene (20 g.) with iodine (15 g.) and iodic acid (10 g.) at 220° (Kekulé, *A.* 137, 157).—6. From benzene, iodine and $FeCl_3$ (Lothar Meyer, *A.* 231, 195).—7. By the action of excess of iodine on phenyl hydrazine (E. v. Meyer, *J. pr.* [2] 36, 115).

Preparation.—By allowing chloride of iodine to drop slowly into a large excess of benzene containing a small quantity of aluminium chloride (Greene, *C. R.* 90, 40).

Properties. — Colourless oil, insol. water. Solidifies when cooled by solid CO_2. Easily reduced by sodium amalgam to benzene. Aqueous HIAq at 250° reduces it to benzene. Not affected by solid KOH at 250°, nor by alcoholic KOH or NH_3 (Kekulé).

Reactions.—1. H_2SO_4 at 100° forms a mixture of iodo-benzene sulphonic acid, di-iodo-benzene, and benzene sulphonic acid, in proportions varying with proportions of materials employed, strength of the acid, temperature, and duration of the experiment (Neumann, *A.* 241, 47).—2. *Silver nitrate* does not act below 135°, but between 140° and 150° a reaction takes place forming tri-nitro-phenol, AgI, and metallic silver (Geuther, *A.* 245, 99).—3. By heating with *aluminium chloride* there is formed benzene, di-iodo-benzenes, HCl, and iodine (Dumreicher, *B.* 15, 1868).

Dichloride $C_6H_5ICl_2$. Formed by passing chlorine into liquid iodobenzene. Formed also by passing chlorine into a solution of iodobenzene (5 g.) in chloroform (15 g.) (Willgerodt, *J. pr.* [2] 33, 154). Begins to decompose at 80°, and at 120° it is all broken up into Cl_2 and C_6H_5I. It may be kept in glass bottles, but if placed over H_2SO_4 it gives off chlorine. It is decomposed by solution in alcohol, but it may be crystallised from chloroform as yellow needles. It dissolves in benzene, glacial acetic acid, light petroleum, CS_2 and ether. As a reagent it displaces iodine by chlorine, turning KI, PbI_2, &c., into KCl, $PbCl_2$, &c., with separation of iodine. May therefore be used as a test for iodides. It also converts alcoholic iodides (*e.g.* MeI) into chlorides. It is hardly attacked by cold aqueous NH_3 or NaOH.

o-Di-iodo-benzene $C_6H_4I_2$ [1:2]. [27°]. (287°).

Preparation.—Iodo-aniline (10 g.) is dissolved in hot water (70 g.) containing H_2SO_4 (9 g.), KNO_2 (4·5 g.) dissolved in a little water is added, and then an excess of solution of KI in aqueous HI (S.G. 1·1). After standing a few hours the oil that has separated is washed with KOHAq and distilled with steam (Körner a. Wender, *G.* 17, 486; *cf.* Körner, *G.* 4, 305). Long prisms or hexagonal tables. Volatile with steam. Sl. sol. water; sol. alcohol.

m-**Di-iodo-benzene** $C_6H_4I_2$ [1:3]. [40°] (K.); [37°] (R.). (285°). From *m*-iodo-aniline by displacing NH_2 by I (Körner). Also from di-iodo-aniline by elimination of NH_2 (Rudolph). Trimetric tables (from ether-alcohol).

p-**Di-iodo-benzene** $C_6H_4I_2$ [1:4]. [127°] (Kekulé); [129°] (Körner). A product of the action of iodine chloride on NaOBz (Schützenberger) and of iodine and iodic acid on benzene (Kekulé). Formed also from *p*-iodo-aniline by the diazo- reaction (Kekulé, *Z.* 1866, 688). Nacreous laminæ. Readily sublimed.

Tri-iodo-benzene $C_6H_3I_3$ [1:2:4]. Mol. w. 456. [76°]. A product of the action of iodine and iodic acid on benzene (Kekulé). Small needles. May be sublimed.

IODO-BENZENE-AZOXY- COMPOUNDS *v.* Azoxy- compounds.

IODO-BENZENE o-SULPHONIC ACID $C_6H_4I.SO_3H$ [1:2]. From *o*-amido-benzene sulphonic acid by the diazo- reaction (Bahlmann, *A.*

186, 325).—KA′aq: crystals, sl. sol. water.—BaA'_2: needles, sl. sol. cold, v. sol. hot, water.

Chloride $C_6H_4I.SO_2Cl$. [51°]. Thick prisms (from ether).

Amide $C_6H_4I.SO_2NH_2$. [170°]. White laminæ, sl. sol. water.

Iodo-benzene *p*-sulphonic acid $C_6H_4I.SO_3H$ [1:4]. From iodo-benzene and fuming H_2SO_4 (Körner a. Paterno, *G.* 2, 448). Formed also from amido-benzene *p*-sulphonic acid by displacing NH_2 by I through the diazo- reaction (Lenz, *B.* 10, 1135). Deliquescent needles.—NH_4A': minute needles.—KA′: needles.—CaA'_2.—BaA'_2: minute plates, sl. sol. water.—PbA'_2.

Chloride $C_6H_4I.SO_2Cl$. [87°]. Laminæ.

Amide $C_6H_4I.SO_2NH_2$. [183°]. Crystalline powder, sl. sol. water, v. sol. alcohol.

o-IODO-BENZOIC ACID $C_6H_4I.CO_2H$. [157°].

Formation.—1. From o-amido-benzoic acid by the diazo- reaction (Griess, *C. J.* 24, 702).—2. By oxidising o-iodo-toluene with dilute HNO_3 (Kekulé, *B.* 7, 1007).—3. From *m*-iodo-nitro-benzene and alcoholic KCy at 200° (Richter, *B.* 4, 554).

Properties.—Long needles; may be readily sublimed. Sl. sol. hot water, v. e. sol. ether and alcohol. Gives salicylic acid when fused with potash.

Salts.—CaA'_2 2aq.—BaA'_2 6aq.

***m*-Iodo-benzoic acid** $C_6H_4I.CO_2H$. [187°].

Formation.—1. From *m*-amido-benzoic acid by the diazo- reaction (Griess, *A.* 113, 334; 117, 1; Cunze a. Hübner, *A.* 135, 108; Grothe, *J. pr.* [2] 18, 324).—2. By heating benzoic acid (1 pt.) with KIO_3 (2 pts.) and dilute H_2SO_4 (Peltzer, *A.* 136, 201).—3. By oxidising o-iodo-toluene with chromic acid mixture (Körner, *Z.* [2] 5, 637).—4. By heating dry silver benzoate with iodine at 150°–180° (Birnbaum a. Reinherz, *B.* 15, 456).

Properties.—Needles, sl. sol. water, v. sol. alcohol. May be sublimed. Gives *p*-oxy-benzoic acid on oxidation. Ammonia forms amido-benzoic acid.

Salts.—NaA′aq.—MgA'_2 4aq.—CaA'_2 2aq: scales.—CaA'_2: nodules.—BaA'_2 4aq: needles, sol. alcohol.—MgA'_2 4aq.

Ethyl ether EtA′. Oil.

Nitrile $C_6H_4I.CN$. [41°]. From *m*-amido-benzonitrile by the diazo- reaction. Needles.

***p*-Iodo-benzoic acid** $C_6H_4I.CO_2H$. [266°] (Beran, *B.* 18, 137; Klingel, *B.* 18, 2693). Formed by oxidation with chromic acid mixture from *p*-iodo-toluene (Körner, *Z.* [2] 5, 327), from *p*-iodo-phenyl-acetic acid (Jackson a. Mabery, *Am.* 2, 253), or from *p*-iodo-acetophenone (Klingel). Nacreous scales (from alcohol). Nearly insol. boiling water. Converted by potash-fusion into *p*-oxy-benzoic acid.

Salts (Glassner, *B.* 8, 562).—NaA′ ½aq: colourless needles, v. sol. water.—KA′.—BaA'_2 1½aq: long trimetric plates.—CaA'_2 aq.—SrA'_2 aq: nacreous laminæ.—ZnA'_2 4aq: cubes.

Methyl ether MeA′. [114°]. Long needles (Schmidt a. Schultz, *A.* 207, 333).

Ethyl ether EtA′. Oil.

o-IODO-BENZOIC ALDEHYDE $C_6H_4I.CHO$. [37°]. Formed from o-nitro-cinnamic acid by successive conversion into amido-, diazo-, and iodo-cinnamic acid, and oxidation of the latter with $KMnO_4$ (Stuart, *C. J.* 53, 140).

***p*-Iodo-benzoic aldehyde** $C_6H_4I.CHO$. [73°]. Needles (Jackson a. White, *B.* 11, 1042; *P. Am. A.* 15, 269).

***p*-IODO-BENZYL ALCOHOL** $C_6H_4I.CH_2OH$. [72°]. Prepared by heating *p*-iodo-benzyl bromide with NaOAc and aqueous NH_3 at 160° Formed also by heating *p*-iodo-benzyl bromide with water for a long time (Jackson, *P. Am. A.* 13, 202; Jackson a. Mabery, *Am.* 2, 251; *B.* 11, 56). Silky scales (from alcohol or CS_2) or long needles (from water). Sl. sol. cold water, v. sol. alcohol, ether, benzene, and CS_2.

o-IODO-BENZYLAMINE C_7H_8IN *i.e.* [2:1] $C_6H_4I.CH_2.NH_2$. From o-iodo-benzyl bromide and alcoholic NH_3 (Mabery a. Robinson, *Am.* 4, 103). Liquid. Absorbs CO_2 from the air.—$B'_2H_2PtCl_6$: minute yellow prisms.

***p*-Iodo-benzylamine** [4:1] $C_6H_4I.CH_2.NH_2$. Formed by heating *p*-iodo-benzyl bromide with alcoholic NH_3 at 120° (Jackson a. Mabery, *Am.* 2, 257). Oil. Absorbs CO_2 from the air forming a carbonate [113°].—B′HCl: slender white needles [240°], sol. water and alcohol, sl. sol. ether.—$B'_2H_2PtCl_6$.

Di-*p*-iodo-di-benzyl-amine $(C_6H_4I.CH_2)_2NH$. [76°]. Formed, together with tri-*p*-iodo-tri-benzylamine, by boiling *p*-iodo-benzyl bromide with alcoholic NH_3 (Jackson a. Mabery, *Am.* 2, 256; *B.* 11, 58; *P. Am. A.* 13, 209). White needles; insol. water, v. sol. hot alcohol, ether, benzene, and CS_2.

Salts.—B′HCl: thick white plates, sol. CS_2 and HOAc, sl. sol. alcohol and benzene.—B′HBr: thick pearly prisms, insol. water, sl. sol. alcohol, sol. ether, benzene, and CS_2.—$B'_2H_2PtCl_6$: minute yellow needles, almost insol. water and alcohol.—$B'_2H_2CO_3$. [113°]. Crystalline.

Tri-*p*-iodo-tri-benzyl-amine $(C_6H_4I.CH_2)_3N$. [115°]. Formed as above (J. a. M.). White needles (from ether); v. sl. sol. hot alcohol, v. sol. ether, benzene, and CS_2.—$B'_2H_2PtCl_6$: yellow needles, nearly insol. water and alcohol.

o-IODO-BENZYL BROMIDE $C_6H_4I.CH_2Br$. [53°]. Prepared by dropping bromine into o-iodo-toluene heated to 190°–200° (Mabery a. Robinson, *Am.* 4, 102; *P. Am. A.* 17, 103). Thick flattened prisms (from ligroïn); v. sol. ether, hot alcohol, benzene, CS_2, and chloroform, insol. water. Its vapour is very pungent. Gives o-iodo-benzoic acid on oxidation with dilute HNO_3.

***p*-Iodo-benzyl bromide** $C_6H_4I.CH_2Br$. [79°]. Prepared by heating *p*-iodo-toluene in bromine vapour at 115°–150° (Jackson, *Am.* 1, 93). Straw-coloured needles, somewhat pungent. Insol. water and cold alcohol, sol. hot alcohol, v. sol. ether. Hardly attacked by CrO_3.

IODO-BENZYL CYANIDE *v. Nitrile* of IODO-PHENYL-ACETIC ACID.

o-IODO-BENZYLIDENE-MALONIC ACID $C_{10}H_7IO_4$ *i.e.* $C_6H_4I.CH:C(CO_2H)_2$. [204°]. Formed by heating equal weights of malonic acid and iodo-benzoic aldehyde for several hours at 100° with half their weight of HOAc (Stuart, *C. J.* 53, 142). Decomposed on melting into CO_2 and o-iodo-cinnamic acid.

α-IODO-BENZYL-MALONIC ETHER $C_6H_5.CH_2.CI(CO_2Et)_2$. From sodium benzyl-malonic ether and iodine (Bischoff a. Hausdörfer, *A.* 239, 110). Oil. Decomposes on hydrolysis

into benzoic aldehyde, alcohol, acetic acid, and CO_2.

p-**IODO-BENZYL SULPHOCYANIDE** $C_6H_4I.SCy$. [40°]. Formed by boiling *p*-iodo-benzyl bromide with an alcoholic solution of potassium sulphocyanide (Jackson, *P. Am. A.* 13, 207; *B.* 11, 58). Long white plates (from alcohol). M. sol. hot alcohol, v. sol. ether, benzene, CS_2, and HOAc.

IODO-BETORCIN $C_6HIMe(OH)_2$. [93°]. Formed by the action of PbO and I (2 pts.) on an ethereal solution (50 pts.) of betorcin (1 pt.). Crystallised from light petroleum (Stenhouse a. Groves, *C. J.* 37, 404). V. sol. ether, CS_2, and benzene.

IODO-BROMO- *v.* Bromo-iodo-.

IODO-BUTANE *v.* Butyl iodides.

Di-iodo-butane $C_4H_8I_2$ *i.e.* $CH_3.CHI.CH_2.CH_2I$. (116° *in vacuo*). S.G. 2·291. From the corresponding di-oxy-butane and HI (Wurtz, *Bl.* [2] 41, 362).

p-**IODO-ISOBUTYL-BENZENE** $C_6H_4(C_4H_9)I$. (256° cor.). Formed by the action of HI on the diazo- compound from *p*-amido-phenyl-butane (Pahl, *B.* 17, 1232). Colourless oil. By HNO_3 it is oxidised to *p*-iodo-benzoic acid.

IODO-BUTYLENE C_4H_7I. *Crotyl iodide.* (132°). From tri-oxy-butane (butenyl-glycerin), iodine, and phosphorus (Lieben a. Zeisel, *M.* 1, 836). Pungent liquid. Combines with mercury forming an unstable crystalline compound.

IODO-ISOBUTYL-TOLUENE $C_6H_3(CH_3)(C_4H_9)I$ [1:3:6]. [c. 35°]. (264°). Formed by diazotising amido-tolyl-isobutane and treating the product with HI (Effront, *B.* 17, 2325). Long white needles. V. sol. alcohol and ether. On oxidation with HNO_3 at 200° it gives nitro-tolyl-isobutyric acid.

α-**IODO-*n*-BUTYRIC ACID** $C_4H_7IO_2$ *i.e.* $CH_3.CH_2.CHI.CO_2H$. [110°] (Fittig, *B.* 9, 1194). From α-crotonic acid and fuming HI at 100° (Hemilian, *A.* 174, 324; *v. infra*). Monoclinic crystals (Haushofer, *Z. K.* 6, 135).

Ethyl ether EtA'. (191°). Formed by boiling α-bromo-butyric ether with alcoholic KI (Hell, *B.* 6, 29).

β-**Iodo-butyric acid** $CH_3.CHI.CH_2.CO_2H$. Formed, in small quantity, in the preparation of the preceding. Liquid.

According to Michael and Freer (*J. pr.* [2] 40, 95) HI unites with solid crotonic acid forming, contrary to the statement of Hemilian, only β-iodo-butyric acid, of low melting-point. The same acid is formed from liquid crotonic acid and HI. Boiling water converts it into β-oxy-butyric acid. Hot NaOHAq gives solid crotonic acid.

γ-**Iodo-butyric acid** $CH_2I.CH_2.CH_2.CO_2H$. [41°]. From the lactone of γ-oxy-butyric acid and HI (Henry, *C. R.* 102, 368; A. Saytzeff, *B.* 14, 2826). Colourless plates, which become yellow in sunlight. Sl. sol. warm water (difference from β-isomeride), v. sol. methyl alcohol, ether, and CS_2.

Methyl ether MoA'. (199°). S.G. $\frac{0}{0}$ 1·666. Oil, with pleasant odour.

Iodo-isobutyric acid $(CH_3)_2CI.CO_2H$ (?). [36°]. From methacrylic acid and fuming HI at 0° (Fittig a. Paul, *A.* 188, 58; 200, 67). Tables (from CS_2) or large prisms (from conc. HIAq). Sl. sol. water.

Di-iodo-isobutyric acid $C_4H_6I_2O_2$. [127°]. Formed by treating tri-oxy-isobutyric acid with HI and P and extracting the product with ether (E. Fischer a. Tafel, *B.* 22, 108). Long needles, v. e. sol. alcohol and ether.

IODO-ISOBUTYRIC ALDEHYDE $(CH_2I)(CH_3)CH.CO.H$ or $(CH_3)_2CI.CO.H$. S.G. $\frac{10}{}$ 2·29.

Preparation.—By treating isobutyric aldehyde (22·5 c.c.) dissolved in 40 c.c. of alcohol, with iodine (25 g.) and iodic acid (10 g.). It is very difficult to obtain pure, 100 g. of the crude body yielding not more than 1 g. sufficiently pure for analysis. Reduced silver removes the excess of iodine with the least loss of substance (Chautard, *A. Ch.* [6] 16, 160).

Properties.—Heavy liquid, colourless when pure. Its vapour is, like its homologues, exceedingly irritating. It is completely decomposed at 100°, and cannot be distilled even *in vacuo*. Forms a crystalline compound with $NaHSO_3$. Is rapidly resinified by solutions of alkalis or mineral acids. Combines with aniline, with elimination of water, giving a di-amine. $Ag(C_2H_3O_2)$ at 100° yields isobutyl acetate (114°). AgCN and AgSCN yield the corresponding cyano- and sulphocyano- derivatives.

IODO-CAMPHOR *v.* Camphor.

IODO-CAPROIC ACID *v.* Iodo-hexoic acid.

IODO-CAPRYL-BENZENE *v.* Iodo-octyl-benzene.

IODO-CARBOSTYRIL *v.* Iodo-oxy-quinoline.

IODO-CHELIDONIC ACID *v.* Chelidonic acid.

IODO-CHRYSIN *v.* Chrysin.

o-**IODO-CINNAMIC ACID** $C_9H_7IO_2$ *i.e.* $C_6H_4I.CH{:}CH.CO_2H$. [214°] (G. a. H.); [207°] (S.). Formed by boiling o-diazo-cinnamic acid with aqueous HI (Gabriel a. Herzberg, *B.* 16, 2037). Formed also by heating o-iodo-benzylidene-malonic acid to its melting-point (Stuart, *C. J.* 53, 142). Crystals (from dilute alcohol).

m-**Iodo-cinnamic acid** $C_6H_4I.C_2H_2.CO_2H$. [182°]. Formed by boiling *m*-diazo-cinnamic acid with HI (G. a. H.). Sol. benzene, petroleum-ether, and hot alcohol, sl. sol. water.

p-**Iodo-cinnamic acid** $C_6H_4I.C_2H_2.CO_2H$. [c. 255°]. Formed by boiling *p*-diazo-cinnamic acid with HI (Gabriel a. Herzberg, *B.* 16, 2040). Crystalline mass.

IODO-CODEÏNE *v.* Codeïne.

IODO-COMPOUNDS. Organic compounds containing iodine attached to carbon.

Formation.—1. Unlike chlorine and bromine, iodine is not capable of directly displacing hydrogen, inasmuch as the HI produced would cause a reverse reaction. But if iodic acid, mercuric oxide, or some other substance capable of removing HI be present, the substitution may take place (Kekulé, *A.* 131, 231). In the case of aniline, the free HI combines with excess of aniline and thus iodo-aniline may be formed. Mercuric oxide will not induce the iodation of fatty compounds, but is especially useful in the case of phenols and oxy-acids (Weselsky, *A.* 174, 99). The operation is performed in boiling alcoholic solution, and an intermediate body appears to be mercuric iodate (Lippmann, *B.* 7, 1773). Aromatic hydrocarbons may be iodated by heating with iodine and dry $FeCl_3$ (L. Meyer, *A.* 231, 195).—2. By the action of HI on hydroxylic compounds.

The alkyl iodides may be prepared in this way by the action of HI or, better, of iodine and phosphorus, on the corresponding alcohols at 100°. The polyhydric alcohols give rise, in this way, to secondary alkyl iodides, the iodine displacing hydrogen attached to a penultimate atom of carbon: thus glycerin gives isopropyl iodide. Iodides of acid radicles are formed by the action of iodide of phosphorus on the dry alkaline salts (Cahours, *A.* 104, 111).—3. By the union of HI with unsaturated compounds. This combination takes place more readily than in the case of HCl and HBr. The iodine attaches itself to that one of the involved atoms of carbon that is combined with the smaller amount of hydrogen, *e.g.*: $CH_3.CH:CH_2 + HI = CH_3.CHI.CH_3$. 4. From aromatic amido- compounds by the diazo-reaction. This may be performed by heating the diazo- compounds with HIAq, or with aqueous KI, *e.g.*: $C_6H_5.N_2.SO_4H + KI = C_6H_5I + N_2 + KHSO_4$. Also by Sandmeyer's reaction, which consists in boiling the diazo- compound with cuprous iodide, *v.* DIAZO- COMPOUNDS.—5. By gradually adding HNO_3 to a hot solution of the amine in HIAq (Losanitsch, *B.* 18, 39).—6. By displacing Cl or Br by I by treatment with a metallic iodide. The elements K, Mg, Ca, Sr, Ba, Al, Mn, and Co prefer chlorine and bromine to iodine, and hence the iodides of these metals when heated with chloro- or bromo- compounds produce iodo-compounds (Köhnlein, *A.* 225, 194). Thus propyl chloride is converted into propyl iodide by CaI_2, SrI_2, MnI_2, and CoI_2, while it is but slightly affected by NiI_2 and FeI_2, is not affected by SnI_2, and is wholly decomposed by PI_3. The conversion of benzyl chloride into benzyl iodide is partially effected by BaI_2 at 15°, by ZnI_2 at 10°, by CdI_2 at 100°, and by PbI_2 at 160°. On the other hand, isobutyl chloride is not converted into iodide at 70° by BaI_2, by ZnI_2, or by CdI_2; while CdI_2 at 135° decomposes it. The substitution of Cl in chloro-acetic acid by I is partly effected by CdI_2 or TlI at 100°, and may be effected by Ba_2I or ZnI_2 at 100° (Brix, *A.* 225, 166). Potassium iodide is a very convenient reagent for the purpose (Perkin a. Duppa, *A.* 112, 125), but cannot be always depended upon; for though it displaces Cl by I in the case of epichlorhydrin, chloro-lactic acid, dichlorhydrin, and mono- and di-chloro-acetone, it does not act on di-chlorinated ether, and it decomposes chloral into chloroform and CO_2. Calcium iodide $CaI_2 3\frac{1}{2}aq$ is also an excellent reagent for converting chloro- and bromo- compounds into the corresponding iodo-derivatives (Spindler, *A.* 231, 257). Thus it converts $CH_2Cl.CH_2Br$ into ethylene iodide, and $CH_3.CHClBr$ into $CH_3.CHI_2$; but it fails with $CH_2Cl.CHCl_2$, with $CHCl_2.CHCl_2$, with $CCl_3.CHCl_2$, with C_2Cl_6, with chloro-benzene, and with chloral. Dry CaI_2 requires a higher temperature (120°) before it reacts, and this decomposes many of the iodo- compounds that should be formed.—7. *Iodine chloride* also acts as an iodating substance, especially upon aromatic amines. Thus it converts aniline (dissolved in HOAc) into di-iodo-aniline (when 2 mols. ICl are used) and tri-iodo-aniline (when 3 mols. ICl are used). It converts acetanilide into acetyl-*p*-iodo-aniline, *m*-nitro-aniline into di-iodo-*m*-nitro-aniline, *p*-nitro-aniline chiefly into iodo-*p*-nitro-aniline, and *p*-toluidine into di-iodo-*p*-toluidine: but it does not act on acetyl-*p*-toluidine (*B.* 11, 107).—8. By heating chloro- compounds with fuming HIAq (Lieben, *Z.* 1868, 712).—9. Nitrogen iodide, acting on dilute alcoholic solutions of the potassium derivatives of phenols, forms iodo-phenols and ammonia (Willgerodt, *J. pr.* [2] 37, 446).

Reactions.—1. The displacement of iodine by chlorine or bromine may be effected by heating with the chloride or bromide of Hg, Cu, Ag, Sn, Pb, As, or Sb (*v.* CHLORO- COMPOUNDS and BROMO-COMPOUNDS).—2. *Chlorine* and *bromine* displace iodine directly.—3. *Sodium* frequently removes iodine with ease, *e.g.* $2C_2H_5I + Na_2 = C_4H_{10} + 2NaI$. In like manner (by what is known as Fittig's reaction): $C_6H_5I + C_2H_5I + Na_2 = C_6H_5.C_2H_5 + 2NaI$. 4. *Water* readily decomposes tertiary alkyl iodides, forming HI and a tertiary alcohol. Methyl and ethyl alcohol at 100° act in like manner, forming a tertiary alcohol and MeI or EtI.—5. *Silver* obtained by reduction sometimes removes iodine: *e.g.* $2CH_2I.CH_2.CO_2H + Ag_2 = 2AgI + CO_2H.CH_2.CH_2.CH_2.CH_2.CO_2H$.

Some aromatic iodo- compounds can take up chlorine, *e.g.* PhI gives $PhICl_2$ (Willgerodt, *J. pr.* [2] 33, 154), C_6H_4BrI gives $C_6H_4BrICl_2$, while $C_6H_2Br_3I$ gives $C_6H_2Br_3ICl_2$, and $C_6H_4(NO_2)I$ gives $C_6H_4(NO_2)ICl_2$. $C_6H_3(NO_2)_2I$ has no action.

IODO-*m*-CRESOL $C_6H_3MeI(OH)$ [1:*x*:3]. Oil Formed by adding iodine to a solution of *m*-cresol in ammonia and alcohol (Willgerodt a. Kornblum, *J. pr.* [2] 39, 289).

Iodo-*p*-cresol $C_6H_3MeI.OH$ [1:3:4]. Formed by the action of dry iodine on sodium-*p*-cresol suspended in CS_2 (Schall a. Dralle, *B.* 17, 2533). Liquid. Volatile with steam.

Methyl ether $C_6H_3MeI(OMe)$: (238°); oil.

Di-iodo-*o*-cresol $C_6H_2MeI_2(OH)$ [1:3:4:2]. [70°]. Formed by the action of iodide of nitrogen upon the sodium compound of *o*-cresol (Willgerodt, *J. pr.* [2] 37, 448, 39, 289).

Acetyl derivative $C_6H_2MeI_2(OAc)$. [56°]. Tables.

Picrate. [204°]. Yellow crystalline aggregates.

Di-iodo-*m*-cresol $C_6H_2MeI_2(OH)$. [76°]. Formed together with iodo-*m*-cresol (W. a. K.). Long needles, sol. usual menstrua.

Di-iodo-*p*-cresol $C_6H_2MeI_2.OH$ [1:3:5:4]. [61°]. Formed together with the preceding (Schall a. Dralle, *B.* 17, 2534). White tables. Easily soluble in alcohol, sparingly in water and ligroïn. Volatile with steam.

Acetyl derivative $C_6H_2MeI_2(OAc)$: [62°], white tables.

Benzoyl derivative $C_6H_2MeI_2(OBz)$: [130°], glistening white prisms.

Ethyl ether $C_6H_2MeI_2(OEt)$. [77°]. White solid, sol. organic solvents (Willgerodt a. Kornblum, *J. pr.* [2] 39, 289).

IODO-CRESOL SULPHONIC ACID

$C_6H_2MeI(OH)SO_3H$ [3:1:2:5]. [155°]. Formed, together with an isomeride, by the action of iodine on the potassium salt of *o*-cresol-sulphonic acid (Kehrmann, *J. pr.* [2] 37, 338). Colourless plates (containing 3aq). Converted by nitric acid into dinitro-cresol [86°]. Chromic acid forms iodo-toluquinone [115°].

Salts.—A'K: fine needles.—A'_2Ba 4aq.

Di-iodo-*m*-cresol sulphonic acid

$C_6HMeI_2(OH)(SO_3H)$[3:6:2:1:4]. [70°]. From potassium *m*-cresol sulphonate by treatment with

iodine (Kehrmann, *J. pr.* [2] 39, 392). Small needles. Oxidised by CrO_3 to di-iodo-toluquinone.

IODO-ψ-CUMENE $C_6H_2IMe_3$[1:2:4:5]. *Iodo-tri-methyl-benzene.* [37°]. (258°). Formed by decomposing ψ-cumene diazopiperidide with HIAq (S.G. 1·73) (Wallach a. Heusler, *A.* 243, 233). Formed also from ψ-cumidine by diazotising and heating the product, dissolved in H_2SO_4 with KI (Kürzel, *B.* 22, 1586). Scales. Treatment with H_2SO_4 forms two isomeric di-iodo-ψ-cumene sulphonic acids: ψ-cumene sulphonic acid and iodo-ψ-cumene sulphonic acid. One of the di-iodo-ψ-cumenes melts at 74°, the other is an oil.

IODO-ψ-CUMENE SULPHONIC ACID $C_6HIMe_3SO_3H$. Formed as above. Scales, m. sol. water.

Salts.—NaA′aq: plates.—BaA'_2aq: needles.

IODO-CYANETHINE *v.* Cyanethine.

IODO-ETHANE *v.* Ethyl iodide.

Di-iodo-ethane *v.* Ethylene iodide and Ethylidene iodide.

Tri-iodo-ethane $C_2H_3I_3$ *i.e.* $CH_3.CI_3$ [95°]. Formed by the action of aluminium iodide upon $CH_3.CCl_3$ (De Boissieu, *Bl.* [2] 49, 16). Yellow octahedra. V. e. sol. CS_2, benzene, and ether; v. sol. petroleum-ether; m. sol. alcohol. Smells faintly of iodoform.

IODO-ETHYL ALCOHOL *v.* Glycol*iodhydrin.*

β-IODO-ETHYL-AMINE $CH_2I.CH_2.NH_2$.

Hydriodide B′HI. [194°]. From vinyl-amine and conc. HIAq (Gabriel, *B.* 21, 1049). Trimetric crystals (from hot alcohol). V. sol. water. When treated with KOH it gives a liquid, soluble in water, with a disagreeable odour.

Picrate $B'C_6H_2(NO_2)_3OH$ ½aq. [c. 105°] (hydrated); [131°] (anhydrous). Short compact yellow prisms.

Di-iodo-ethyl-amine $EtNI_2$ *v. Ethyl-di-iodo-amine*, vol. ii. p. 474.

ωα-DI-IODO-ETHYL-BENZENE $C_8H_8I_2$ *i.e.* $C_6H_5.CHI.CH_2I$. *Styrene di-iodide.* From styrene and a concentrated solution of iodine in KIAq (Berthelot, *Bl.* 6, 295; 7, 277). Crystals; v. sol. ether. Rapidly decomposes into iodine and metastyrene.

IODO-ETHYLENE C_2H_3I *i.e.* CH_2:CHI. *Vinyl iodide.* (56°). S.G. $\frac{0}{}$ 2·08. Formed by distilling ethylene iodide with conc. alcoholic potash, the receiver being kept very cool, and the distillate finally mixed with water (Regnault, *A.* 15, 69; E. Kopp, *C. R.* 18, 871). Also from ethylidene iodide (Gustavson, *B.* 7, 731). Formed also by the union of HI with acetylene (Berthelot, *A.* 132, 122; Semenoff, *Z.* 1865, 725). Oil; v. sol. alcohol and ether, with alliaceous odour.

Di-iodo-ethylene $C_2H_2I_2$ *i.e.* CHI:CHI. *Acetylene di-iodide.* [73°]. (192° cor.). S.G. $\frac{21}{}$ 3·302. Formed by passing acetylene over iodine moistened with alcohol (Sabanejeff, *A.* 178, 109; 216, 275; Plimpton, *C. J.* 41, 392). Elastic needles (from alcohol). It appears to be accompanied by a small quantity of a liquid isomeride. S.G. $\frac{21}{}$ 2·942. With alcoholic $AgNO_3$ it forms long needles of a compound $C_2H_2I_24AgNO_3$, which is decomposed by HCl, giving off acetylene.

Tetra-iodo-ethylene CI_2:CI_2. *Di-carbon-tetra-iodide.* [c. 165°]. Prisms. Formed by the action of a solution of iodine in aqueous KI upon the cuprous compound of potassium propargylate. Formed also by the action of the iodine solution upon acetylene copper (Homolka a. Stolz, *B.* 18, 2283).

IODO-ETHYLIDENE DI-ETHYL DI-SULPHONE $CH_3.CI(SO_2Et)_2$. [109°]. From ethylidene di-ethyl di-sulphone by boiling with iodine (Fromm, *A.* 253, 146). Needles.

IODO-DI-ETHYL OXIDE C_4H_9IO *i.e.* $CH_2I.CH_2.OEt$. (155°). S.G. $\frac{0}{}$ 1·692. V.D. 6·91 (obs. and calc.). Formed by heating ethylene iodide with alcohol at 75° (Baumstark, *B.* 7, 1172). Formed also from the mono-ethyl derivative of glycol by treatment with iodide of phosphorus (Demole, *B.* 9, 746). Pungent oil, not decomposed by water. Alcoholic potash attacks it energetically, yielding CH_2:CH.OEt (35°), and $CH_2(OEt).CH_2(OEt)$ (122°). Boiling with reduced silver does not affect it.

IODO-(β)-ETHYL-THIOPHENE $C_4H_2(C_2H_5)IS$. Oil. Formed by the action of iodine upon (β)-ethyl-thiophene in presence of HgO (Bonz, *B.* 18, 551)

IODO-FLUORO-BENZENE *v.* Fluoro-iodo-benzene.

IODOFORM CHI_3. *Tri-iodo-methane.* Mol. w. 394. [119°]. S.G. 2.

Depression of freezing-point of benzene by iodoform: Raoult, *A. Ch.* [6] 2, 88; Paterno, *B.* 22, 465.

Formation.—1. By heating alcohol with iodine and caustic or carbonated alkali (Serullas, *A. Ch.* [2] 25, 314). Iodoform is formed in like manner by the action of iodine and potash on aldehyde, acetone, lactic acid, and many other substances (*cf.* vol. i. p. 96).—2. From chloroform and HI (Baeyer, *B.* 5, 1094).—3. By heating chloroform with CaI_2 at 75° (Spindler, *A.* 231, 263).—4. Together with carbamic ether, by the action of iodine on sodium carbamic ether (Mulder, *R. T. C.* 7, 333).

Preparation.—1. Alcohol containing about 20 p.c. aldehyde is mixed with ten times its weight of aqueous NaOH, iodine is added, and the mixture stirred from time to time. The iodoform quickly separates in the cold (Günther, *Ar. Ph.* [3] 25, 373).—2. To prepare iodoform R. Rother (*Ph.* [3] 4, 593) heats 32 pts. iodine, 32 potassium carbonate, 16 alcohol of 95 per cent. and 80 water, till the mixture becomes colourless; then decants the clear liquid, collects the separated crystals of iodoform, and mixes the filtered liquid with 16 to 24 pts. hydrochloric acid and 2 to 3 pts. potassium dichromate. The liquid is then neutralised with potassium carbonate, and 32 pts. more of that salt are added, together with 6 pts. iodine and 16 alcohol. The reaction having been completed at the heat of the water-bath, the product is treated as above, whereby a fresh quantity of iodoform is obtained.—3. By the action of excess of sodium hypochlorite on an aqueous solution of acetone (6 pts.), potassium iodide (50 pts.), and NaOH (2 pts.) (Suillot a. Raynaud, *Bl.* [3] 1, 3).

Properties.—Hexagonal yellow tables; $a:c$ = 1: ·9015 (Rammelsberg a. Kokscharoff, *C. C.* 1857, 524; *cf.* Dogiel, *N. Petersb. Acad. Bull.* 20, 337). Above its melting-point it partly decomposes, giving off iodine and HI. Has a peculiar persistent odour. Volatile with steam. Insol. water, acids, and alkalis; v. sol. alcohol, ether, and fixed and volatile oils. An alcoholic solution of iodoform is decomposed under the influence of

light. The decomposition is accelerated by dry oxalic acid; iodine and methylene iodide are produced (Mulder, *R. T. C.* 7, 316; *cf.* Humbert, *J. Ph.* [3] 29, 352). Does not in the least hinder the putrefaction of pancreas at 35° (Boillat, *J. pr.* 133, 308).

Detection.—An alcoholic solution of iodoform warmed with aqueous KOH and a little phenol forms a red substance, which dissolves in dilute alcohol, giving it a crimson colour (Lustgarten, *M.* 3, 717).

Reactions.—1. *Heated* in a sealed tube at 150°, either alone or with iodine, it yields methylene iodide and brown products (Hofmann, *C. J.* 13, 65).—2. *Bromine* gives bromoform (Löscher, *B.* 21, 410); but an excess of Br at high temperatures forms CBr_4.—3. Distilled with $HgCl_2$ it yields $CHCl_2I$ (Schlagdenhauffen, *J. Ph.* [3] 29, 247).—4. *Mercuric oxide* forms CO, formic acid, HgI_2, and water.—5. Boiling aqueous KOH forms a little potassium formate.—6. Boiling *alcoholic potash* forms methylene iodide (Bruning, *A.* 104, 187; Butlerow, *C. R.* 47, 595).—7. NaOEt forms methylene iodide, NaI, aldehyde, acrylic acid, and $CH_3.CH(OEt).CO_2H$ (Butlerow, *A.* 107, 110; 114, 204; 118, 325).—8. K_2SO_3 forms $CH_2(SO_3K)_2$ (Strecker, *A.* 148, 90).—9. By the copper-zinc couple iodoform may be reduced to methane (Gladstone a. Tribe, *C. J.* 28, 508).—10. Unites with PEt_3 forming $C_{19}H_{46}P_3I_3$ (Hofmann, *Pr.* 10, 189).—11. PCl_5 forms chloroform. 12. When made into a paste with moist finely-divided silver, acetylene is at once given off. A mixture of ppd. silver and copper is even more effective (Cazeneuve, *C. R.* 97, 1371).—13. *Silver nitrate* acts readily at ordinary temperatures, forming AgI, nitric acid, and CO, so that by nitrating the liberated acid an estimation of the quantity of iodoform present may be formed (Greshoff, *R. T. C.* 7, 342).—14. Iodoform exposed to direct sunlight is completely oxidised by air, forming CO_2, iodine, and water (Daccomo, *G.* 16, 247).—15. *Mercuric acetate* is reduced by iodoform to mercurous acetate, CO_2 being evolved. It does not reduce mercuric nitrate (although chloral forms, in this case, mercurous chloride) (Cotton, *J. Ph.* [5] 16, 481).—16. Isobutyl alcohol (200 g.) mixed with sodium (20 g.) and iodoform (100 g.) gives a violent reaction, the products being formic acid, isobutyric acid, pentenoic acid, $CMe_2:CH.CO_2H$ [70°], isobutyl-oxy-isobutyric acid $C_4H_9O.CMe_2.CO_2H$, a lactone of an oxy-octoic acid, isobutylene, methyl isobutyl oxide, methylene di-isobutyl oxide, a compound $C_{12}H_{26}O_3$, and other bodies (Gorboff a. Kessler, *J. R.* 1887, 428).

IODO-FUMARIC ACID $C_2HI(CO_2H)_2$. *Iodo-maleic acid.* [184°]. Formed by dissolving acetylene-di-carboxylic acid in strong aqueous HI (Baudrowski, *B.* 15, 2697). Fine glistening crystals. Very soluble in water, alcohol, and ether.

Salts.—A″HK: small sparingly soluble crystals.—$A''Ag_2$: crystalline pp.—A″Pb 2aq: crystalline pp.

IODO-HENDECOIC ACID $C_{11}H_{21}IO_2$ *i.e.* $CH_2I.CH_2.(CH_2)_8.CO_2H$. [24°]. From hendecenoic acid and HI (Ph. Brunner, *B.* 19, 2224). Crystalline.

IODO-HEPTOIC ALDEHYDE $C_6H_{12}I.CHO$. S.G. $\frac{20}{}$ 2·31. Formed by treating heptoic (œnanthic) aldehyde (75 g.) diluted with alcohol (100 c.c.) with iodine (50 g.) and iodic acid (20 g.). The crude product is purified by treatment with reduced silver. The yield is very bad (Chautard, *A. Ch.* [6] 16, 170). Very unstable liquid with irritating odour. Decomposed by heat. Easily decomposed by KOH, NaOH, ammonia, and mineral acids.

Reactions.—1. *Nitric acid* gives heptoic aldehyde and heptoic acid.—2. *Silver acetate* forms octyl acetate (208°).—3. By heating iodo-heptoic aldehyde (120 g.) dissolved in alcohol with *silver cyanide* (67 g.) there is formed $C_6H_{12}Cy.CHO$ (177°) S.G. $\frac{15}{}$ ·913. This is a colourless liquid which reduces Fehling's solution and ammoniacal $AgNO_3$ but does not form crystalline compounds with aniline or phenyl-hydrazine.—4. *Silver sulphocyanide* forms the corresponding sulphocyano-heptoic aldehyde.—5. Heating with aniline forms $C_7H_{13}I(NHC_6H_5)_2$.

IODO-HEPTYLENE $C_7H_{13}I$ *i.e.* $Pr.CH_2.CI:CHMe$ or $Pr.CH:CI.CH_2Me$. (140°–150°). From heptinene (*q. v.*) and HI (Morris, *C. J.* 41, 179).

IODO-HEXANE *v.* Hexyl iodide.

Di-iodo-hexane $C_6H_{12}I_2$ *i.e.* $CH_3.CHI.CH_2.CH_2.CHI.CH_3$. *Hexylene iodide.* S.G. $\frac{0}{}$ 2·024. Formed by heating di-allyl in a sealed tube for 5 hours with excess of conc. HIAq at 100° (Wurtz, *A. Ch.* [4] 3, 129); or better, by passing gaseous HI into strongly cooled diallyl (Sorokin, *J. pr.* [2] 23, 18). Oil; gives off iodine when heated. With sodium it gives hexylene and hexenyl iodide. Alcoholic potash forms diallyl. Silver acetate forms hexylene acetate $C_6H_{12}(OAc)_2$, whence baryta forms di-oxy-hexane.

Tetra-iodo-hexane $C_6H_{10}I_2$. [above 100°]. From diallyl and iodine (Berthelot a. De Luca, *A.* 100, 363).

TETRA-IODO-HEXINENE *v. Tetra-iodide* of Dipropargyl.

IODO-HEXOIC ACID $C_6H_{11}IO_2$. Formed by mixing hydrosorbic acid with conc. HIAq at 0° (Fittig, *A.* 200, 44). Oil, turning yellow on exposure to light. May be reduced by sodium-amalgam to *n*-hexoic acid.

IODO-HEXYLENE $C_6H_{11}I$ *i.e.* $CH_2:CH.CH_2.CH_2.CHI.CH_3$. *Hexenyl iodide. Diallyl hydroiodide.* (165°). S.G. $\frac{0}{}$ 1·497. Formed, together with di-iodo-hexane, by the action of HI on diallyl (Wurtz, *A. Ch.* [4] 3, 155). Formed also by the action of alcoholic potash or of an alloy of tin and sodium on di-iodo-hexane $CH_3.CHI.CH_2.CH_2.CHI.CH_3$. When treated for 24 hours with moist Ag_2O it forms diallyl, hexylene, and two liquids $C_6H_{12}O$ (c. 135°) and $C_{12}H_{22}O$ (180°).

Iodo-hexylene $C_6H_{11}I$. (131°). S.G. $\frac{10}{}$ 1·92. Formed from the hexenyl alcohol obtained by distilling glycerin with lime (Destrem, *A. Ch.* [5] 27, 58).

Iodo-hexylene $C_6H_{11}I$. (142°–145°). From pinacone hydrate and HI at 160° (Bouchardat, *Z.* 1871, 699). Reduced by tin and HCl to hexylene. Bromine gives crystalline $C_6H_{10}Br_4$.

IODO-HIPPURIC ACID $C_9H_8INO_3$ *i.e.* $NHBz.CHI.CO_2H$ (?). Formed by treating a boiling alcoholic solution of hippuric acid with iodine (Maier, *Z.* 1865, 415). White needles. Decomposes at 90°. All its salts are soluble in water excepting the silver salt.

Iodo-hippuric acid $C_6H_4I.CO.NH.CH_2.CO_2H$. Formed by the action of aqueous HI on the sulphate of diazo-hippuric acid (Griess, *Z.* [2] 4, 725; *B.* 1, 190). Laminæ, v. sol. cold alcohol and ether, m. sol. hot water, nearly insol. cold water. The iodine is not easily removed.

IODO-HYDROCINNAMIC ACID *v.* Iodo-phenyl-propionic acid.

DI-IODO-HYDROQUINONE $C_6H_2I_2(OH)_2$ [5:3:4:1]. [145°]. Formed by boiling di-iodo-quinone [180°] with a dilute solution of $SnCl_2$ (Seifert, *J. pr.* [2] 28, 438; Kehrmann, *J. pr.* [2] 37, 337). Long colourless needles (from hot water). Volatile with steam.

Di-iodo-hydroquinone $C_6H_2I_2(OH)_2$. [142°]. From di-iodo-quinone [159°] and aqueous SO_2 (Metzeler, *B.* 21, 2555). White needles, v. sol. hot water, alcohol, ether, and HOAc; m. sol. benzene. Reoxidised by $FeCl_3$ to di-iodo-quinone.

Di-acetyl derivative $C_6H_2I_2(OAc)_2$. [148°]. Needles or plates (from alcohol); insol. water, v. sol. alcohol and ether, sl. sol. cold HOAc.

IODO-HYDROTHYMOQUINONE $C_6HMePrI(OH)_2$ [5:2:6:4:1]. [74°]. Obtained by reducing iodo-thymoquinone with $SnCl_2$ (Kehrmann, *J. pr.* [2] 39, 392). Colourless prisms, v. sol. organic solvents.

IODO-HYDRO-TOLUQUINONE $C_6H_2MeI(OH)_2$ [6:2:4:1]. [111°]. From the corresponding quinone, by reduction with $SnCl_2$ (Kehrmann, *J. pr.* [2] 39, 392). Soft silky aggregates of needles, sol. organic solvents.

IODOL *v.* Tetra-iodo-pyrrole.

IODO-LACTIC ACID *v.* Iodo-oxy-propionic acid.

IODO-MALEÏC ACID *v.* Iodo-fumaric acid.

IODO-MELILOTIC ACID. *Methyl derivative.* $C_{10}H_{11}IO_3$ *i.e.* $C_6H_4(OMe).C_2H_3I.CO_2H$. From the methyl derivatives of (α) and of (β) coumaric acid and fuming aqueous HI in the cold (Perkin, *C. J.* 39, 429). Aqueous Na_2CO_3 forms $C_6H_4(OMe).CH:CH_2$ and CO_2.

IODO-METHANE *v.* Methyl iodide.

Di-iodo-methane *v.* Methylene iodide.

Tri-iodo-methane *v.* Iodoform.

Tetra-iodo-methane CI_4. *Carbon tetra-iodide.* S.G. $\frac{20}{}$ 4·32. Formed by mixing CCl_4 with aluminium iodide dissolved in CS_2 (Gustavson, *A.* 172, 173; *C. R.* 78, 882). Formed also by heating CCl_4 with $CaI_2\,3\frac{1}{2}aq$ at 75° (Spindler, *A.* 231, 264). Dark-red regular octahedra (Friedel, *Bl.* [2] 21, 482). Sol. CS_2, alcohol, ether, and MeI. May be kept for some days, but gradually decomposes. The decomposition is hastened by both CS_2 and CO_2. Above 80° it quickly splits up into carbon and iodine. Converted into iodoform by boiling with aqueous HI, and even by boiling with water. Scarcely attacked by aqueous potash or H_2SO_4. Chlorine converts it into CCl_4. Br gives CBr_4.

IODO-DI-METHYL-AMINE *v.* *Di-methyl-iodo-amine* under Di-methyl-amine.

IODO-DI-METHYL-ANILINE $C_8H_{10}IN$ *i.e.* $C_6H_4I.NMe_2$. [79°]. Formed by adding iodine to a solution of di-methyl-aniline in CS_2 (Weber, *B.* 10, 765). Formed also by the action of cyanogen iodide on di-methyl-aniline in the cold, heat being evolved and HCy given off (Merz a. Weith, *B.* 10, 757). White laminæ, sol. alcohol and HClAq. Not attacked by caustic soda. When heated above 80° it gives off HI and leaves a residue which forms a deep violet solution in alcohol.—$B'_2H_2PtCl_6$.

IODO-TRI-METHYL-BENZENE *v.* Iodo-ψ-cumene.

IODO-METHYL-BUTYL-BENZENE *v.* Iodo-butyl-toluene.

DI-IODO-METHYLENE DI-ETHYL DI-SULPHONE $CI_2(SO_2Et)_2$. [177°]. Formed from methylene di-ethyl di-sulphone, I, and KIAq, by exposure to sunlight (Fromm, *A.* 253, 161). Needles, sl. sol. boiling water.

DI-IODO-DI-METHYL OXIDE $C_2H_4I_2O$ *i.e.* $(CH_2I)_2O$. (219°). From dry 'oxymethylene' (formic paraldehyde) and gaseous HI (Tishtschenko, *J. R.* 1887, 464). Oil.

IODO-TRI-METHYL-PIPERIDINE $C_8H_{16}IN$. [60°]. Formed by heating ethylidene diacetonine with HI (E. Fischer, *B.* 17, 1796). Colourless rectangular prisms. Nearly insol. water.—B'HI: very sparingly soluble.

Iodo-tetra-methyl-piperidine $C_9H_{18}NI$. [90°]. Formed by heating triacetonine with HI at 150° (E. Fischer, *B.* 17, 1791). Easily soluble in alcohol and ether, insol. water. Colourless tables (from ether).

IODO-DI-METHYL-THIOPHENE C_6H_7IS *i.e.*

CI :CMe\
| >S. (97°). From di-methyl-thiophene
CH:CMe/

(from coal tar), iodine, and HgO (Messinger, *B.* 18, 1638). Oil.

Iodo-tri-methyl-thiophene C_7H_9IS *i.e.*

CMe:CMe\
| >S. Formed by the action of iodine
CMe:CI /

(48 g.) and HgO (21 g.) on tri-methyl-thiophene (12 g.) dissolved in ligroïn (24 g.) (Zelinsky, *B.* 21, 1837). Non-volatile oil.

(α)-IODO-NAPHTHALENE $C_{10}H_7I$. (305°).

Formation.—1. By adding iodine to a solution of mercury dinaphthyl: $Hg(C_{10}H_7)_2 + 2I_2 = HgI_2 + 2C_{10}H_7I$ (Otto, *A.* 147, 173).—2. From diazo-naphthalene sulphate and HI (Nölting, *B.* 19, 135).

Properties.—Thick yellowish oil, not solidified at −17°. Miscible with alcohol, ether, CS_2, and benzene. Alcoholic potash at 160° forms some naphthalene. Boiling HIAq (127°) completely converts it into naphthalene. When a solution in CS_2 is boiled with aluminium chloride there is formed naphthalene, iodine, and tarry matter, but no (β)-iodo-naphthalene (Roux, *Bl.* [2] 45, 517).

Picric acid compound [127°]. Golden yellow needles.

(β)-Iodo-naphthalene $C_{10}H_7I$. [55°]. Prepared by the action of HI on (β)-diazo-naphthalene sulphate (P. Jacobson, *B.* 14, 804). Colourless plates; sol. ether, alcohol, and HOAc. Volatile with steam.

(α_1 α_4)-Di-iodo-naphthalene $C_{10}H_6I_2$ [1:4]. [110°]. From (α)-iodo-(α)-nitro-naphthalene by reduction, and treatment of the resulting iodo-naphthylamine with H_2SO_4 and $NaNO_2$, followed by HI (Meldola, *C. J.* 47, 522). Needles (from alcohol).

($\alpha_1\beta_2$)-Di-iodo-naphthalene $C_{10}H_6I_2$ [1:2]. [81°]. From (β)-iodo-(α)-nitro-naphthalene in

the same way as the preceding (Meldola). Scales (from alcohol).

(β) - **IODO - NAPHTHALENE SULPHONIC ACIDS** $C_{10}H_6I.SO_3H$. Two isomerides are formed by sulphonating (β)-iodo-naphthalene (Armstrong a. Wynne, *C. J. Proc.* 3, 22). One of the isomerides forms the salts KA′ aq and $BaA'_2 4\frac{1}{2}$aq, both crystallising in hexagonal scales, the other forms the salts KA′ aq crystallising in laminæ, and BaA'_2 2aq in flat needles.

(1, 5)-**Iodo-naphthalene sulphonic acid** $C_{10}H_6I(SO_3H)$ [1:5]. [129°]. Formed from (α)-diazo-naphthalene sulphonic acid and warm HIAq (40 p.c.) (Mauzelius, *B.* 22, 2820). Colourless tables (containing 2aq): v. sol. water.

Salts.—A′K aq: plates: m. sol. water.—A′Na aq: indistinct needles.—A′Ag: plates: S. ·66.—A'_2Ca 2aq: scales; sl. sol. water.—A'_2Ba aq: scales: S. ·23 (in the cold). S. 1 at 100°.—A'_2Mg: needles: sl. sol. water.—A′Zn 6aq: scales; m. sol. water.—A'_2Cu 4aq: greenish-white needles; sl. sol. water.—A'_2Pb 4aq: sl. sol. water.—A'_2Mn 4aq: indistinct crystals: sl. sol. water.

Methyl-ether MeA′. [60°]. Prisms: v. sol. Et_2O; sl. sol. cold EtOH.

Ethyl-ether EtA′. [74°]. Six-sided tables: v. sol. Et_2O.

n-Propyl-ether PrA′. [67°]. Colourless tables.

Isopropyl-ether PrA′. [90°]. Prisms.

Chloride $C_{10}H_6ISO_2Cl$. [114°]. Monoclinic prisms: v. sol. hot AcOH; sl. sol. ligroïn.

Bromide [153°]. Prisms.

Amide $C_{10}H_6I(SO_2NH_2)$. [239°]. Scales.

(α)-**IODO-(β)-NAPHTHOL** $C_{10}H_6I(OH)$ [1:2] [94·5°] (M.); [c. 100°] (W.). Prepared by dissolving equal parts (20 g.) of (β)-naphthol, lead acetate, and dried sodium acetate in HOAc, cooling, and gradually adding iodine (35·2 g.) dissolved in hot HOAc. The product is ppd. by water and recrystallised from dilute alcohol (Meldola, *C. J.* 47, 527). Formed also by the action of iodide of nitrogen on a dilute alcoholic solution of sodium (β)-naphthol (Willgerodt, *J. pr.* [2] 37, 448).

Properties.—Long colourless needles; sl. sol. boiling water; v. sol. organic solvents. Volatile with steam. Sol. cold dilute KOHAq; decomposed by hot alkalis. Nitric acid liberates iodine. $KMnO_4$ gives phthalic acid.

(α)-**IODO-(α)-NAPHTHYLAMINE** $C_{10}H_6I(NH_2)$ [4:1]. From (α)-iodo-(α)-nitro-naphthalene, zinc-dust, and HOAc (Meldola, *C. J.* 47, 521). Its solution rapidly oxidises in the air forming a red colouring matter.—$B'_2H_2SO_4$: tolerably stable white needles.

Acetyl derivative $C_{10}H_6I(NHAc)$. [196°]. From the preceding by boiling with Ac_2O (M.). Needles (from alcohol). Gives a nitro- derivative [236°].

IODO-*o*-NITRO-ANILINE $C_6H_3I(NO_2)(NH_2)$ [5:2:1]. Formed by heating di-iodo-nitro-benzene [168°] with alcoholic NH_3 at 170° for several days (Körner, *G.* 4, 386). Large steel-blue laminæ (from alcohol in sealed tubes), yellow by transmitted light. Does not melt at 220°. Not attacked by nitrous ether.

Iodo-o-nitro-aniline $C_6H_3I(NO_2)(NH_2)$ [4:2:1]. [122°]. Formed by warming a solution of the acetyl derivative of *p*-iodo-aniline in HOAc with HNO_3 (Michael a. Norton, *B.* 11, 109). Long orange-yellow needles (from alcohol).

Iodo-*p*-nitro-aniline $C_6H_3I(NO_2)(NH_2)$ [2:4:1]. [105·5°]. Prepared by the action of iodine chloride (2 pts.) on *p*-nitro-aniline (1 pt.) dissolved in dilute HClAq (Michael a. Norton, *Am.* 1, 262; *B.* 11, 113). Long yellow needles.—B′HCl [163°].

Di-iodo-*m*-nitro-aniline $C_6H_2I(NO_2)_2(NH_2)$ [4:2:3:1]. [145·5°]. Formed by passing iodine chloride (3 pts.) into a solution of *m*-nitro-aniline (1 pt.) in HClAq (Michael a. Norton, *Am.* 1, 255; *B.* 11, 112). Long slender yellow needles, v. sol. cold alcohol, sl. sol. acetic ether, insol. water. Its hydrochloride is not decomposed by water.

Di-iodo-*p*-nitro-aniline $C_6H_2I_2(NO_2)(NH_2)$ [6:2:4:1]. [244°]. Prepared by the action of iodine chloride (2 mols.) on *p*-nitro-aniline dissolved in chloroform (M. a. N.). Yellow prisms with blue fluorescence (from alcohol). Sl. sol. hot alcohol, sol. $CHCl_3$ and EtOAc, v. sol. hot nitro-benzene. It is not basic.

o-**IODO-NITRO-BENZENE** $C_6H_4I(NO_2)$ [1:2]. [49°]. Formed, together with the *p*-isomeride, by treating iodo-benzene with HNO_3 (Körner, *G.* 4, 305). The *p*-isomeride crystallises first from alcohol. Long flat lemon-yellow needles. Gives a little o-iodo-aniline and much aniline on reduction.

***m*-Iodo-nitro-benzene** $C_6H_4I(NO_2)$ [1:3]. [36°]. (c. 280°). Formed from *m*-nitro-aniline by displacing NH_2 by I through the diazo- reaction (Griess, *Z.* 1866, 218). Monoclinic plates; $a:b:c = 2·296:1:1·129$ (Panebianco, *G.* 9, 360). The same body is perhaps formed by the action of ICl on sodium *m*-nitro-benzoate (Schützenberger a. Segenwald, *Rép. Chim. pure*, 1862, 144).

***p*-Iodo-nitro-benzene** $C_6H_4I(NO_2)$ [1:4]. [171°]. The chief product of the action of fuming HNO_3 upon iodo-benzene (Kekulé, *A.* 137, 129). Obtained also from *p*-nitro-aniline by the diazo-reaction. Pale yellow needles.

Di-chloride $C_6H_4(NO_2)ICl_2$. Formed by passing Cl into a solution of iodo-nitro-benzene in chloroform (C. Willgerodt, *J. pr.* [2] 33, 160). Hardly sol. CS_2, Et_2O, or light petroleum. Sol. $CHCl_3$ and benzene. At 150° it gives off Cl_2, leaving $C_6H_4(NO_2)I$. With alcohol it reacts forming aldehyde, HCl and $C_6H_4(NO_2)I$.

Iodo-di-nitro-benzene $C_6H_3I(NO_2)_2$ [1:2:4]. [89°]. Obtained by nitrating o- or *p*-iodo-nitro-benzene with H_2SO_4 and HNO_3 (Körner, *J.* 1875, 322). Yellow triclinic crystals, $a:b:c = 1·634:1:·940$ (La Valle, *G.* 10, 3). V. sl. sol. cold alcohol. Hot dilute KOH forms di-nitro-phenol. Alcoholic NH_3 gives di-nitro-aniline, though the decomposition is incomplete in the cold.

Iodo-di-nitro-benzene $C_6H_3I(NO_2)_2$ [1:2:6]. [114°]. Formed in small quantity, together with the preceding, by treating *o*-iodo-nitro-benzene with HNO_3 mixed with H_2SO_4 (Körner, *G.* 4, 305). Orange triclinic tables (from alcohol). More sol. alcohol and ether than the preceding. Converted by heating with alcoholic NH_3 into di-nitro-aniline [138°]. May be reduced to phenylene-*m*-diamine.

Iodo-tri-nitro-benzene $C_6H_2I(NO_2)_3$ [1:2:4:6]. [164°]. From chloro-tri-nitro-benzene and alcoholic KI (Hepp, *A.* 215, 361). Golden needles.

Converted by boiling aqueous KOH into picric acid.

Di-iodo-nitro-benzene $C_6H_3I_2(NO_2)$ [1:3:4]. [168°]. Obtained from *m*-di-iodo-benzene by dissolving in hot fuming HNO_3 (Körner). Trimetric octahedra; $a:b:c = \cdot 647:1:\cdot 458$ (La Valle, *G.* 10, 2). Sl. sol. ether, v. sl. sol. cold alcohol. By heating for a few days with alcoholic NH_3 at 170° it forms iodo-nitro-aniline.

Di-iodo-nitro-benzene $C_6H_3I_2(NO_2)$ [1:2:4?]. [112·5°]. Formed by dissolving o-di-iodo-benzene in fuming HNO_3 and, after a few minutes, diluting with water (Körner a. Wender, *G.* 17, 491). Lemon-yellow needles or small prisms (from alcohol).

(α)-IODO-NITRO-BENZOIC ACID $C_7H_4INO_4$ *i.e.* $C_6H_3I(NO_2)(CO_2H)$ [3:2or6:1]. [235°]. Formed, together with the two following, by heating *m*-iodo-benzoic acid with conc. HNO_3 (Grothe, *J. pr.* [2] 18, 324; Cunze a. Hübner, *A.* 135, 106). Sl. sol. water, especially if HCl be present. —Gives o-amido-benzoic acid on reduction. NH_4A'aq.—NaA′ 3aq.—CaA′ 2aq.—SrA'_2 4aq.—BaA'_2 3aq.

Ethyl ether EtA′. [84°].

(β)-Iodo-nitro-benzoic acid $C_6H_3I(NO_2)(CO_2H)$ [3:6or2:1]. [174°]. Formed as above. V. sol. water, especially if HCl be present. Melts under water. May be reduced to o-amido-benzoic acid. —NH_4A'aq.—LiA′aq.—NaA′ 4aq.—KA′3aq.—CaA′.—SrA'_2.—BaA'_2 6aq.

Ethyl ether EtA′. [64°]. Yellow plates.

(γ)-Iodo-nitro-benzoic acid $C_6H_3I(NO_2)(CO_2H)$ [3:x:1]. [192°]. Formed as above. V. sol. water, but does not melt under it. —NaA′aq: silky yellow needles.—CaA'_2 3½aq.—SrA'_2 4aq.—BaA'_2 3aq.

Iodo-nitro-benzoic acid $C_6H_3I(NO_2)(CO_2H)$ [4:3:1]. [210°]. Formed by heating *p*-iodo-benzoic acid with fuming HNO_3 (Glassner, *B.* 8, 562). Nearly insol. water, v. sol. alcohol.—NaA′aq.—KA′aq.—CaA'_2 1½aq.

($\alpha_4\alpha_1$)-IODO-NITRO-NAPHTHALENE $C_{10}H_6I(NO_2)$ [4:1]. [123°]. Formed from acetyl-(α)-naphthylamine by nitration, saponification, diazotisation, and treatment with HI (Meldola, *C. J.* 47, 519). Minute white needles (from hot alcohol). Sol. benzene, HOAc, and acetone. May be reduced to (α)-naphthylamine.

($\alpha_1\beta_2$)-Iodo-nitro-naphthalene $C_{10}H_6I(NO_2)$ [1:2]. [108·5°]. Formed from the mother-liquor of the preceding (Meldola). Yellow scales. May be reduced to (β)-napthylamine.

($\beta_2\alpha_1$)-Iodo-nitro-naphthalene $C_{10}H_6I(NO_2)$ [2:1]. [88·5°]. From acetyl-(α)-nitro-(β)-naphthylamine by saponifying with hot dilute H_2SO_4, and subsequent displacement of NH_2 by I (Meldola, *C. J.* 47, 520).

(α_1)-IODO-(β_2)-NITRO-(α_1)-NAPHTHOL $C_{10}H_5I(NO_2)(OH)$[4:2:1]. [146°]. Formed by boiling acetyl (4, 2, 1)-iodo-nitro-naphthylamine with strong caustic alkali (Meldola, *C. J.* 47, 524). Yellow needles (from alcohol). Insol. cold water, sl. sol. hot water and hot benzene, v. sol. alcohol, acetic acid, and acetone. Yields phthalic acid on oxidation. Its K and Na derivatives form minute orange needles, m. sol. cold water.—$\{C_{10}H_5I(NO_2)\}_2$Ba 3aq: bright red amorphous powder, almost insol. boiling water; deflagrates on ignition.

(α_1)-IODO-(β_2)-NITRO-(α_1)-NAPHTHYLAMINE. *Acetyl derivative* $C_6H_5I(NO_2)(NHAc)$[4:2:1]. [236°]. From acetyl-iodo-naphthylamine by warming its solution in HOAc with HNO_3 at 75° (Meldola, *C. J.* 47, 524). Straw-coloured needles (from alcohol). Sublimes while melting. More difficult to saponify by H_2SO_4 than the bromo- compound.

IODO-NITRO-o-OXY-BENZOIC ACID $C_7H_4INO_5$ *i.e.* $C_6H_2I(NO_2)(OH)(CO_2H)$. From (5, 2, 1)-nitro-oxy-benzoic acid by treatment in alcoholic solution with I and HgO (Weselsky, *A.* 174, 108). Slender yellow needles.—KA′ 2aq. —$C_7H_2K_2NO_5$ 3aq.—BaA'_2 6aq.

Iodo-nitro-o-oxy-benzoic acid $C_6H_2I(NO_2)(OH)(CO_2H)$. [204°]. From (5, 2, 1)-iodo-oxy-benzoic acid by nitration (Hübner, *B.* 12, 1347).

Iodo-nitro-*m*-oxy-benzoic acid $C_6H_2I(NO_2)(OH)(CO_2H)$. Formed by treating an alcoholic solution of nitro-*m*-oxy-benzoic acid with I and HgO (Weselsky, *A.* 174, 109). Lemon-yellow crystals; sl. sol. water, v. sol. cold alcohol.—BaA'_2 6aq: minute red needles.

Iodo-nitro-*p*-oxy-benzoic acid $C_6H_2I(NO_2)(OH)(CO_2H)$. From nitro-*p*-oxy-benzoic acid, iodine, and HgO (W.). Lemon-yellow needles.—BaA'_2 4aq: flat red needles. $BaC_7H_2INO_5$ 2aq: short dark-red needles.

DI-IODO-DI-NITRO-DI-OXY-DI-PHENYL SULPHONE $C_{12}H_6I_2N_2SO_8$ *i.e.* $SO_2(C_6H_2I(NO_2)OH)_2$. [205°]. Formed by heating iodine (50 g.) dissolved in alcohol with a mixture of di-nitro-di-oxy-di-phenyl sulphone (34 g.) and HgO (21·6 g.) at 100° (Annaheim, *B.* 9, 660). Needles (from HOAc); insol. water and alcohol. Decomposes alkaline carbonates.—$Na_2C_{12}H_4I_2N_2SO_8$ 2aq.

IODO-*o*-NITRO-PHENOL $C_6H_4INO_3$ *i.e.* $C_6H_3I(NO_2)(OH)$. [110°] (Armstrong, *Watts' Dict.* Ed. i. *Suppl.* 2, 917; *B.* 6, 649). Formed by the action of iodine and HgO on *o*-nitro-phenol dissolved in HOAc (Busch, *B.* 7, 462; *cf.* Armstrong). Short yellow needles, v. sol. hot water, alcohol, and ether. Moderately volatile with steam.—KA′aq: garnet-red plates with green lustre (A.), v. e. sol. hot water and alcohol.

Iodo-*p*-nitro-phenol $C_6H_3I(NO_2)(OH)$[2:4:1]. [93°] (Körner; Armstrong). Formed by the action of iodine and HgO on *p*-nitro-phenol dissolved in HOAc (Körner, *Bull. Acad. Belg.* [2] 24, 166; Busch, *B.* 7, 462). Also from nitro-amido-phenol by the diazo- reaction (K.). Yellow needles.—NaA′ 2½aq (K.).—KA′ ½aq (B.). Nitric acid converts it into iodo-di-nitro-phenol [106°].

Iodo-di-nitro-phenol $C_6H_2I(NO_2)_2(OH)$[6:4:2:1]. [106°] (A.); [108°] (W.). Formed from (4, 2, 1)-di-nitro-phenol by treatment with iodine, potassium iodate, and potash (Körner, *G.* 4, 397) or with iodine and HgO (Armstrong, *B.* 6, 649; Weselsky, *A.* 174, 111). Formed also from di-nitro-amido-phenol by the diazo- reaction (A.), and by the nitration of the preceding iodo-nitro-phenol (A.). Long slender lemon-yellow needles (from hot water). Sl. sol. hot water.—KA′: deep orange needles, v. sol. hot, sl. sol. cold, water.—$CaA'_2$5aq: orange-red plates, v. sol. hot water.

Iodo-di-nitro-phenol $C_6H_2I(NO_2)_2(OH)$[4:6:2:1]. [113°]. Formed from (6, 2, 1)-di-nitro-phenol by treatment with iodine

and iodic acid (Körner, *G.* 4, 397) or with iodine and HgO (Armstrong, *B.* 6, 649). Long, lemon-yellow needles (from water); v. sl. sol. water and alcohol. The potassium derivative forms magnificent crimson needles with green and golden lustre; sl. sol. water. The silver derivative forms small brownish-red needles.

Di-iodo-*o*-nitro-phenol $C_6H_2I_2(NO_2)(OH)[6:4:2:1]$. [98°]. From o-nitro-phenol, iodine, and iodic acid in alkaline solution (Körner). Slender dark-yellow needles (from ether-alcohol); sl. sol. water, v. sol. boiling alcohol and ether.—NaA'aq: dark-brown prisms, with golden lustre.—KA': very soluble reddish-brown needles.

Di-iodo-*p*-nitro-phenol $C_6H_2I_2(NO_2)(OH)[6:2:4:1]$. [157°] (K.). From *p*-nitro-phenol, iodine, KIO_3 and potash (K.; *cf.* Seifert, *J. pr.* [2] 28, 437). Also from *p*-nitro-phenol o-sulphonic acid, iodine in alcoholic solution, and HgO (Post a. Brackebusch, *A.* 205, 91). Formed also by treating nitro-*o*-oxy-benzoic acid with iodine and HgO (Weselsky, *A.* 174, 107). Large colourless prisms (from ether) turning yellow on exposure to air. Decomposes a little above its melting-point.—KA': golden needles with violet iridescence.—NaA'2aq: efflorescent orange laminæ.

Di-iodo-nitro-phenols appear also to have been obtained by Piria (*A.* 198, 268).

IODO-NITRO-PHENOL SULPHONIC ACID $C_6H_4INSO_6$ *i.e.* $C_6H_2I(NO_2)(OH)(SO_3H)[2:6:1:4]$. Formed when iodine and HgO are added to an alcoholic solution of o-nitro-phenol *p*-sulphonic acid (Armstrong a. Brown, *C. J.* 25, 869).—KA': yellow scales, composed of short needles, sl. sol. water.—$K_2C_6H_2INSO_6$: red crystals.—$BaA'_2$4aq: pale-yellow silky needles, sl. sol. water.

Iodo-nitro-phenol sulphonic acid $C_6H_2I(NO_2)(OH)(SO_3H)[6:4:1:2]$. Formed, together with di-iodo-*p*-nitro-phenol, by treating an alcoholic solution of *p*-nitro-phenol *o*-sulphonic acid with iodine and mercuric oxide (Post a. Brackebusch, *A.* 205, 88).—Salts.—$CaC_6H_2INSO_6$3aq: coarse yellow needles, m. sol. water.—$BaC_6H_2INSO_6$3aq: long yellow needles, m. sol. water.—$Pb_2(OH)_2C_6H_2INSO_6 2\frac{1}{2}$aq: yellow crystalline pp.

DI-IODO-NITRO-RESORCIN $C_6HI_2(NO_2)(OH)_2$. From nitro-resorcin in alcoholic solution by alternate addition of iodine and mercuric oxide (Weselsky, *A.* 174, 111). Golden needles.

IODO-NITRO-THIOPHENE $C_4H_2I(NO_2)S$. [74°]. Formed by nitration of iodo-thiophene (Kreis, *B.* 17, 2073). Glistening yellow prisms.

IODO-NITRO-TOLUENE $C_7H_6INO_2$ *i.e.* $C_6H_3MeI(NO_2)$ [1:4:2]. [61°]. (286°). From (4,2,1)-di-nitro-toluene (Heynemann, *A.* 158, 337). Pale yellowish crystals. V. e. sol. CS_2 and ether.

Iodo-nitro-toluene $C_6H_3MeI(NO_2)$ [1:4:3]. [56°]. From *p*-toluidine by nitration and displacement of NH_2 by I (Beilstein a. Kuhlberg, *A.* 158, 344). Large flat needles; v. sol. boiling alcohol.

Iodo-nitro-toluene $C_6H_3MeI(NO_2)$ [1:2:*x*]. [104°]. Formed by nitrating o-iodo-toluene (B. a. K.). Minute needles.

Iodo-nitro-toluene (?). [109°]. Formed by nitrating *m*-iodo-toluene (B. a. K.). Small needles.

Iodo-di-nitro-toluene $C_6H_2MeI(NO_2)_2$[1:4:5:3]. [138°]. Formed by nitrating *p*-iodo-toluene (Glassner, *B.* 8, 561). Crystals.

IODO-OCTINOIC ACID $C_8H_{11}IO_2$ *i.e.* $(C_3H_5)_2CI.CO_2H$. *Iodo-di-allyl-acetic acid.* From $(C_3H_5)_2C(OH).CO_2H$ (17 g.) and cold fuming HIAq (45 g.) (Schatzky, *J. R.* 17, 78). Crystals, insol. water, v. sol. alcohol and ether. Easily decomposed.

p-**IODO-*n*-OCTYL-BENZENE** $C_{14}H_{21}I$ *i.e.* $C_6H_4(C_8H_{17})I$ [1:4]. (319°). Heavy oil. Formed by diazotising *p*-amido-phenyl-octane, aud treating the diazo-octyl-benzene with HI (Beran, *B.* 18, 136). On oxidation with CrO_3 it gives *p*-iodo-benzoic acid. Iodo-octyl-benzene obtained by the action of iodine and HgO upon *n*-octyl-benzene is described by Ahrens (*B.* 19, 2720) as an oil, solidifying at −4°, and completely decomposed by distillation.

p-Iodo-*sec*-octyl-benzene $C_6H_4(C_8H_{17})I$ [1:4]. *p-Iodo-capryl-benzene.* (305° uncor.). Formed by diazotising *p*-amido-phenyl-*sec*-octane and treating the diazo-capryl-benzene with HI. Heavy oil. V. sol. ether and acetic acid, sl. sol. alcohol. It is oxidised by CrO_3 to *p*-iodo-benzoic acid (Beran, *B.* 18, 142).

IODO-(α)-OCTYL-THIOPHENE $C_{12}H_{19}IS$ *i.e.* $C_4H_2SI(C_8H_{17})$. [c. 0°]. S.G. $\frac{20}{20}$ 1·2614. From octyl-thiophene (10 g.) in ligroïn by treatment with iodine (10 g.) and HgO (11 g.) (Schweinitz, *B.* 19, 644). V. sol. ether, cannot be distilled.

IODO-OLEIC ACID *v.* Iodo-stearidenic acid.

IODO-ORCIN $C_7H_7IO_2$ *i.e.* $C_6H_2MeI(OH)_2$. [86·5°]. Formed by dissolving orcin (1 pt.) and iodine (2 pts.) in ether (6 pts.), and gradually adding finely powdered litharge (9 pts.). The ether is distilled off, and the residue recrystallised from benzene (Stenhouse, *Pr.* 22, 53). Prisms; decomposing when heated alone or with water. Sl. sol. cold water, v. sol. hot water, alcohol, and ether. Has not the astringent sweet taste of orcin.

Tri-iodo-orcin $C_7H_5I_3O_2$ *i.e.* $C_6MeI_3(OH)_2$. Formed by adding to a dilute aqueous solution of orcin a quantity of ICl_3, not quite sufficient to ppt. all the orcin, and crystallising the pp. first from CS_2 and then from boiling alcohol (Stenhouse, *C. J.* 17, 327). Large transparent plates, tinged with brown. V. sol. CS_2, v. e. sol. ether, m. sol. alcohol, insol. water. Becomes brown at 100°. Dissolves with decomposition in aqueous KOH. Decomposed by hot H_2SO_4 and by hot HNO_3.

Iodo-(β)-orcin *v.* Iodo-betorcin.

DI-IODO-ORSELLIC ACID. *Methyl ether* $C_9H_8I_2O_4$ *i.e.* $C_8H_5I_2O_4Me$. *Methyl di-iodo-di-oxy-toluate.* Formed by adding a dilute solution of chloride of iodine, containing excess of iodine, to a cold saturated aqueous solution of methyl orsellate (Stenhouse, *A.* 149, 295). Needles from CS_2); sol. benzene, CS_2, alcohol, and boiling water. Decomposed on fusion.

Ethyl-ether $C_8H_5I_2O_4Et$. Formed in like manner. Small needles; almost insol. cold water, m. sol. benzene, CS_2, and boiling alcohol. Decomposed on fusion.

IODO-o-OXY-BENZOIC ACID $C_7H_5IO_3$ *i.e.* $C_6H_3I(OH)(CO_2H)$ [3:2:1]. *Iodo-salicylic acid.* [198°]. Formed, together with the following compound, by boiling a solution of salicylic acid

and iodine in alcohol, and separated by fractionally crystallising the product from water (A. Miller, *C. J.* 41, 406; *A.* 220, 124). Long needles; v. sol. water. Gives a violet colouration with $FeCl_3$. Gives the corresponding di-oxy-benzoic acid on potash-fusion.—$BaA'_2 3\frac{1}{2}aq$: concentrically grouped needles. S. ·5 at 8°.

Iodo-o-oxy-benzoic acid $C_6H_3I(OH)(CO_2H)$ [5:2:1]. [196°] (G.); [193·5°] (F.); [197°] (M.). S. ·11 at 20°; 1 at 100° (L.).

Formation.—1. As above.—2. Together with di- and tri-iodo-oxy-benzoic acids, by fusing salicylic acid (1 mol.) with iodine (1 mol.), and treating the product with aqueous KOH (Kolbe a. Lautemann, *A.* 115, 157).—3. By dissolving equal weights of iodine and salicylic acid in 80 p.c. alcohol, boiling for 3 hours, evaporating, and dissolving in aqueous Na_2CO_3 (Lautemann, *A.* 120, 299).—4. From salicylic acid, iodine, and HgO (Hlasiwetz a. Weselsky, *B.* 5, 380; *A.* 174, 99).—5. By agitating a hot solution of salicylic acid (1 pt.) in water (25 pts.) with a mixture of iodine (1 pt.) and iodic acid ($\frac{1}{5}$ pt.), keeping the liquid hot for some time. The resulting acid is converted into sodium salt, and the satiny-needles of the salt of the di-iodo-acid separated, if uecessary by hand-picking, from the lancet-shaped laminæ of the mono-iodo-acid (Liechti, *A. Suppl.* 7, 129; H. Fischer, *A.* 180, 346).—6. From the corresponding nitro-oxy-benzoic acid by reduction to oxy-amido-benzoic acid and exchange of NH_2 for I by the diazo- reaction (Goldberg, *J. pr.* [2] 19, 368; P. F. Frankland, *C. J.* 37, 749).—7. By warming dry silver salicylate with iodine (Birnbaum a. Reinherz, *B.* 15, 458).

Properties.—Long needles (from water); sl. sol. water, v. sol. alcohol and ether. Gives a violet colour with $FeCl_3$. Ou potash-fusion at 200° it gives di-oxy-benzoic acid [197°]. When suddenly heated it splits up into CO_2 and iodo-phenol.

S a l t s.—NaA'aq. S. 7·7 at 20° (L.).—KA'3aq: laminæ. S. 19 at 20° (L.).—NH_4A' $3\frac{1}{2}aq$: needles. S. 9·5 at 20° (L.).—$BaA'_2 4aq$: warty scales. S. (of BaA'_2) ·8 at 8° (M.); 1·3 at 20° (L.).—$BaC_7H_3IO_3$ 2aq: tufts of small needles (L.).—$CaA'_2 6aq$.—$MgA'_2 6aq$.—PbA'_2.—AgA': yellowish pp.

E t h y l e t h e r EtA'. [71°] (Schmitt, *Z.* 1864, 321).

Iodo-*m*-oxy-benzoic acid $C_6H_3I(OH)(CO_2H)$ [*x*:3:1]. Formed, together with di-iodo-phenol, by alternately adding iodine and HgO to oxy-benzoic acid dissolved in 90 p.c. alcohol, and separated by solution in boiling water (Weselsky, *A.* 174, 105). Slender needles; sl. sol. cold water.

Iodo-*p*-oxy-benzoic acid $C_6H_3I(OH)(CO_2H)$ [3:4:1]. [160°] (P.). S. ·18 in the cold.

Formation.—1. By boiling a solution of *p*-oxy-benzoic acid for a few minutes with iodine and iodic acid (Peltzer, *A.* 146, 288).—2. From *p*-oxy-benzoic acid dissolved in alcohol by alternate addition of iodino and HgO (Weselsky, *A.* 174, 99).

Properties.—Small needles (from water). Decomposes at 192°. May bo sublimed below its melting-point. V. e. sol. alcohol and ether. Gives with $FeCl_3$ a dingy brown pp.

S a l t s. NaA' 6aq: monoclinic efflorescent crystals. $Na_2C_7H_3IO_3$ 6aq: hygroscopic silky needles (from alcohol).—$BaA'_2 7aq$: trimetric tables.—AgA': white pp.

M e t h y l d e r i v a t i v e $C_6H_3I(OMe)CO_2H$. *Iodo-anisic acid.* [235°]. S. (cold ether) ·7. Formed by heating anisic acid with iodine and iodic acid at 150° (P.). Formed also by oxidation of the methyl ether of iodo-*p*-cresol (Schall a. Dralle, *B.* 17, 2533). The same, or an isomeric acid, is formed from amido-anisic acid by the diazo- reaction (Griess, *Pr.* 10, 309). Plates (S. a. D.) or needles (G.). Nearly insol. boiling water, m. sol. alcohol.—NaA'2aq: concentrically grouped needles.—$BaA'_2 3aq$: vitreous prisms.—$CaA'_2 3aq$: nacreous laminæ.—PbA'_2 (at 100°): curdy pp.—AgA': micro-crystalline laminæ.

Di-iodo-o-oxy-benzoic acid $C_6H_2I_2(OH)(CO_2H)$. *Di-iodo-salicylic acid.* S. ·07 at 15°; ·15 at 100° (L.). Formed, together with iodo-o-oxy-benzoic acid, by the action of iodiue and aqueous potash, of iodiue and iodic acid, or of iodine and HgO upou salicylic acid (Lautemann, *A.* 120, 304; Liechti, *A. Suppl.* 7, 141; Demole, *B.* 7, 1439; Weselsky, *A.* 174, 103). Formed also by heatiug dry silver salicylate with iodine (Birnbaum a. Reinherz, *B.* 15, 459). White felted mass (from hot water). V. sol. alcohol and ether. At 197° (L.) or 220° (W.) it begins to decompose, giving off iodine. It gives a violet colouration with $FeCl_3$. On potash-fusion it gives tri-oxy-benzoic (? gallic) acid and pyrogallol.

S a l t s.—NaA' $2\frac{1}{2}aq$: long flat needles, mostly grouped in druses. S. 2 at 20°; much less soluble in water than iodo-o-oxy-benzoic acid.—KA' $\frac{1}{2}aq$: minute thick prisms. S. ·553 at 20°. V. sol. alcohol, sl. sol. ether.—NH_4A' $\frac{1}{2}aq$: arborescent groups of small needles. S. ·32 at 20°.—$BaA'_2 3aq$: needles. S. ·074 at 18°. V. sl. sol. alcohol.—$BaC_7H_2I_2O_3$ $1\frac{1}{2}aq$: small silky tablets, v. sl. sol. water, forming an alkaline solution.—$CaA'_2 5aq$: needles. S. ·086 at 18°.

Di-iodo-*p*-oxy-benzoic acid $C_6H_2I_2(OH)(CO_2H)$. Formed, together with iodo-*p*-oxy-benzoic acid, by iodation of *p*-oxy-benzoic acid (Peltzer). Small needles (from dilute alcohol). Nearly insol. boiling water, v. e. sol. alcohol and ether. Decomposes when heated without previous fusion. Cannot be sublimed.—NaA' 7aq: tufts of delicate, iridescent, efflorescent needles, v. sol. water.—$Na_2C_7H_2I_2O_3$ 6aq: trimetric tables.—BaA'_2: gelatinous pp. got by adding alcohol to its aqueous solutiou.—$CaA'_2 2aq$: nacreous lamiuæ.—PbA'_2: bulky pp. Swells up like mercuric sulphocyauide wheu heated.—AgA'.—$Ag_2C_7H_2I_2O_3$.

Tri-iodo-o-oxy-benzoic acid $C_6HI_3(OH)(CO_2H)$. [c. 157°]. Obtained in small quantity in preparing mono-, aud di-iodo-o-oxy-benzoic acids by the action of iodino and KOH on salicylic acid (Lautemann). Weselsky (*A.* 174, 104) could not obtain it by treating salicylic acid with iodine and HgO. Tufts of needles (from alcohol). Insol. water, sol. alcohol and ether. Decomposed by alkalis into CO_2 and a red body $C_6H_2I_2O$ (?). Its s o d i u m s a l t is a grey-green mass, v. sl. sol. water.

IODO-*p*-OXY-BENZOIC ALDEHYDE $C_7H_5IO_2$ *i.e.* $C_6H_3I(OH).CHO$. [199°]. Formed by heating the dilute alcoholic solution of *p*-oxy-benzoic aldehyde with iodine for some hours (Herzfeld, *B.* 10, 2196). Sl. sol. water and benzene, v. sol.

alcohol and ether. Converted by potash-fusion into protocatechuic acid.

Iodo-di-oxy-benzoic aldehyde. *Methyl derivative* $C_8H_7IO_3$ *i.e.* $C_6H_2I(OH)(OMe).CHO$. *Iodo-vanillin.* [174°]. Formed by warming vanillin with an alcoholic solution of iodine (Carles, *Bl.* [2] 17, 12). Needles. Sl. sol. cold alcohol and ether.

Di-iodo-di-oxy-benzoic aldehyde. *Methyl derivative* $C_6HI_2(OH)(OMe).CHO$. Formed like the preceding, using more iodine (C.). Crystals; insol. chloroform, sol. alcohol and ether.

α-IODO-β-OXY-PHENYL-PROPIONIC ACID $C_9H_9IO_3$ *i.e.* $C_6H_5.CH(OH).CHI.CO_2H$. [138°]. Formed by treating cinnamic acid with an aqueous solution of iodine chloride, the compound $C_6H_5.CHCl.CHI.CO_2H$ being probably first formed (Erlenmeyer a. Rosenhek, *B.* 19, 2464). Large crystals (from benzene). With HCl it gives the compound $C_{18}H_{16}ClIO_4$, which may possibly be $C_6H_5.CH:CH.C(OH){<}{}^{O}_{O}{>}C(OH).CHI.CHCl.C_6H_5$.

Exo-**Iodo-*o*-oxy-phenyl-propionic acid.** *Methyl derivative* $C_6H_4(OMe).C_2H_3I.CO_2H$. Formed by the combination of the methyl derivative of (α)- or (β)-coumaric acid with HI (Perkin, *C. J.* 39, 429). Decomposed by aqueous Na_2CO_3 into CO_2, HI, and $C_6H_4(OMe).C_2H_3$.

TETRA-IODO-DI-OXY-DI-PHENYL SULPHONE $C_{12}H_6I_4SO_4$ *i.e.* $SO_2(C_6H_2I_2.OH)_2$. [260°–270°]. S.G. $\frac{19}{}$ 2·797. From di-oxy-di-phenyl sulphone by treatment in alcoholic solution with iodine and HgO (Annaheim, *B.* 9, 1150). Minute needles (from HOAc). Decomposes on fusion. Insol. cold alcohol, nearly insol. boiling alcohol and HOAc.

β-IODO-α-OXY-PROPIONIC ACID $C_3H_5IO_3$ *i.e.* $CH_2I.CH(OH).CO_2H$. *Iodo-lactic acid.* [101°] (M.); [85°] (G.). Formed by treating β-chloro-α-oxy-propionic acid with KI at 50° (Glinsky, *B.* 6, 1257). Prepared by the addition of HI to sodium glycidate (Melikoff, *B.* 14, 937). Large prisms, v. sol. water, alcohol, and ether. Converted by alcoholic KOH into glycidic acid.—AgA′: white unstable pp.—ZnA'_2: crystalline powder (M.) or tables (G.).—CaA'_2 3aq: amorphous (M.).

DI-IODO-OXY-PYRIDINE $C_5NH_2I_2(OH)$ [2:4:5] (?). [259°]. Formed by heating an alkaline solution of pyridine di-carboxylic acid (quinolinic acid) with iodine and KI at 180°–200°. Small flat needles. Sol. hot acetic acid and amyl alcohol, v. sl. sol. boiling water, alcohol, ether, or chloroform. Dissolves in dilute alkalis.—$C_5NH_2I_2(ONa)$ 3aq: colourless glistening scales, sl. sol. aqueous NaOH (Pfeiffer, *B.* 20, 1352).

IODO-(*Py.* 3)-OXY-QUINOLINE C_9H_6NOI *i.e.* $C_6H_4{<}{}^{CI:CH}_{N:C(OH)}$ or $C_6H_4{<}{}^{CH:CI}_{N:C(OH)}$. *Iodo-carbostyril.* [276°]. Formed by boiling *o*-amido-phenyl-propiolic acid $C_6H_4(NH_2).C⋮C.CO_2H$ with dilute HI (Baeyer a. Bloem, *B.* 15, 2149). Sublimable.

DI-IODO-DI-OXY-TOLUIC ACID *v.* Di-iodo-orsellic acid.

IODO-PENTANE *v.* Amyl iodide.

Di-iodo-pentane $C_5H_{10}I_2$ *i.e.* $(CH_3.CHI)_2CH_2$. (c. 182°). Formed by heating methylene di-methyl diketone $(CH_3.CO)_2CH_2$ with HI at about 90° (Combes, *A. Ch.* [6] 12, 235). Liquid, begins to decompose at its boiling-point.

IODO-PENTINENE C_5H_7I *i.e.* $(CH_3)_2CH.C⋮CI$. (140°). Formed from the silver derivative of $(CH_3)_2CH.C⋮CH$ by treatment with a solution of iodine in KI (Eltekoff, *J. R.* 9, 225). Liquid. Gives $(CH_3)_2CH.C⋮CH$ when heated with NaOEt.

DI-IODO-DIPHENIC ACID *v.* Di-iodo-di-phenyl di-carboxylic acid.

o-IODO-PHENOL C_6H_5IO *i.e.* [2:1]$C_6H_4I(OH)$. [43°].

Formation.—1. Probably occurs among the products of the iodation of phenol (Schützenberger a. Sengenwald, *C. R.* 54, 197; Körner, *A.* 137, 197; Hlasiwetz a. Weselsky, *Sitz. W.* 60 [2] 290; Lobanoff, *B.* 6, 1251).—2. By the action of iodine on sodium phenol suspended in CS_2 (Schall, *B.* 16, 1897).—3. By heating the chloride or sulphate of o-diazo-phenol with KI, distilling the product with steam, and recrystallising from water (Nölting a. Wrzesinsky, *B.* 8, 820; Nölting a. Stricker, *B.* 20, 3018; *Bl.* [2] 49, 659; Neumann, *A.* 241, 68).—4. By adding powdered iodine to a dilute alcoholic solution of phenol, mixed with ammonia (Willgerodt, *J. pr.* [2] 37, 446).

Properties.—White needles, v. sol. water and other ordinary menstrua. According to Schall (*B.* 20, 3363) it forms in crystalline branches, melting at 43° or needles melting at 40°. Nitric acid attacks it, setting iodine free, but chlorine does not do so, but forms chloro-iodo-phenol. Potash-fusion at 165°–250° yields pyrocatechin. Not affected by air and light. Cold conc. H_2SO_4 produces di-iodo-phenol (Neumann, *B.* 20, 581).

***m*-Iodo-phenol** [3:1] $C_6H_4I(OH)$. [40°]. Prepared from *m*-iodo-aniline by diazo- reaction. The product is distilled with steam, extracted with ether, and recrystallised from ligroïn (N. a. S.). It may be prepared in like manner from *m*-amido-phenol, by diazotising and heating the product with aqueous KI. Needles (from ligroïn). May be sublimed. V. sol. alcohol and ether. It does not give off iodine when treated either with HNO_3 or with chlorine. It yields resorcin when fused with KOH.

***p*-Iodo-phenol** [4:1] $C_6H_4I(OH)$. [94°].

Formation.—1. In the iodation of phenol.—2. From *p*-amido-phenol by diazotising and heating the product with KIAq (N. a. S.).—3. A by-product, together with di- and tri-iodo-phenol, in the formation of *o*-iodo-phenol from iodine, ammonia, and an alcoholic solution of phenol (Willgerodt, *J. pr.* [2] 37, 446).

Properties.—Long needles. Nitric acid sets iodine free, but chlorine does not do so. When heated with conc. H_2SO_4 it gives (1, 3, 6)-di-iodo-phenol [72°]. Potash-fusion gives resorcin at high temperatures.

Di-iodo-phenol $C_6H_3I_2(OH)$ [4:2:1]. [72°]. Formed by mixing o-iodo-phenol (10 g.) with H_2SO_4 (30 g.) at −10° (Neumann, *A.* 241, 71). Formed also in like manner from *p*-iodo-phenol. White needles (from water). Volatile with steam. Boiling HNO_3 converts it into picric acid.

Acetyl derivative $C_6H_3I_2(OAc)$. [76°]. Long flat trimetric prisms (from dilute alcohol); $a:b:c = ·731:1:·832$.

Di-iodo-phenol $C_6H_3I_2(OH)$ [68°]. Formed as a by-product in the action of iodine upon phenol-sodium suspended in CS_2 (Schall, *B.* 16, 1899, 1902; 20, 3364). Apparently formed also in the action of iodine chloride on phenol (S. a. S.). White glistening plates. Volatile with steam.—$C_6H_3I_2.ONa$: needles.

Acetyl derivative $C_6H_3I_2(OAc)$: [107° uncor.], small prisms.

Benzoyl derivative $C_6H_3I_2(OBz)$: [96° uncor.].

Di-iodo-phenol $C_6H_3I_2(OH)$. [150°]. Formed by the action of iodine and HgO on an alcoholic solution of phenol (Hlasiwetz a. Weselsky, *Sitz. W.* 60 [2] 290; *C. C.* 1870, 63). Silky felted needles (from dilute alcohol); v. sol. alcohol, ether, and CS_2. May be sublimed. Not affected by boiling alcoholic KOH.

Tri-iodo-phenol $C_6H_2I_3(OH)$ [6:4:2:1]. [155°].

Formation.—1. By treating phenol with a considerable quantity of ICl, and exhausting the product with boiling alcohol in which tri-iodo-phenol is not very soluble (Schützenberger, *Bl.* [2] 4, 102).—2. From phenol, iodine, and KOH (Lautemann, *A.* 120, 307).—3. From phenol, iodine, and iodic acid (Körner, *A.* 137, 213).—4. From salicylic acid, iodine and iodic acid (Kekulé, *A.* 131, 231).—5. Formed as a by-product from the action of iodine on phenol-sodium suspended in CS_2 (Schall, *B.* 16, 1899).—6. By the action of iodide of nitrogen on a dilute alcoholic solution of sodium phenolate (Willgerodt, *J. pr.* [2] 37, 447).

Properties.—Needles (from dilute alcohol). Decomposed on fusion. M. sol. alcohol. Converted by excess of ICl into per-chloro-phenol. HNO_3 gives picric acid. HCl and $KClO_3$ give chloranil.

DI-IODO-PHENOL SULPHONIC ACID $C_6H_2I_2(OH)(SO_3H)$ [6:2:1:4]. [120°]. Formed by adding a solution of KI and KIO_3 to one of phenol *p*-sulphonic acid in aqueous HCl (Kehrmann, *J. pr.* [2] 37, 11, 334, 359; Ostermayer, *J. pr.* [2] 37, 215). Monoclinic prisms, v. e. sol. water, but ppd. by HCl or H_2SO_4, decomposes at 190°. Converted by nitric acid into picric acid. Chromic acid oxidises it to di-iodo-quinone.

Salts.—KA′ 2aq: long needles or thick prisms.—NaA′ 3aq: sol. water, commercially known as 'sozodole.'—$C_6H_2K_2I_2SO_4$: dimetric prisms.—BaA'_2 3aq: shining needles, v. sl. sol. water.—ZnA'_2 6aq: long needles. The copper salt is greenish-white and v. sol. water.

DI-*p*-IODO-DIPHENYL $C_{12}H_8I_2$ *i.e.* $C_6H_4I.C_6H_4I$. [202°]. Formed by the action of HI on the diazo- compound derived from benzidine (Schmidt a. Schultz, *B.* 12, 489). Yellow leaflets.

o-**IODO-PHENYL-ACETIC ACID** $C_8H_7IO_2$ *i.e.* $C_6H_4I.CH_2.CO_2H$. [96°]. Prepared by digesting its nitrile with fuming HCl for four hours at 126°. The nitrile is formed by treating o-iodo-benzyl bromide with KCy (Mabery a. Robinson, *Am.* 4, 102). Slender needles (from water), sol. hot water, alcohol, ether, CS_2, and ligroïn.—AgA: curdy pp.; sl. sol. water.

p-Iodo-phenyl-acetic acid $C_6H_4I.CH_2.CO_2H$. [135°]. Prepared by heating its nitrile with fuming HClAq in sealed tubes at 100° (Jackson, a. Mabery, *Am.* 2, 253; *P. Am. A.* 13, 205; *B.* 11, 56). Narrow white plates (from water) with agreeable odour like sweet allysium; v. sol. hot water, alcohol, ether, benzene, and CS_2. Gives *p*-iodo-benzoic acid on oxidation.—BaA'_2 aq: minute white needles, v. sol. water.—AgA′: glistening plates, sl. sol. boiling water.

Nitrile $C_6H_4I.CH_2.CN$. *p-Iodo-benzyl cyanide.* [50·5°]. Prepared by boiling *p*-iodo-benzyl bromide with alcoholic KCy. Pearly plates, insol. water, v. sol. alcohol, ether, and CS_2.

IODO-PHENYL-ACETYLENE $C_6H_5.C:CI$. Obtained from phenyl-acetylene (Holleman, *B.* 20, 3080). Brownish-yellow liquid.

IODO-PHENYL-ACRYLIC ACID *v.* Iodo-cinnamic acid.

Exo-**IODO-DI-PHENYL-AMYLIDENE-DI-AMINE** $C_{17}H_{21}N_2I$ *i.e.* $C_5H_9I(NHPh)_2$. Formed by heating iodo-isovaleric aldehyde with aniline (Chautard, *A. Ch.* [6] 16, 169). Large brownish-yellow needles; v. sol. water and alcohol, m. sol. other solvents. Decomposed on fusion. Forms uncrystallisable salts.

DI-IODO-DIPHENYL-DI-CARBOXYLIC ACID $C_{14}H_8I_2O_4$ *i.e.* $C_6H_3I(CO_2H).C_6H_3I.CO_2H$. [262°]. Prepared by the action of HI on the diazo- derivative of di-amido-di-phenyl dicarboxylic acid (Schultz, *B.* 11, 217; *A.* 196, 21; 203, 95). Amorphous; v. sl. sol. boiling water, v. sol. alcohol, acetone, and ether.

DI-IODO-PHENYLENE OXIDE so called. $C_6H_2I_2O$. *Tetra-iodo-diphenylene quinone.* Formed in the action of iodine and KOH upon o-, *m*-, or *p*-oxy-benzoic acid and on phenol (Lautemann, *A.* 120, 309; Kämmerer a. Benzinger, *B.* 11, 557). Formed also by boiling tri-iodo-phenol with aqueous Na_2CO_3(L.), and by distilling di-iodo-diphenyl dicarboxylic acid with lime (Schultz, *B.* 11, 217). Reddish-brown powder, insol. water, alcohol, ether, chloroform, and benzene. Dissolves in CS_2 with deep-red colour. Boiling KOHAq has little action on it. Conc. HNO_3 forms picric acid. It decomposes at 200°. Aqueous SO_2 at 100° forms colourless $C_{12}H_6I_4O_2$.

DI-*exo*-IODO-DI-PHENYL-ETHYLENE $C_{14}H_{10}I_2$ *i.e.* CIPh:CIPh. Formed by heating di-phenyl-acetylene (tolane) with dry iodine and crystallising from chloroform (E. Fischer, *A.* 211, 233). Rose-coloured plates; v. sl. sol. alcohol. Decomposed by heat.

ω-**IODO-DI-PHENYL-ETHYLIDENE-DI-AMINE** $C_{14}H_{15}IN_2$ *i.e.* $CH_2I.CH(NHPh)_2$. Obtained by heating iodo-acetic aldehyde with excess of aniline (Chautard, *A. Ch.* [6] 16, 155). Yellow needles or tables. Cannot be melted without decomposition. V. sol. alcohol, sol. ether, benzene and CS_2. With strong acids it forms uncrystallisable salts, v. sol. water and alcohol.

DI-*p*-IODO-DI-PHENYL-GUANIDINE $C_{13}H_{11}I_2N_3$ *i.e.* $CN_3H_3(C_6H_4I)_2$? From *p*-iodo-aniline in ethereal solution and CyCl (Hofmann, *A.* 67, 148). Crystalline.—$B'_2H_2PtCl_6$.

Tri-*p*-iodo-tri-phenyl-guanidine $C_{19}H_{14}I_3N_3$. From di-*p*-iodo-di-phenyl-thio-urea and iodine (Losanitsch, *B.* 5, 158).

Exo-**IODO-DI-PHENYL-HEPTYLIDENE-DIAMINE** $C_7H_{13}I(NHC_6H_5)_2$. Formed by heating iodo-heptoic aldehyde with aniline (Chautard, *A. Ch.* [6] 16, 173). Lemon-yellow deliquescent tables; v. sol. alcohol, sl. sol. benzene and $CHCl_3$. Decomposes on heating. Does not give crystalline salts.

p-**IODO-PHENYL-HYDRAZINE** $C_6H_7IN_2$ *i.e.* $C_6H_4I.NH.NH_2$. [103°]. Formed by reducing the diazo- derivative of *p*-iodo-aniline [60°] with an excess of $SnCl_2$ (Neufeld, *A.* 248, 98). Silky needles (from hot water); v. sol. alcohol, ether, chloroform, benzene, and dilute HOAc. With acetone it forms $C_6H_4I.N_2H:CMe_2$ crystallising from petroleum-ether in white plates [114°]. With acetic aldehyde it gives $C_6H_4I.N_2H:CHMe$ [107°] crystallising from petroleum-ether in yellow needles.

Di-iodo-phenyl-hydrazine $C_6H_3I_2(N_2H_3)$ [4:2:1]. [112°]. From di-iodo-aniline by diazotising and reducing with $SnCl_2$ (Neufeld, *A.* 248, 99). White silky needles, v. sol. alcohol, ether, and benzene, sl. sol. hot water and petroleum-ether. The hydrochloride [162°] crystallises from water in white needles.

Di-iodo-*s*-di-phenyl-hydrazine $C_{12}H_{10}I_2N_2$ *i.e.* [3:1] $C_6H_4I.NH.NH.C_6H_4I$ [1:3]. *Hydrazo-di-iodo-benzene.* [90°]. Formed by heating the azoxy- compound $C_6H_4I.N_2O.C_6H_4I$ with alcoholic ammonium sulphide at 100° (Gabriel, *B.* 9, 1408). V. sol. ordinary solvents.

Di-iodo-*s*-di-phenyl-hydrazine [4:1] $C_6H_4I.NH.NH.C_6H_4I$ [1:4]. Formed by heating the corresponding azoxy- compound with alcoholic ammonium sulphide at 100° (G.). Flat needles; decomposed before melting.

p-**IODO-PHENYL-OXAMIC ACID** $C_6H_4I.NH.CO.CO_2H$. [c. 200°]. S. ·072 at 25°. Formed by the action of alcoholic potash on the di-iodo-di-anilide of oxalic acid (Dyer a. Mixter, *Am.* 8, 357). Long white fibres. Sol. alcohol and ether.—$^xBaA'_2$: white pp.—$^xAgA'$: white pp.—KA′: sol. hot water.

p-**IODO-PHENYL PHTHALIMIDE**

(1)C=O

C_6H_4< >O

(2)C=N.C_6H_4I. [227°–228°]. Prepared by heating *p*-iodo-aniline with phthalic anhydride (Gabriel, *B.* 11, 2261). Needles. V. sol. C_6H_6, less sol. ether.

o-**IODO-PHENYL-PROPIONIC ACID** $C_9H_9IO_2$ *i.e.* $C_6H_4I.C_2H_4.CO_2H$. *o-Iodo-hydrocinnamic acid.* [103°]. Plates (from water). Formed by reduction of *o*-iodo-cinnamic acid (Gabriel a. Herzberg, *B.* 16, 2037).

m-**Iodo-phenyl-propionic acid** $C_6H_4I.C_2H_4.CO_2H$. *m-Iodohydro-cinnamic acid.* [66°]. Colourless plates. Formed by reduction of *m*-iodo-cinnamic acid (Gabriel a. Herzberg, *B.* 16, 2039).

p-**Iodo-phenyl-propionic acid** $C_6H_4I.C_2H_4.CO_2H$ *p-Iodo-hydrocinnamic acid.* [141°]. White prisms. Formed by reduction of *p*-iodo-cinnamic acid with HI and P (Gabriel a. Herzberg, *B.* 16, 2040).

β-**Iodo-phenyl-propionic acid** $C_6H_5.CHI.CH_2.CO_2H$. [120°]. Formed by adding fuming HIAq to a concentrated aqueous solution of *β*-oxy-phenyl-propionic acid (Glaser, *A.* 147, 97). Formed also from cinnamic acid and conc. HIAq in the cold (Fittig a. Binder, *A.* 195, 133). Small crystals (from CS_2). Decomposed on fusion. Boiling with water converts it into HI and cinnamic acid. Aqueous Na_2CO_3 gives HI, styrene, and CO_2.

ω-**IODO-DI-PHENYL-PROPYLIDENE-DI-AMINE** $C_{15}H_{17}IN_2$ *i.e.* $CH_2I.CH_2.CH(NHPh)_2$. Formed by heating *β*-iodo-propionic aldehyde with excess of aniline (Chautard, *A. Ch.* [6] 16, 159). Brownish-yellow needles or tables, v. sol. all ordinary solvents. Decomposed by heat without previous fusion. Gives no crystalline salts.

DI-IODO-DI-PHENYL SULPHIDE $C_{12}H_8I_2S$ *i.e.* $(C_6H_4I)_2S$. [139°]. Formed by heating di-phenyl sulphide with iodine and iodic acid in sealed tubes. Got also from di-amido-di-phenyl sulphide by the diazo- reaction (Krafft, *B.* 7, 1165). Laminæ.

p-**IODO-PHENYL THIOCARBIMIDE** $C_6H_4I.N\,CS$. [65°]. Formed by the action of iodine on an alcoholic solution of di-*p*-iodo-di-phenyl-thio-urea (Losanitsch, *B.* 5, 158). Crystals.

DI-*p*-IODO-DI-PHENYL-THIO-UREA $C_{13}H_{10}I_2N_2S$ *i.e.* $CS(NH.C_6H_4I)_2$. [173°]. From *p*-iodo-aniline, alcohol, and CS_2 (Losanitsch, *B.* 5, 157). V. sl. sol. alcohol and ether.

IODO-*iso*-PHTHALIC ACID $C_6H_3I(CO_2H)_2$ [6:3:1]. [204°]. Formed by oxidation of iodo-tolyl methyl ketone $C_6H_3MeI.CO.CH_3$ [1:2:5] with CrO_3 (Klingel, *B.* 18, 2701). Fine white needles. Sublimable. V. sol. alcohol, acetic acid, and ether, insol. cold water.

Salts.—A″Ba: very sparingly soluble fine white needles.—$A''Ca^x$: microscopic needles.—$A''Ag_2{}^x$: white crystalline pp.—$A''Cu^x$: green crystalline pp.

IODO-PROPANE *v.* PROPYL IODIDE.

Di-iodo-propane $C_3H_6I_2$ *i.e.* $CH_3.CHI.CH_2I$. *Propylene iodide.* S.G. $\frac{18.5}{}$ 2·49. From propylene and iodine (Berthelot a. De Luca, *C. R.* 39, 748). From allyl iodide and gaseous HI at −18° (Malbot, *C. R.* 107, 114; *Bl.* [2] 50, 449). Liquid. Split up by alcoholic potash into iodine and propylene.

Di-iodo-propane $CH_2I.CH_2.CH_2I$. *Tri-methylene iodide.* (227°); (169° at 170 mm.). S.G. $\frac{10}{4}$ 2·5631; $\frac{4}{4}$ 2·5962; $\frac{25}{25}$ 2·5614. Obtained by heating *s*-di-oxy-propane (trimethylene glycol) with fuming HIAq at 100° (Freund, *M.* 2, 640). Also from trimethylene bromide, alcohol, and KI (Perkin, jun., *C. J.* 51, 12).

Di-iodo-propane $CH_3.CI_2.CH_3$. *Allylene di-hydro-di-iodide.* (148°). S.G. $\frac{0}{}$ 2·15 (O.); 2·45 (S.). Obtained by direct combination of allylene with HI (in conc. solution) (Oppenheim, *Bl.* [2] 4, 434; Semenoff, *Bl.* [2] 5, 446). Heavy oil. Partly decomposed by distillation, but may be distilled with steam or with any indifferent gas. Sl. sol. alcohol, v. sol. ether. Becomes coloured in air and light. Alcoholic potash forms $CH_3.CI:CH_2$. Ag_2O gives acetone (Sorokin, *Z.* 1871, 264).

IODO-PROPIOLIC ACID C_3HIO_2 *i.e.* $I.C{:}C.CO_2H$. *Iodo-propargylic acid. Iodo-acetylene carboxylic acid.* [140°]. Small colourless prisms or glistening needles.

Formation.—1. By saponification of the ethyl ether.—2. By the action of a solution of iodine in KI upon the cuprous compound of calcium or barium propargylate.

Reactions.—It combines with HBr to form brom-iodo-acrylic acid [96°]; with HI it yields *β*-di-iodo-acrylic acid [133°]; with bromine dissolved in chloroform it yields di-bromo-iodo-acrylic acid [147°]; with an ethereal solution of iodine, tri-iodo-acrylic acid [207°]; and with iodine bromide, bromo-di-iodo-acrylic acid [182°].

On the other hand, an aqueous solution of bromine converts it into di-bromo-iodo-ethylene IBrC:CHBr with evolution of CO_2.

Salts.—A′K: small glistening very hygroscopic needles.—A′Ag: white pp., decomposed by warming with water forming AgI.—A'_2Ba: easily soluble amorphous solid.—A'_2Cu.

Ethyl ether A′Et: [68°]; large colourless prisms. Formed by the action of a solution of iodine in KI upon the cuprous compound of propargylic ether (Baeyer, *B.* 18, 2274; Homolka a. Stolz, *B.* 18, 2282; 19, 536).

α-IODO-PROPIONIC ACID $C_3H_5IO_2$ *i.e.* $CH_3.CHI.CO_2H$. Prepared by digesting syrupy lactic acid (1 mol.) with PI_2 (1 mol.), pouring the product into water and extracting with ether (Wichelhaus, *A.* 144, 352). Oil, nearly insol. water.

β-Iodo-propionic acid $CH_2I.CH_2.CO_2H$. [82°].

Formation.—1. By the action of iodide of phosphorus on glyceric acid (Beilstein, *A.* 120, 226; 122, 366; Erlenmeyer, *A.* 191, 284).—2. From acrylic acid and conc. HIAq (Wislicenus, *A.* 166, 1).

Preparation.—The product of the oxidation of glycerin with nitric acid is evaporated on the water-bath, and the syrupy residue diluted with water until it possesses S.G. 1·26. This solution (30 c.c.) is then poured into a flask containing iodide of phosphorus prepared from iodine (50 g.) and yellow phosphorus (6·5 g.). After the vigorous action has taken place, the solid residue is recrystallised from water (V. Meyer, *B.* 19, 3294; 21, 24).

Properties.—Colourless laminæ; v. sol. hot, v. sl. sol. cold, water; v. e. sol. alcohol and ether. May be converted into propionic acid by HI or by sodium-amalgam (Moldenhauer, *A.* 131, 328). By boiling with water it is converted into hydracrylic acid and a little acrylic acid. Boiling with water and Ag_2O forms hydracrylic acid, para-adipi-malic acid $C_6H_{10}O_5$, dihydracrylic acid $C_6H_{10}O_5$, and paracrylic acid $C_3H_4O_2$ [69°] (Beilstein; Wislicenus, *Z.* [2] 4, 683; Socoloff; Klimenko, *Bl.* [2] 34, 321; *v.* also Acrylic acid). β-Iodo-propionic acid is converted into adipic acid by heating with reduced silver (W.). $AgNO_3$ gives in an aqueous solution of β-iodo-propionic acid an immediate pp. of AgI.

Methyl ether MeA′. (188°). S.G. $\frac{7}{}$ 1·841 (Henry, *C. R.* 100, 114). Colourless oil, turning brown in light. Is not pungent. Formed from the acid, alcohol, and H_2SO_4.

Ethyl ether EtA′. (202°) (Fittig a. Wolff, *A.* 216, 128). S.G. $\frac{8}{}$ 1·707 (Henry). Formed by heating an alcoholic solution of the acid after adding a few drops of H_2SO_4. Formed also by dissolving the acid (1 pt.) in alcohol (3 pts.) and saturating with HCl; the yield is only 50 p.c., for much EtI is evolved (Lewkowitsch, *J. pr.* [2] 20, 167; Wichelhaus, *B.* 1, 25; Wislicenus, *A.* 192, 129). Oil. Partly decomposed on distillation.

Amide $CH_2I.CH_2.CONH_2$. [101°]. Formed by the action of aqueous NH_3 on the methyl ether in the cold (Henry). Colourless tables, turning yellow in light. V. sol. water. Its solution gives a pp. with $AgNO_3$.

β-IODO-PROPIONIC ALDEHYDE $CH_2I.CH_2.CO.H$. S.G. $\frac{15}{}$ 2·21. Prepared by the action of iodine (25 g.) and iodic acid (10 g.) on propionic aldehyde (18 c.c.) diluted with alcohol (50 c.c.). It is washed with KOH solution and poured into water (Chautard, *A. Ch.* [6] 16, 157).

Properties.—Heavy colourless liquid, not inflammable, with an exceedingly irritating vapour. Miscible with alcohol, ether, and acetone; sl. sol. water. Is totally decomposed at 100°. Very dilute solutions of KOH, NaOH, or NH_4HO attack it slowly in the cold. Conc. solutions resinify it. Mineral acids behave similarly. HNO_3 oxidises it to $CH_2I.CH_2.CO_2H$ [82°]. $Ag(C_2H_3O_2)$ forms propyl acetate (90°). AgCN and silver sulphocyanide give $CH_2.(CN).CH_2.CO.H$ and $CH_2.(CNS).CH_2.CO.H$. Aniline gives the compound $CH_2I.CH_2.CH.(NH.C_6H_5)_2$.

IODO-PROPYL ALCOHOL *v. Iodhydrin* of Propylene glycol.

Di-iodo-propyl alcohol $C_3H_6I_2O$ *i.e.* $CH_2I.CHI.CH_2OH$. *Di-iodide of allyl alcohol.* [45°]. Prepared by dissolving iodine in allyl alcohol (Hübner a. Lellmann, *B.* 13, 460; 14, 207). Colourless needles. Easily decomposed by light or heat. Sol. alcohol, ether, and benzene, insol. water. On heating the chloroform solution it gives a compound crystallising in colourless prisms [160°], which is probably an iodo-allyl alcohol.

Di-iodo-isopropyl alcohol $CH_2I.CH(OH).CH_2I$. *Glycerin di-iodhydrin.* [c. −18°]. S.G. $\frac{15}{}$ 2·4. Prepared by heating the *s*-dichlorhydrin of glycerin with KI and water on a salt-bath (Nahmacher, *B.* 5, 353; Claus, *A.* 168, 24). Faintly yellowish oil. Decomposes when distilled.

***p*-IODO-PROPYL-BENZENE** $C_6H_4(C_3H_7)I$ [1:4]. [250°]. Formed by heating *p*-diazo-propyl-benzene with HI (Louis, *B.* 16, 110). Volatile with steam. Colourless oil. Sol. ether, m. sol. alcohol, almost insol. water. On oxidation with cold CrO_3 in acetic acid it gives *p*-iodo-benzoic acid.

***p*-Iodo-iso-propyl-benzene** $C_6H_4(C_3H_7)I$. (234°). Prepared by heating *p*-diazo-iso-propyl-benzene with HI (Louis, *B.* 16, 114). Colourless oil. On oxidation it gives *p*-iodo-benzoic acid.

ω-IODO-PROPYLENE *v.* Allyl iodide.

α-Iodo-propylene $CH_3.CHI:CH_2$. *Allylene hydro-iodide.* (82°) (S.); (93°–103°) (O.). S.G. $\frac{0}{}$ 1·835; $\frac{16}{}$ 1·803. Formed by decomposing di-iodo-propane $CH_3.CI_2.CH_3$ (1 mol.) with alcoholic KOH (1 mol.), and mixing the distillate with water (Semenoff, *Bl.* [2] 5, 446; *Z.* 1865, 725; Oppenheim, *Bl.* [2] 4, 434; *Z.* 1865, 719).

Di-iodo-propylene $C_3H_4I_2$ *i.e.* $CH_3.CI:CHI$. *Allylene di-iodide.* (198°). Obtained by exposing allylene for two months to a solution of I in aqueous KI in sunshine (Oppenheim). Oil. Turns brown in light. Yields allylene with alcoholic KOAc.

Tri-iodo-propylene $CHI:CI.CH_2I$. *Di-iodo-allyl iodide. Propargyl tri-iodide.* [41°]. Formed by the combination of propargyl iodide with iodine (Henry, *B.* 17, 1132). Small colourless needles.

Tri-iodo-propylene $CH_3.CI:CI_2$. *Iodo-allylene di-iodide.* [64°]. From silver allylene and iodine in ethereal solution (Liebermann, *A.* 135, 273). Needles. Decomposes at 78°. V. e. sol. ether, m. sol. alcohol. Alcoholic potash gives iodo-allylene.

IODO-PROPYLENE-GLYCOL *v. Iodhydrin* of Glycerin.

IODO-PROPYL-THIOPHENE C_7H_9IS *i.e.* $C_4H_2IS.C_3H_7$. From *n*-propyl-thiophene (Rufei, *B.* 20, 1743). Oil, volatile with steam.

Ita-**IODO-PYROTARTARIC ACID** $C_5H_7IO_4$. [135°]. From itaconic acid and HI at 150° (Swarts, *Z.* 1866, 722). Nodules. Reduced by further treatment with HI to pyrotartaric acid.

TETRA-IODO-PYRROLE C_4I_4NH. '*Iodol.*' S. ·02; S. (90 p.c. alcohol) 6 at 15°; S. (ether) 50. Formed by the action of an ethereal solution of iodine on pyrrole-potassium (Ciamician a. Dennstedt, *G.* 13, 18; *B.* 15, 2582), and by the action of iodine on an alkaline solution of pyrrole (Ciamician a. Silber, *G.* 16, 543; *B.* 18, 1766). Long yellowish-brown flat prisms or minute yellow needles (from dilute alcohol). Sol. ether, acetic acid, and hot alcohol, nearly insol. cold alcohol, insol. water and aqueous acids. Decomposes at about 140°–150°. Gives a white pp. with $AgNO_3$ instantly blackening; green colouration with $HgCl_2$. Has no basic properties. It is not decomposed by boiling water, but boiling HClAq blackens it. It does not dissolve in aqueous KOH, but alcoholic potash dissolves it forming a potassium derivative which is decomposed by acids (even CO_2) but not by water. Zinc-dust and KOH reduce it to pyrrole (Ciamician a. Silber, *B.* 19, 3027). When heated gently with conc. H_2SO_4 it gives at first a green, then a dirty violet colouration. Its alcoholic solution gives a red colour with nitric acid (Vulpius). It is employed pharmaceutically as a substitute for iodoform for suppurating sores, fungoid growths, hay fever, &c., having the advantage of possessing no odour, and exerting no poisonous effect upon the system.

IODO-QUINOLINE C_9H_6IN. [63°]. (above 300°). S.G. 1·93. Prepared by heating quinoline with a KI solution of iodine and HIO_3 (La Coste, *B.* 18, 780). Monoclinic prisms, or long thin needles. Easily volatile with steam.

Salts.—$B'HCl\ \frac{1}{2}aq$: small yellow needles.—$B'_2H_2PtCl_6$ 2aq: long orange needles, sl. sol. water.—$B'_2H_2Cr_2O_7$: sparingly soluble yellow needles or plates.

Methylo-iodide B'MeI: glistening golden plates; sol. hot water, v. sl. sol. cold water and alcohol, insol. ether.

Methylo-chloride B'MeCl aq: fine yellowish needles or thick yellow prisms, dimorphous (Lehmann, *Z. K.* 12, 377), v. sol. water.—$(B'MeCl)_2PtCl_4$: fine orange crystals, sl. sol. cold water.

(*Py.* 3)-Iodo-quinoline $C_6H_4\left<\begin{matrix}CH{:}CH\\ \vert\\ N\ :\ CI\end{matrix}\right.$. [53°]. Formed by heating (*Py.* 3)-chloro-quinoline with HI (Friedländer a. Weinberg, *B.* 18, 1531). White needles. Sl. sol. water, v. sol. other solvents.—B'HI: long needles.—$B'_2H_2Cl_2PtCl_4$ aq: red needles.

Di-iodo-quinoline $C_9H_7I_2N$. [90° uncor.]. Formed by the action of iodine in CS_2 on quinoline (Claus a. Istel, *B.* 15, 824). Dull-green metallic needles. Sol. alcohol, ether, and acetic acid.

DI-IODO-QUINONE $C_6H_2I_2O_2$. [159°]. Formed by the action of iodic acid on the diacetyl derivative of hydroquinone (Metzler, *B.* 21, 2555). Yellow needles (from alcohol). Is converted by the action of sulphurous acid into the hydroquinone [142°].

Di-iodo-quinone $C_6H_2I_2O_2$ [3:5:4:1]. [180°]. From di-iodo-*p*-amido-phenol (*q. v.*), H_2SO_4 and $K_2Cr_2O_7$ (Seiffert, *J. pr.* [2] 28, 438). Formed also by oxidising di-iodo-phenol sulphonic acid with CrO_3 (Kehrmann, *J. pr.* [2] 37, 336). Golden plates (from benzoline). Readily sublimes, almost insol. cold, v. sl. sol. boiling, water. With HCl and $SnCl_2$ it gives di-iodo-hydroquinone [145°]. $FeCl_3$ reconverts this into di-iodo-quinone.

Di-iodo-quinone-chlorimide $C_6H_2I_2<\!{}^{O}_{NCl}\!>$. [123°]. From $C_6H_2I_2(NH_2)(OH)$, hydric chloride, and bleaching-powder solution (Seiffert, *J. pr.* [2] 28, 438). With NMe_2Ph it gives $C_6H_2I_2<\!{}^{O}_{N}\!>C_6H_4NMe_2$.

IODO-RESORCIN $C_6H_5IO_2$ *i.e.* $C_6H_3I(OH)_2$. [67°]. Formed by agitating an ethereal solution containing resorcin (10 pts.) and iodine (24 pts.) with PbO (110 pts.), distilling off the ether and recrystallising from benzene (Stenhouse, *C. N.* 26, 279; *A.* 171, 311). Trimetric prisms, sol. water.

Tri-iodo-resorcin $C_6HI_3(OH)_2$. [145°] (M. a. N.); [154°] (C.). Formed, together with a brown substance insoluble in CS_2, when ICl is added to an aqueous solution of resorcin (Michael a. Norton, *B.* 9, 1752). Formed also by adding an aqueous solution of resorcin to a solution of KIO_3, iodine, and KI (Claasen, *B.* 11, 1443). Prepared by adding bleaching powder to a dilute alkaline solution of resorcin (1 mol.) and KI (7 mols.), and then acidifying (Degener, *J. pr.* [2] 20, 324). Needles (from CS_2), sl. sol. hot water, v. sol. alcohol and ether. May be sublimed. Boiling HNO_3 gives tri-nitro-resorcin.

Di-acetyl derivative $C_6HI_3(OAc)_2$. [170°]. Needles, v. sol. alcohol and ether.

IODO-RESORCIN SULPHONIC ACID $C_6H_2I(OH)_2(SO_3H)$. From potassium resorcin sulphonate and iodine (H. Fischer, *M.* 2, 340).—KA' 3aq: minute crystals.

Iodo-resorcin disulphonic acid $C_6HI(OH)_2(SO_3H)_2$. Formed by digesting potassium resorcin disulphonate (30 g.) with iodine (33 g.) in dilute alcoholic solution at 100° (F.).—KA': long needles.

IODO-SALICYLIC ACID *v.* IODO-*o*-OXY-BENZOIC ACID.

IODO-STEARIC ACID $C_{18}H_{35}IO_2$. From di-oxy-stearic acid and HI (A. Saytzeff, *J. pr.* [2] 33, 309). Oil.

Iodo-stearic acid $C_{18}H_{35}IO_2$. From oleïc acid, PI_3, and a little water. The product is mixed with water and extracted with ether (M. C. a. A. Saytzeff, *J. pr.* [2] 35, 384).

Properties.—Oil. Resembles the preceding acid.

Reactions.—1. Reduced by Zn and HCl to stearic acid.—2. Moist Ag_2O forms a substance that is unsaturated (taking up 55 p.c. I from its solution in $HgCl_2Aq$), but is converted by alcoholic KOH into oxy-stearic acid.—3. Alcoholic KOH forms solid iso-oleïc acid [45°], and also ordinary oleïc acid.

Iodo-stearic acid $C_{18}H_{35}IO_2$. Formed by heating iso-oleïc acid with tri-iodide of phosphorus and water (Const a. Saytzeff, *J. pr.* [2] 37, 276; *Bl.* [2] 47, 169). Oil, sol. ether.

Reactions.—1. Yields an oxy-stearic acid [85°] on treating with silver oxide.—2. Alcoholic potash regenerates iso-oleïc acid [40°–45°], but forms no oleïc acid.—3. Alkaline $KMnO_4$ oxidises it to di-oxy-stearic acid [78°].

IODO-STEARIDENIC ACID $C_{18}H_{33}IO_2$. *Iodo-oleïc acid.* From ricinoleïc acid $C_{18}H_{34}O_3$, water, P, and iodine at 100° (Claus, *B.* 9, 1917). Oil. Reduced by boiling with zinc and HClAq to stearic acid. Combines with bromine.

DI-IODO-SUCCINAMIC ACID $CO_2H.CH_2.CI_2.CONH_2$.

Ethyl ether A'Et: [134°]; long needles; slightly soluble in cold water. Formed by the action of iodine upon diazo-succinamic ether $CO_2Et.CH_2.CN_2.CONH_2$ in ethereal solution (Curtius a. Koch, *B.* 19, 2462; *J. pr.* [2] 38, 485)

IODO-TARCONINE *v.* Narcotine.

IODO-THIENYL METHYL KETONE $C_4SH_2I.CO.CH_3$. *Iodo-acetothiënone.* [129°]. Formed by the action of acetyl chloride upon mono- or di-iodo-thiophene in presence of Al_2Cl_6 (Gattermann a. Römer, *B.* 19, 692). Long colourless needles (from alcohol). Very volatile with steam. Strong odour. By alkaline $KMnO_4$ it is oxidised to iodo-thiophene carboxylic acid [131°].

Phenyl-hydrazide $C_4SH_2I.C(N_2HPh).CH_3$: [134°]; yellow tables; sl. sol. alcohol.

(α)-IODO-THIOPHENE C_4H_3IS *i.e.*

CH:CH
| >S. (182° cor.). Oil. Formed by the
CH:CI

action of iodine and HgO on thiophene at the ordinary temperature (Meyer a. Kreis, *B.* 17, 1558; Egli, *B.* 18, 544). With sodium and EtI it gives ethyl-thiophene. With Na and *n*-butyl bromide it forms *n*-butyl-thiophene (182°). Gives an iodo-nitro-thiophene [74°] (Kreis, *B.* 17, 2073).

Di-iodo-thiophene $C_4H_2I_2S$. [40½°]. White crystals. Formed by the action of 2 mols. of iodine and HgO on thiophene at the ordinary temperature (Meyer a. Kreis, *B.* 17, 1558).

IODO-THIOPHENE CARBOXYLIC ACID $C_4SH_2I(CO_2H)$. *Iodo-thiophenic acid.* [131°]. Formed by oxidation of iodo-thiënyl methyl ketone with alkaline $KMnO_4$ (Gattermann a. Römer, *B.* 19, 693). Colourless silky needles (from water). Sublimes in glistening tables.—NH_4A': needles, sl. sol. cold water.

(α)-IODO-THIOPHENE-(β)-DI-SULPHONIC ACID $C_4HIS(SO_3H)_2$. Formed by sulphonation of (α)-iodo-thiophene. On reduction with sodium-amalgam it yields thiophene-(β)-di-sulphonic acid (Langer, *B.* 18, 559).

IODO-THIOXENE is Iodo-di-methyl-thiophene (*q. v.*).

IODO-THYMOL $C_6H_2MePr(OH)I$ [1:4:3:6]. [69°]. Prepared by adding iodine (8·5 g.) to a solution of thymol (5 g.) in ammonia (6 c.c.) mixed with alcohol (2 c.c.) and distilling the oily product with steam (Willgerodt a. Kornblum, *J. pr.* [2] 39, 289). Lustrous white needles, insol. water, sol. other solvents. Oxidised by MnO_2 and H_2SO_4 or by $FeCl_3$ to thymoquinone. Not attacked by aqueous KOH at 300°. HNO_3 forms nitro-thymol, displacing I by NO_2. H_2SO_4 forms a sulphonic acid.

Ethyl derivative $C_6H_2MePrI(OEt)$. [52°]. Opaque white trimetric tables, insol. cold water, sl. sol. hot water and alcohol.

Acetyl derivative $C_6H_2MePrI(OAc)$. [71°]. White needles.

Benzoyl derivative $C_6H_2MePrI(OBz)$. [95°]. Large tables.

Picryl derivative: [155°]; yellowish crystalline aggregates.

IODO-THYMOL SULPHONIC ACID $C_6HMePr(OH)ISO_3H$ [1:4:3:2:6]. From thymol by successive sulphonation and iodation (Kehrmann, *J. pr.* [2] 39, 392). Gives an iodo-thymoquinone on oxidation. HNO_3 gives di-nitro-thymol [53°].—KA' 2aq: crystals, melting in water of crystallisation at 80°, decomposed at 120°.—BaA'_2.—AgA'.

IODO - THYMOQUINONE $C_6HMePrIO_2$ [5:2:6:4:1]. [61°]. Formed by oxidising iodo-thymol sulphonic acid with CrO_3 (Kehrmann, *J. pr.* [2] 39, 392). Yellowish-red prisms. Reduces to an iodo-hydrothymoquinone [74°].

Oxim $C_6HMePrIO(NOH)$ [5:2:6:4:1]. [130°]. Formed by heating the quinone with hydroxylamine hydrochloride in diluted (75 p.c.) alcoholic solution. Long yellow prisms and needles, sol. alcohol and ether, insol. cold water. Its acetyl derivative $C_6HMePrIO(NOAc)$ crystallises in golden needles [70°]. Its sodium derivative crystallises in greenish laminæ.

Iodo-thymoquinone $C_6HMePrIO_2$ [5:2:3:4:1]. [66°]. From iodo-carvacrol sulphonic acid by oxidation with chromic acid mixture (Kehrmann, *J. pr.* [2] 40, 188). Garnet-red tables, sol. alcohol and ether. More volatile with steam than its isomeride. Smells like quinone. Hydroxylamine slowly forms an oxim.

o-IODO-TOLUENE C_7H_7I *i.e.* $C_6H_4I.CH_3$ [2:1]. (205°) (B. a. K.); (211° i. V.) (K.). S.G. $\frac{20}{}$ 1·697 (B. a. K.). Formed from o-toluidine by the diazo- reaction (Beilstein a. Kuhlberg, *Z.* 3, 102; *A.* 158, 347; Kekulé, *B.* 7, 1007; Mabery a. Robinson, *Am.* 4, 101). Oil.

Reactions.—1. Oxidised by dilute nitric acid to *o*-iodo-benzoic acid [157°].—2. With $ClCO_2Et$ and Na it forms $C_6H_4Me.CO_2Et$.—3. CrO_2Cl_2 gives $C_6H_4I.CHCl_2$ and a little $C_6H_4I.CHO$ (Stuart a. Elliott, *C. J.* 53, 805).—4. When heated with H_2SO_4 it forms iodo-toluene sulphonic acid, di-iodo-toluene, and tri-iodo-toluene (Neumann, *A.* 241, 62).

m-**Iodo-toluene** $C_6H_4I.CH_3$ [3:1]. (204°). S.G. $\frac{20}{}$ 1·698. From *m*-toluidine by the diazo-reaction (B. a. K.).

p-**Iodo-toluene** $C_6H_4I.CH_3$ [4:1]. [35°]. (211·5°). From *p*-toluidine by the diazo- reaction (Körner, *Bull. Acad. Belg.* 1867, 157). The same body appears to be formed from mercury ditolyl and iodine, although the melting-point is given as 20° (Dreher a. Otto, *A.* 154, 171). Laminæ. May be sublimed. Gives *p*-iodo-benzoic acid when oxidised by chromic acid mixture. H_2SO_4 forms iodo-toluene sulphonic acid and di- and tri-iodo-toluene (Neumann, *A.* 241, 58).

ω-**Iodo-toluene** *v.* Benzyl iodide.

o-IODO-TOLUENE SULPHONIC ACID $C_7H_7ISO_3$ *i.e.* $CH_3.C_6H_3I.SO_3H$. From *o*-iodo-toluene and SO_3 (Mabery a. Palmer, *Am.* 6 170). Syrupy liquid.—BaA'_2 1½ aq: needles.—CaA'_2 2½aq.—PbA'_2 2aq.

p-**Iodo-toluene** (α)**-sulphonic acid** $CH_3.C_6H_4I.SO_3H$. Formed, together with the (β)-isomeride, by gradually adding *p*-iodo-toluene to SO_3, both dissolved in chloroform (Glassner, *B.* 8, 560).—BaA'_2 4aq: needles; v. e. sol. water.

p-**Iodo-toluene** (β)**-sulphonic acid** $CH_3.C_6H_4I.SO_3H$. Formed as above. Deliquescent crystalline mass.—KA'aq: very soluble laminæ. —NaA' ½aq: dense aggregates of whetstone-shaped very soluble crystals.—CaA'_2 3aq: very soluble silky needles.—BaA'_2 aq: thin laminæ, sl. sol. water.—CuA'_2 6aq: light-blue needles, v. sol. water.

Amide $C_6H_3MeI.SO_2NH_2$. [179°]. Crystals; m. sol. hot water, v. sol. alcohol.

Iodo-toluene disulphonic acid $C_6H_2MeI(SO_3H)_2$ [1:4:3:*x*]. From $C_6H_2Me(NH_2)(SO_3H)_2$ by diazo- reaction (E. Richter, *A.* 230, 325; Limpricht, *B.* 18, 2179). Slender white needles; v. sol. alcohol and water.—BaA″6aq: prisms, v. sol. water.—K_2A'' 2aq: small prisms.

Chloride $C_6H_2MeI(SO_2Cl)_2$: [143°]. After one fusion it melts at 126°. Long white prisms; sl. sol. ether.

Amide [130°–132°]. White needles (from water).

IODO-o-TOLUIDINE $C_6H_3MeI(NH_2)$ [1:4:2]. [49°]. (273°). From iodo-o-nitro-toluidine by reduction (Heynemann, *Z.* [2] 6, 402; *A.* 158, 338). Needles. Boils, with rapid decomposition, at 273°. V. e. sol. alcohol, ether, and CS_2.—$B'HNO_3$: colourless nacreous laminæ. S. ·95 at 16°.

Iodo-toluidine $C_6H_3MeI(NH_2)$ [1:4:3]. [189°]. From *p*-iodo-toluene by nitration and reduction (Glassner, *B.* 8, 561). Needles or plates; v. sol. alcohol.—B″HCl: needles.—$B'HNO_3$: plates.—$B'H_2SO_4$: needles.

Di-iodo-*p*-toluidine $C_6H_2MeI_2(NH_2)$ [1:3:5:4]. [124·5°]. Formed by the action of ICl on *p*-toluidine dissolved in HClAq (Michael a. Norton, *B.* 11, 115; *Am.* 1, 263). Ramified groups of slender needles; m. sol. cold alcohol, sl. sol. hot water.

IODO-TOLUIDINE SULPHONIC ACID $C_6H_2Me(NH_2)I(SO_3H)$ [1:2:4:5]. From the diazo-derivative of $C_6H_2Me(NO_2)(NH_2)(SO_3H)$ [1:2:4:5] and conc. HI at 140° (Limpricht a. Foth, *A.* 230, 308; *B.* 18, 2185). Satiny needles (containing aq). Sl. sol. cold water, m. sol. hot water.—BaA'_2x: trimetric tables; v. sol. water.

IODO-TOLUQUINONE $C_6H_2MeIO_2$ [6:3:4:1]. [117°]. Formed by oxidising a solution of iodo-cresol sulphonic acid in sulphuric acid with chromic acid (Kehrmann, *J. pr.* [2] 37, 340; 39, 392). Long reddish-yellow needles; m. sol. ether. Reduced by stannous chloride to iodo-hydrotoluquinone [111°]. With hydroxylamine it gives the mono-oxim crystallising in short yellow prisms [156°].

Di-iodo-toluquinone $C_6HMeI_2O_2$ [3:6:2:4:1]. [113°]. From di-iodo-*m*-cresol sulphonic acid and CrO_3 (Kehrmann, *J. pr.* [2] 39, 392). Garnet-red laminæ; v. sol. organic solvents. May be sublimed.

DI-IODO-DITOLYL [3:4:1] $C_6H_3MeI.C_6H_3MeI$ [1:3:4]. [100°]. From di-amido-ditolyl by Sandmeyer's modification of the diazo-reaction (Stolle, *B.* 21, 1096). Yellow needles.

ω-IODO-DI-TOLYL-ETHYLIDENE-DI-AMINE $CH_2I.CH(NHC_6H_4Me)_2$. Obtained by heating iodo-acetic aldehyde with *p*-toluidine (Chautard, *A. Ch.* [6] 16, 156). Orange-yellow prisms or tables; decomposed by heat. Does not furnish crystalline salts.

IODO-TOLYL METHYL KETONE $C_6H_3MeI.CO.CH_3$ [1:2:5]. [39°]. Formed by heating diazo-tolyl methyl ketone (from amido-tolyl methyl ketone [102°]) with an excess of HI (Klingel, *B.* 18, 2700). Yellowish prisms. V. sol. alcohol and ether; sl. sol. ligroïn and benzene; insol. water. By CrO_3 it is oxidised to iodo-iso-phthalic acid [204°].

β-IODO-VALERIC ACID $C_5H_9IO_2$ *i.e.* $(CH_3)_2CI.CH_2.CO_2H$. [80°]. Solidifies at 59°. Separates as crystals when HI is passed into a concentrated solution of β-oxy-isovaleric acid (Schirokoff, *J. pr.* [2] 23, 285). Converted by sodium-amalgam to isovaleric acid.

Iodo-valeric acid $CEtMeI.CO_2H$ (?). *Hydro-iodide of tiglic acid.* [86·5°]. Formed by the combination of tiglic (methyl-crotonic) acid with HI which may be effected in the cold (Schmidt a. Berendes, *A.* 191, 117). Formed also, together with the following, when angelic acid is heated with HIAq (Schmidt, *A.* 208, 254). Needles; sl. sol. cold water; decomposed by boiling with water. Converted by zinc and dilute H_2SO_4 into $CEtMeH.CO_2H$. Aqueous $AgNO_3$ gives AgI, tiglic acid and CO_2.

Iodo-valeric acid $CH_3.CHI.CHMe.CO_2H$. [46°]. *Hydro-iodide of angelic acid.* From angelic acid and conc. HIAq in the cold (Fittig, *A.* 216, 162). Prisms, v. sol. water. Zinc and dilute H_2SO_4 converts it into $CEtMeH.CO_2H$. Aqueous $AgNO_3$ gives AgI, tiglic acid, and CO_2. Aqueous Na_2CO_3 at 0° gives CO_2, ψ-butylene $CH_3.CH:CH.CH_3$, and HI. *V.* also ANGELIC ACID, vol. i. p. 266.

IODO-ISOVALERIC-ALDEHYDE C_5H_9IO *i.e.* $(CH_3)_2CH.CHI.CHO$ (?). S.G. $\frac{17}{}$ 2·17.

Preparation.—Isovaleric aldehyde (24 c.c.) dissolved in alcohol (50 c.c.) is treated with iodine (20 g.), and iodic acid (8 g.). The reaction takes place at the ordinary temperature, and is complete in about 15 days. The liquid is poured into excess of water, and decolourised by alkali or reduced silver (Chautard, *A. Ch.* [6] 16, 160).

Properties.—Colourless liquid, blackening on exposure to light, and having an extremely irritating and suffocating odour. It is completely decomposed at 100°, and is not solidified at −20°. V. sol. alcohol and ether, less sol. benzene, $CHCl_3$ and CS_2. Sl. sol. water.

Reactions.—Rapidly decomposed by alkalis. The action of ammonia is complex, giving valeric aldehyde-ammonia, valeridine $C_{10}H_{19}N$, and valeritrine $C_{15}H_{27}N$. Forms a crystalline compound with $NaHSO_3$. $Ag(C_2H_3O_2)$ at 100° yields amyl acetate (138°). AgCN and AgSCN react forming AgI and the corresponding derivatives. Forms a mono- and a di-anilide with aniline.

IODO-VANILLIN *v. Methyl derivative* of IODO-DI-OXY-BENZOIC ALDEHYDE.

DI-IODO-VINYL-AMINE $CI_2:CH(NH_2)$. [192° with decomposition]. Formed by the action of cold aqueous NH_3, CO_2 and alcohol being eliminated upon the di-iodo-oxy-acrylic ether $CI_2:C(OH).CO_2Et$, obtained by treating diazo-oxy-acrylic ether $CN_2:C(OH).CO_2Et$ with an ethereal solution of iodine (Buchner a. Curtius, *B.* 19, 851). Small yellowish prisms. Very

sparingly soluble in cold water and ether, more easily in hot water and hot alcohol. Volatile with steam. It is stable towards acids, but alkalis set free NH_3 in the cold.

DI-ω-IODO-o-XYLENE $C_6H_4(CH_2I)_2$. *o-Xylylene-iodide.* [110°]. Prismatic crystals. Formed by heating phthalyl alcohol (di-ω-oxy-xylene) with HI (Leser, *B.* 17, 1826).

Di-ω-iodo-*p*-xylene $C_6H_4(CH_2I)_2$. [c. 170°]. Obtained by boiling [4:1] $C_6H_4(CH_2OH)_2$ with conc. HIAq for a few minutes (Grimaux, *Z.* 1870, 395). Slender needles, sl. sol. ether, v. sol. boiling alcohol and chloroform. Turns yellow in air. Not very volatile with steam.

IODOPLUMBIC ACID H_2PbI_4, *v.* LEAD, IODIDE OF, *Combinations*, No. 3.

IONS. The elements or radicles into which a compound is primarily separated by electrolysis (*v.* PHYSICAL METHODS, section *Electrical methods*).

IPECUANIC ACID $C_{14}H_{18}O_7$. An acid existing, according to Willigk (*A.* 76, 342), along with emetine (*q. v.*) in the root of *Cephalis Ipecacuanha.* It is extracted by boiling alcohol, ppd. by basic lead acetate, and the pp. decomposed by H_2S. Reddish-brown, very bitter, amorphous mass, m. sol. ether, v. sol. alcohol and water. Colours ferric salts green, the colour being changed to violet by ammonia. Its dilute solution does not ppt. $Pb(OAc)_2$ but ppts. basic lead acetate. Its alkaline solution absorbs oxygen from the air. It thus somewhat resembles gallic acid. Podwyszotzky (*Ph.* [3] 10, 642) by extracting ipecacuanha with ether and light petroleum obtained an acid ('Erythrocephaleïn'), which formed a purple-red alkaline salt, and which crystallised from chloroform in coloured needles.

IPOMIC ACID $C_6H_{10}O_4$. [104°]. Produced by the action of nitric acid on jalapin (Mayer, *A.* 83, 143; Poleck a. Samelson, *C. C.* 1884, 813). Resembles sebacic acid.

IRIDIUM. Ir. At. w. 192·5. Mol. w. unknown. [2200°] (Van der Weyde); [1950°] (Violle, *C. R.* 89, 702); [2500°] (Pictet, *C. R.* 88, 1317). S.G. 22·42 at 17·5° (Deville a. Debray, *P. M.* [4] 50, 651). S.H. 0°–100° = ·0323, 0°–1400° = ·0401 (Violle, *C. R.* 89, 702). C.E. linear ·000007 (Fizeau, *C. R.* 68, 1125).

Occurrence.—As metal, alloyed with Pt, Os, Ru, Rh, and Pd. Specimens of platin-iridium, osm-iridium, &c., contain from 25 to 78 p.c. Ir (*v.* Deville a. Debray, *A. Ch.* [3] 56, 431; Berzelius, *P.* 13, 435, 527; 15, 208). In 1802 Tennant (*T.* 1804. 411) noticed a metallic residue when he dissolved Pt ore in *aqua regia*; this residue was examined by Descotils (*Gehlen's Journ. Chem.* 2, 273), and Fourcroy a. Vauquelin (*Gehlen's Journ. Chem.* 3, 362). In 1804 Tennant (*l.c.*) showed that the residue contained two new metals; to one he gave the name *Iridium* because of the varied colours of its oxides, and to the other the name *Osmium* because of the peculiar smell of its volatile oxide.

Formation.—1. By digesting Ir_2O_3 or $IrCl_3$ with formic acid.—2. By action of sunlight on an alcoholic solution of Ir sulphate.

Preparation.—When Pt ore is heated with *aqua regia* osm-iridium and platin-iridium remain as black insoluble scales. Ir is prepared from the residue by various methods: 1. W. von Schneider (*A. Suppl.* 5, 261) mixes the insoluble in *aqua regia* with NaCl, and heats to low redness in a stream of Cl; Os is thus removed. The residual mixed chlorides are triturated with the smallest possible quantity of water, and then washed on to a filter; the solution is treated with Cl, mixed with a little HClAq, and shaken up with excess of KCl; the pp. is washed with water, and then with saturated KClAq. The pp. is now nearly pure K_2MCl_6, M = Ir, Ru, and Pt. The pp. is dissolved in much boiling water, and H is passed in for several days (the flask being closed by a caoutchouc cork) until the supernatant olive-green liquid treated with potash becomes colourless and then blue or turbid. Pt and Ru are thus wholly ppd. as metals, and most of the Ir remains in solution as $IrCl_3$. H is removed by a stream of CO_2—otherwise explosions occur on opening the flask from the action of the ppd. Pt and Ru on the H and O in the flask—the cork is removed, and the liquid is again saturated with H; Ir is ppd. on the surface of the liquid in large lustrous laminæ.—2. Matthey (*Pr.* 28, 463) prepares Ir free from all metals except Pt as follows. Ordinary Ir, finely divided, is fused with 10 times its weight of Pb; the Pb is dissolved in HNO_3Aq, and the insoluble is digested for a long time with *aqua regia*; the insoluble is fused with $KHSO_4$ (to remove Rh), and then melted with 10 times its weight of KOH and 3 times its weight of KNO_3 in a gold crucible; the cold mass is treated with cold water, in which K iridate remains insoluble. The insoluble is well washed with water containing a little KOH and NaClO, and then with water; fairly conc. cold NaClOAq is added to the residual blue solid; after a time the water is distilled off; the residue is again fused with KNO_3 and KOH, and treatment with dilute NaClOAq and KOHAq is repeated. The blue solid is now dissolved in *aqua regia*, the liquid is evaporated to dryness, and the residue is redissolved and filtered; the dark-coloured liquid is slowly poured into conc. NaOHAq containing NaClO, and Cl is passed in, the liquid being kept in a distilling apparatus; the blue oxide of Ir thus obtained is collected, washed, dried, and reduced in a mixture of CO and CO_2 (made by gently warming oxalic acid with sulphuric acid). Metallic Ir is thus obtained, while any Fe present remains as oxide. The mass is heated to redness with $KHSO_4$, and repeatedly washed with ClAq to remove Au, and with HFAq to remove SiO_2; it is finally washed with water and dried. Pt may be removed by dissolving in *aqua regia*, saturating with NH_4Cl, dissolving the double NH_4-Ir and NH_4-Pt chlorides in hot water, reducing by SO_2 when $IrCl_3.3NH_4Cl$ is formed, and dissolves with olive-green colour, while $PtCl_4.2NH_4Cl$ remains insoluble; the reduction should be stopped before the whole of the $IrCl_4.2NH_4Cl$ is reduced (the presence of a little of this salt gives a deep-red colour to the mixed chlorides). The solution is oxidised by HNO_3, NH_4Cl is added, and the ppd. $IrCl_4.2NH_4Cl$ is washed with NH_4ClAq, and strongly heated, when Ir remains as a grey metallic powder (Claus, *J. pr.* 42, 251). Wöhler a. Mucklé (*A.* 104, 368) reduce the mixed Pt-NH_4 and Ir-NH_4 chlorides by digesting with slightly warm KCNAq till the undissolved is light yellow-brown, taking care to avoid excess; $IrCl_3.3NH_4Cl$ is formed and

dissolves, while $PtCl_4.2NH_4Cl$ remains unreduced and insoluble. For other methods of preparing Ir *v.* Deville a. Debray (*A. Ch.* [3] 56, 431); Claus (*C. C.* 1862. 129); Wöhler (*P.* 31, 161; 104, 368; 107, 357); Fremy (*A. Ch.* [3] 44, 385); Martius (*A.* 107, 360); Bunsen (*A.* 146, 274).

Properties. — As prepared by heating $IrCl_4.2NH_4Cl$, Ir forms a grey spongy mass; Ir as a grey powder is produced by heating $IrCl_4.2KCl$ with excess of Na_2CO_3, washing and reducing in H; by heating to whiteness and compressing, a compact lustrous mass is obtained. When fused in a very powerful O-H flame, Ir forms a white, lustrous mass resembling polished steel; brittle when cold, somewhat malleable at red heat (D. a. D.). Harder than iron. S.G. of porous Ir varies from 16 to 19. Ir which has been very strongly heated is insoluble in all acids; Ir black is sol. in *aqua regia.* Heated in Cl, Ir black forms $IrCl_3$.

The atomic wt. of Ir has been determined by heating $IrCl_4.2KCl$ in H (Berzelius, *P.* 13, 435, 527; 15, 208); by reducing $IrCl_4.2NH_4Cl$ in H and weighing the residual Ir, and by reducing the double Ir-K chloride in H and dissolving out the KCl (Seubert, *B.* 11, 1767). As no compound of Ir has been gasified, the valency of the atom of Ir in gaseous molecules is not determined. From the crystalline form of osm-iridium G. Rose (*P.* 77, 143) concluded that Os and Ir are isomorphous, and that both belong to the hexagonal system.

In its chemical reactions, Ir is closely related to Os and Pt, and less closely but very distinctly related to Ru, Rh, and Pd; all these elements are metallic, but the instability of their salts, the solubility of the hydrated oxides MO_2 in alkalis, and the formation of acids H_2MCl_6 and H_3MBr_6, show the non-metallic tendencies of the Pt metals (*v.* NOBLE METALS).

Ir is used alloyed with Pt for making instruments, &c., which remain unchanged in air, *e.g.* for making the normal metre preserved as the standard of reference. Stylographic pens are sometimes tipped with Ir. When Ir powder is heated to whiteness with $\frac{1}{2}$ its weight of P, the whole melts; on cooling, the mass may be readily worked; by strongly heating with lime, the P is entirely removed.

Reactions and Combinations.—1. Heated in *oxygen*, compact Ir is not oxidised; Ir black is oxidised to Ir_2O_3, which decomposes again at c. 1000° (Deville a. Debray, *C. R.* 1878. 441; *cf.* DISSOCIATION, vol. ii. p. 397).—2. Ir black is oxidised by fusion with *nitre, potash, potassium carbonate,* or *potassium-hydrogen-sulphate.*—3. Heated in *chlorine* $IrCl_3$ is formed; mixed with NaCl or KCl, and heated in Cl, soluble $IrCl_4.2Na(K)Cl$ is formed.—4. Heated in an *alcohol flame*, Ir becomes covered with a blackish layer which disappears on heating in air, leaving a portion of the Ir combined with C (*v.* IRIDIUM CARBIDE).—5. Ir probably combines with *phosphorus* when the elements are heated together; when the product is heated in air, Ir and a phosphate of Ir are formed.

Iridium, alloys of. Faraday a. Stodart (*A. Ch.* 21, 73); Deville a. Debray (*C. R.* 81, 839); Fizeau (*C. R.* 78, 1205); Morin (*C. R.* 78, 1502); Wöhler (*A.* 146, 375).

Osmium-iridium alloy. Occurs in South America, California, Australia, Ural Mountains, &c. Hexagonal prisms; lustrous, steel-grey. Slightly malleable; S.G. 19·3 to 21·1. Analyses show composition approximating to formulæ Ir_3Os, IrOs and $IrOs_3$, with Ir more or less replaced by Pt, Rh, and Ru; but it is probably non-homogeneous (D. a. D.). Heated in air, OsO_4 is given off; heated with KNO_3 and KOH K osmate and iridate are formed. Scarcely acted on by *aqua regia.* Alloys with Fe (F.).

Platinum-iridium alloy. Occurs native in octahedra. 1 pt. Ir heated in O-H flame with 10 pts. Pt gives a ductile alloy; Pt alloyed with 15–20 p.c. Ir is insoluble in *aqua regia.* For accounts of the Pt-Ir alloy used for making the normal standard metre *v.* D. a. D. and also M. Alloys of Ir with Pt and Rh, and with Pt, Rh, and Sn were prepared by D. a. D. Alloys of Ir with Cu, Au, Pb, Hg, Ru, and Sn have been prepared.

Iridium, ammonio-salts of, or Irid-ammonium salts. (*Ammoniacal iridium bases.*) $IrCl_2$ dissolves in $(NH_4)_2CO_3Aq$ and on neutralising with HClAq, the compound $IrCl_2.2NH_3$ is produced; treated with H_2SO_4Aq, this compound yields $IrSO_4.2NH_3$. $IrCl_2.2NH_3$ dissolves in boiling NH_3Aq, and the compound $IrCl_2.4NH_3$ forms on cooling; this compound gives a sulphate and nitrate, SO_4 and $2NO_3$ replacing Cl_2. From $IrCl_3.3NH_4Cl$ is obtained $IrCl_3.5NH_3$, and this again yields a basic hydroxide $Ir(OH)_3.5NH_3$, a carbonate $Ir_2(CO_3)_3.10NH_3$, and other salts. Finally by treating $IrCl_2.2NH_3$ with conc. HNO_3Aq the compound $IrCl_2(NO_3)_2.4NH_3$ is obtained; $AgNO_3Aq$ does not ppt. Cl from this salt; treated with HClAq the salt $IrCl_2.Cl_2.4NH_3$ is produced from which $AgNO_3Aq$ ppts. only half the Cl. The foregoing compounds may be formulated as double salts of $IrCl_2$, $IrCl_3$, $IrCl_4$, &c., with NH_3; but many of their reactions are better explained if we regard them as salts of condensed ammoniums containing Ir. The following classification is that usually adopted:—

1. IRIDOSAMMONIUM COMPOUNDS: $N_2H_6.Ir.X^I_2$ and $N_4H_{12}Ir.X^I_2$; or $NH_2(NH_4)Ir.X_2$, and $N_2H_4(NH_4)_2Ir.X_2$, &c., obtained from $IrCl_2$.

Iridosammonium chloride $N_2H_6Ir.Cl_2$. (simplest formula $IrCl_2.2NH_3$ = *di-ammonio-iridium dichloride*). A yellow, curdy pp., obtained by dissolving $IrCl_2$ in excess of $(NH_4)_2CO_3Aq$ and neutralising the greenish-yellow liquid with HClAq. Insol. hot and cold water. Heated gives NH_4Cl, HCl and Ir (Skoblikoff, *A.* 84, 275). Heated with H_2SO_4Aq, easily soluble orange-coloured *iridosammonium sulphate*, $N_2H_6Ir.SO_4$, is produced.

Iridoso-diammonium chloride $N_4H_{12}Ir.Cl_2$ or $N_2H_4(NH_4)_2Ir.Cl_2$ (simplest formula $IrCl_2.4NH_3$ = *tetrammonio-iridium dichloride*). $IrCl_2.2NH_3$ is boiled with NH_3Aq until almost all dissolved, the solution is filtered and allowed to cool. Nearly white pp., insol. in cold water; heated, or placed in boiling water, goes to $IrCl_2.2NH_3$ (Skoblikoff, *l.c.*). The *sulphate*, $N_4H_{12}Ir.SO_4$, is obtained by the action of H_2SO_4Aq on the chloride; and the nitrate, $N_4H_{12}Ir.(NO_3)_2$, by addition of $Ba2NO_3Aq$ to a solution of the sulphate in warm water.

2. IRIDO-AMMONIUM COMPOUNDS $N_{10}H_{30}Ir_2.X^I_6$ or $N_4H_6(NH_4)_6Ir_2.X^I_6$; obtained from $IrCl_3$.

Irido-pentammonium chloride $N_{10}H_{30}Ir_2.Cl_6$ (simplest formula $Ir_2Cl_6.10NH_3$ = *decammonio-*

iridium trichloride). $IrCl_3.3NH_4Cl$ is dissolved in water, an equal volume of conc. NH_3Aq is added, a flask is quite filled with the liquid, and allowed to stand for several weeks in a warm place until the olive-green colour of the liquid has changed to deep rose-red; after gentle warming, to remove excess of NH_3, the liquid is saturated with HClAq and evaporated to dryness; the greenish-yellow salt which separates during evaporation is washed with cold water, and then crystallised from water acidified with HCl. Flesh-coloured, crystalline, powder; v. sl. sol. water (Claus, *J. pr.* 63, 99; *A.* 98, 317).

Irido-pentammonium hydroxide $N_{10}H_{30}Ir_2.(OH)_6$. Known only in solution which is obtained by digesting the chloride with moist Ag_2O. Solution is alkaline; neutralised by acids gives *carbonate*, *nitrate*, and *sulphate*.

3. Iridi-ammonium compounds $N_4H_{12}IrCl_2.X^I_2$ or $N_2H_4(NH_4)_2Cl_2.Ir.X^I_2$; obtained from series 1 by oxidation.

Iridi-diammonium chloride ? better *chloriridi-diammonium chloride* $N_4H_{12}IrCl_2.Cl_2$ (simplest formula $IrCl_4.4NH_3$ = *tetrammonio-iridium tetrachloride*). Obtained by slowly warming iridosammonium chloride ($N_2H_6Ir.Cl_2$) with conc. HNO_3Aq, dissolving the salt which separates in hot water, adding excess of HClAq, and crystallising from hot water. Violet octahedra; $AgNO_3Aq$ ppts. only ½ the Cl from this salt. The salt which separates after treating $N_2H_6Ir.Cl_2$ with HNO_3 is the *nitrate*, $N_4H_{12}IrCl_2.(NO_3)_2$; $AgNO_3Aq$ does not ppt. Cl from this salt. When this salt is evaporated with dilute H_2SO_4Aq, the *sulphate*, $N_4H_{12}IrCl_2.SO_4$, is obtained (Skoblikoff, *l.c.*). Palmer (*B.* 22, 15) describes $N_5H_{15}Ir.Cl.Cl_2$, $N_5H_{15}IrCl.SO_4.2H_2O$, $N_5H_{15}IrCl.(NO_3)_2$, $N_4H_{12}IrCl_2.Cl$, and $(N_4H_{12}IrCl_2)_2SO_4.2H_2O$.

References.—For other memoirs besides those referred to, *v.* Weltzien, *A.* 97, 19; Gibbs a. Genth, *J.* 1858. 214; Birnbaum, *B.* 12, 1544.

Iridium, boride of. When Ir is heated with B to a very high temperature a fusible mass is obtained; no definite boride has been isolated (Wöhler a. Deville, *A. Ch.* [3] 52, 71).

Iridium, bromides of (Birnbaum, *A.* 133, 161). Only one bromide has been isolated, $IrBr_3.4H_2O$; there are indications of the existence in solution of a tetrabromide, $IrBr_4$. Ir does not combine directly with Br; nor is it soluble in a mixture of HNO_3 and HBrAq.

Iridium tribromide $IrBr_3.4H_2O$ (*Iridobromide. Iridium sesquibromide*). When the blue hydrate IrO_4H_4 (obtained by heating a solution of $IrCl_4$ with alkali) is dissolved in HBrAq and evaporated *in vacuo*, olive-green six-sided crystals separate, and then steel-blue needles. The olive-green crystals are $IrBr_3.4H_2O$, and the steel-blue crystals are $IrBr_3.3HBr.3H_2O$. The bromide loses $3H_2O$ at 100°-120°; it is sol. water, insol. alcohol or ether; aqueous solution is green, but becomes blue probably with formation of $IrBr_4$.

Irido-bromhydric acid $IrBr_3.3HBr.3H_2O(=H_3IrBr_6.3H_2O)$. Crystallises in steel-blue crystals which melt at 100°, giving off $3H_2O$; deliquescent; easily sol. water, alcohol, ether; oxidised by HNO_3, probably to $IrBr_4$.

Ammonium-iridium tribromide, or *Ammonium iridobromide* or *bromiridite* $2(IrBr_3.3NH_4Br).3H_2O$, is obtained by reducing $IrBr_4.2NH_4Br$ (formed by adding $IrCl_4.2NH_4Cl$ to hot NaBrAq and cooling) by SO_2 and neutralising by $(NH_4)_2CO_3$. The following other double salts are described by Birnbaum (*A.* 133, 161): $IrBr_3.3HgBr$, $IrBr_3.3AgBr$, $IrBr_3.3KBr.3H_2O$, $IrBr_3.3NaBr.12H_2O$.

Iridium tetrabromide (*Iridibromide*). When IrO_4H_4 is dissolved in HBrAq, or when $IrBr_4.2KBr$ is decomposed by H_2SiF_6Aq, a solution is obtained which loses Br on evaporation, and on addition of HNO_3Aq, after evaporation, gives a deliquescent, blue, crystalline mass, easily sol. in water and alcohol. The blue solution probably contains $IrBr_4.2HBr$ (Birnbaum). This solution does not yield double compounds with other metallic bromides.

Ammonium-iridium tetrabromide, or *Ammonium iridibromide* or *bromiridate* $IrBr_4.2NH_4Br$ ($(NH_4)_2IrBr_6$). Dark-blue octahedra; by adding $IrCl_4.2NH_4Cl$ to hot NaBrAq, and cooling.

Potassium bromiridate $IrBr_4.2KBr(K_2IrBr_6)$. When solution of $IrCl_4$, or $IrCl_4.2NaCl$, or $IrCl_4.2NH_4Cl$ is warmed with conc. KBrAq, a greenish-blue liquid is obtained from which very dark-blue crystals of K_2IrBr_6 separate; the salt is recrystallised from hot water.

Sodium bromiridate also exists.

Iridium, carbide of (? IrC_4). When a coherent mass of Ir is held in the flame of a spirit-lamp, black masses appear on the surface; these burn when heated in air and leave 80·2 p.c. Ir (Berzelius, *P.* 15, 213).

Iridium, chlorides of. Three chlorides are known: $IrCl_2$, $IrCl_3$, and $IrCl_4$; as none has been gasified the formulæ are not necessarily molecular (*v. Iridium, haloid compounds of*). When Ir black is heated in Cl, $IrCl_3$ is formed; when Cl is passed over a heated mixture of Ir black and KCl, $IrCl_4.2KCl$ is produced.

Iridium dichloride (*Iridosochloride*). $IrCl_2$. A blackish-green, insoluble, solid. By passing Cl over Ir black heated to low redness (Berzelius, *P.* 13, 470). The change is not complete, as the temperatures of formation and decomposition are nearly the same (Claus, *A.* 59, 249). By heating Ir sulphite in Cl (Fellenberg, *P.* 50, 66). By carefully heating $IrCl_4$ (Skoblikoff, *A.* 84, 275). Seubert (*B.* 11, 1761) describes an acid $IrCl_2.H_2SO_3.4NH_4Cl$ from which salts of NH_4 and Na are obtained.

Iridium trichloride (*Iridochloride. Iridium sesquichloride*). $IrCl_3$. Olive-green solid, insol. in acids or alkalis (Claus, *A.* 107, 129). Obtained by heating Ir black in Cl, also by strongly heating an alkali double salt of $IrCl_3$ with conc. H_2SO_4 and pouring into cold water (Berzelius, *P.* 13, 470). A soluble hydrate $IrCl_3.4H_2O$ is obtained by dissolving IrO_4H_4 in HClAq, reducing by H_2S, and evaporating.

Double salts. *Ammonium-iridium trichloride* (*Ammonium chloriridite*) $2(IrCl_3.3NH_4Cl.)3H_2O$; formed by slowly evaporating mixed solutions of $IrCl_3.3NaCl$ and NH_4Cl, or by reducing $IrCl_4.2NH_4ClAq$ by H_2S, adding conc. NH_4ClAq, filtering if necessary, and slowly evaporating (Claus, *J. pr.* 42, 351; Seubert, *B.* 11, 1761); olive-green, rhombic plates.

Potassium chloriridite $IrCl_3.3KCl.3H_2O$. By reducing $IrCl_4.2KClAq$ by H_2S, and evaporating with addition of KCl. Olive-green efflorescent prisms. The following double salts are also known:—$2IrCl_3.(12NH_3.Co_2)Cl_6$; $IrCl_3.3HgCl$; $IrCl_3.3AgCl$; $IrCl_3.3NaCl.12H_2O$ (Claus, *l.c.*; Karmrodt a. Uhrlaub, *A.* 81, 120).

IRIDIUM TETRACHLORIDE (*Iridichloride*). $IrCl_4$. The solution obtained by decomposing $IrCl_4.2NH_4Cl$ suspended in water by Cl contains $IrCl_4$ (Vauquelin, *A.Ch.* 89, 150, 225); a solution of $IrCl_4$ is also obtained by dissolving IrO_4H_4 in HClAq, digesting $IrCl_3Aq$ with *aqua regia*, or decomposing $IrCl_4.2KCl$ with H_2SiF_6Aq (Berzelius, *P.* 13, 470). By evaporating these solutions to dryness at temperatures not above 40°, $IrCl_4$ is obtained as a black mass, translucent with dark-red colour at the edges; very deliquescent; decomposed by heat to $IrCl_3$ and Cl, and then to Ir; combines with alkali chlorides to form double salts. *Ammonium-iridium tetrachloride* (*Ammonium chloriridate*) $IrCl_4.2NH_4Cl$; obtained by mixing conc. solutions of NH_4Cl and $IrCl_4$ or $IrCl_4.2NaCl$. Crystallises from hot water in dark red-brown octahedra, isomorphous with $PtCl_4$. $2NH_4Cl$. S. 5 in cold water. Reduced by SO_2 to the more soluble $IrCl_3.3NH_4Cl$.

Potassium chloriridate $IrCl_4.2KCl$. Formed by mixing conc. solutions of its constituent salts; also by dissolving IrO_4H_4 in HClAq (solution probably contains H_2IrCl_6) and adding KCl; also by passing Cl at a gentle heat over an intimate mixture of Ir black and KCl, dissolving in hot water, filtering from Ir, evaporating to dryness with addition of *aqua regia*, dissolving out KCl by small quantities of cold water, dissolving in hot water, adding a little *aqua regia*, and evaporating to the crystallising point. Black octahedra; very sl. sol. cold water, much more sol. hot water, insol. alcohol. Heated, goes to $IrCl_3.3KCl$, and at higher temperature to Ir and KCl.

The following *chloriridates* have also been obtained:—$IrCl_4.2(NH_3.CH_3Cl)$ (Vincent, *C. R.* 100, 112); $IrCl_4.2NaCl.6H_2O$ (Vauquelin, *l.c.*; Berzelius, *l.c.*).

Iridium, cyanides of, also **Iridicyanides**, *v.* vol. ii. p. 332.

Iridium, haloid compounds of. The only haloid compound certainly formed by direct union of the elements is $IrCl_3$. When an intimate mixture of Ir black and KCl is heated in Cl, or of Ir black and KI is heated in I, the double salt K_2IrCl_6 or K_2IrI_6 is obtained. The following formulæ present the composition of the haloid compounds and the double salts which they form with alkali haloid compounds:—

			Double salts.		
IrX_2	IrX_3	IrX_4	$IrX_2.2MX$	$IrX_3.3MX$	$IrX_4.2MX$
—	Br_3	? Br_4 in solution	—	Br_3	Br_4
Cl_2	Cl_3	Cl_4	Cl_2	Cl_3	Cl_4
? I_2	I_3	I_4	I_2	I_3	I_4

None of the Ir haloid compounds has been gasified. The formulæ are given from the analogies between these compounds and those of other Pt metals. The only binary compound of a Pt metal which has been gasified is OsO_4. The acid H_3IrBr_6 has been obtained. The double alkali-iridium haloid salts are probably better regarded as salts of the acids H_2IrX_4, H_3IrX_6 and H_2IrX_6. The chloriridates (salts of H_2IrCl_6) are readily reduced to chloriridites (salts of H_3IrCl_6).

Iridium, hydroxides of, *v. Iridium, oxides and hydrated oxides of.*

Iridium, iodides of (Oppler, *Ueber Iodverbindungen des Iridiums* [Göttingen, 1857]; *J.* 1857. 263). Two iodides, IrI_3 and IrI_4, have been isolated. There are indications of the existence of IrI_2. Ir and I do not directly combine.

IRIDIUM DI-IODIDE (*Iridoso-iodide*). The brown solid obtained by leading SO_2 into IrI_4 suspended in water is perhaps IrI_2. When a solution of $IrCl_4.2NH_4Cl$ in boiling KIAq is allowed to cool, a black crystalline powder separates; this is *ammonium iridium di-iodide*, $IrI_2.2NH_4I$.

IRIDIUM TRI-IODIDE (*Irido-iodide. Iridium sesqui-iodide*) IrI_3. A black crystalline pp.; by adding NH_4Cl to $IrI_4.2KIAq$. Very slightly sol. cold water, more sol. hot water.

Double salts.—*Ammonium-iridium tri-iodide* (*Ammonium iodiridite*) $2(IrI_3.3NH_4I).H_2O$. Crystalline needles; by dissolving $IrCl_4.2NH_4Cl$ in boiling KIAq, cooling, filtering from $IrI_2.2NH_4I$, concentrating, and recrystallising from hot water.

Potassium iodiridite, $IrI_3.3KI$. Green lustrous crystalline powder; by reducing $IrCl_4$ by H_2S with addition of KIAq. *Silver iodiridite*, $AgI.3KI$, has also been obtained.

IRIDIUM TETRA-IODIDE (*Iridi-iodide*) $IrCl_4$. A black powder; by boiling $IrCl_4Aq$ with KI in presence of a little HCl.

Double salts.—*Ammonium-iridium tetra-iodide* (*Ammonium iodiridate*) $IrI_4.2NH_4I$. Separates after some weeks from solution of $IrCl_4.2NH_4Cl$ in cold conc. KIAq; dark-brown lustrous crystals, easily decomposed by heat; aqueous solution gently heated deposits IrI_4 and $IrI_2.2NH_4I$. *Potassium iodiridate*, K_2IrI_6. Separates, after IrI_4, from solution of $IrCl_4$ in KIAq. Also formed by dissolving IrI_4 in KIAq, and allowing to crystallise; also, in small quantity, by action of I vapour on an intimate mixture of Ir black and KI at 60°–70°. *Sodium iodiridate*, $IrI_4.2NaI$, has also been obtained.

Iridium, oxides and hydrated oxides of. The only oxides of Ir which have been certainly isolated are Ir_2O_3 and IrO_2. The former forms a hydrate with $3H_2O$, and another hydrate probably with $5H_2O$. IrO_2 forms the hydrate $IrO_2.2H_2O$. Hydrated Ir_2O_3 dissolves in alkalis probably with formation of *iridites*; $IrO_2.2H_2O$ dissolves in some acids, but no salts have thus been prepared. Alkaline *iridates* appear to exist. There are indications of the existence of an oxide with less O than Ir_2O_3, probably IrO. When Ir black is heated in O, Ir_2O_3 is formed; the oxide decomposes again at c. 1000°. IrO_2 is the most

stable oxide; $Ir_2O_3.xH_2O$ rapidly absorbs O from the air, and passes into $IrO_2.xH_2O$.

IRIDOUS OXIDE (*Iridium monoxide*). IrO. When $IrCl_2$ is boiled with KOHAq a black powder separates; this is probably IrO (Berzelius, *P.* 13, 479). Claus (*A.* 59, 249) thinks that this oxide is obtained by heating one of the double salts of $IrSO_3$ with K_2CO_3 in a stream of CO_2. On adding KClAq to $IrCl_3.3NaClAq$, and filtering, a solution of $IrCl_2$ is obtained; when K_2CO_3Aq is added to this liquid (or to $IrCl_3.3KClAq$) a greyish-green pp. is formed, which is probably a hydrate of IrO; the pp. is sol. in excess of K_2CO_3Aq (Berzelius, *l.c.*). A few salts derived from IrO are known, *e.g.* $IrSO_3.4H_2O$; they are not, however, formed directly from the oxide, but by reducing $IrO_2.2H_2O$ or chloriridates by SO_2.

IRIDIC OXIDE AND HYDRATE (*Iridium dioxide*) IrO_2 and $IrO_2.2H_2O$. By adding excess of alkali to $IrCl_4Aq$ and heating, a heavy indigo-blue pp. $IrO_2.2H_2O$ is produced. The same compound is obtained by using $IrCl_3Aq$ in place of $IrCl_4$, and allowing the pp. to stand in the air, when it absorbs O. The pp. is soluble in HClAq with formation of $IrCl_4$; it is insoluble in dilute H_2SO_4Aq or HNO_3Aq. When the hydrate is heated in a stream of CO_2, IrO_2 remains as a black powder quite insoluble in acids (Claus, *A.* 59, 249). No salts corresponding with IrO_2 have been prepared. By adding CaOAq to a solution of IrO_4H_4 in HClAq a blue pp. is obtained, which is a compound of IrO_2 with CaO. When Ir black is fused for some time with KNO_3, and the blackish-green mass is treated with water, part dissolves, forming a deep indigo-blue solution, and part remains as a black crystalline powder. The quantity of K in this powder is variable, but the ratio of Ir:O is always 1:3 (Claus, *A.* 59, 249). The powder is probably an iridate of K, $IrO_2.xK_2O$.

IRIDO-IRIDIC OXIDE AND HYDRATES (*Iridium sesquioxide*) Ir_2O_3 and $Ir_2O_3.xH_2O$. The oxide Ir_2O_3 is obtained by heating $IrCl_4.2KCl$ with 2 parts K_2CO_3, or Na_2CO_3, in a stream of CO_2, washing the fused mass with boiling water, and then with water containing NH_4Cl, heating to remove NH_4Cl, treating with acid to remove alkali, and again washing with water (Claus, *A.* 59, 249). A hard blue-black powder; decomposed by heating to c. 1000° into Ir and O (Deville a. Debray, *C. R.* 1878. 441; *cf.* DISSOCIATION, vol. ii. p. 397). Reduced to Ir by H at the ordinary temperature. The *hydrate* $Ir_2O_3.3H_2O(=IrO_3H_3)$ is obtained by adding to $IrCl_4.2NaClAq$ so much KOHAq that all remains dissolved, and then heating or ppg. by alcohol. Black pp. insol. in acids except conc. HClAq, which dissolves it very slightly. By adding a little KOHAq to solution of an alkaline chloriridate, and quite filling a flask with the liquid, a yellow-green pp. forms, which is probably $Ir_2O_3.5H_2O$; it oxidises very easily to the blue $IrO_2.2H_2O$; easily soluble in the slightest excess of alkali. De Boisbaudran (*C. R.* 96, 1236, 1406, 1551) describes a violet-coloured pp., which is probably $Ir_2O_3.xH_2O$, obtained by adding alkali to $Ir_2(SO_4)_3.3K_2SO_4Aq$ (this salt is formed by heating Ir compounds with $KHSO_4$, and treating the product with K_2SO_4Aq). A few salts, and some double and basic salts, corresponding with Ir_2O_3 are known; they are produced indirectly. The sulphites and double sulphites are produced by reducing IrO_22H_2O or chloriridates by SO_2. By adding CaOAq to $IrCl_3Aq$ a yellow pp. of $Ir_2O_3.3CaO$ is produced (Claus, *A.* 59, 249). Compounds of Ir_2O_3 with NO_2 and with nitrites are described by Gibbs (*B.* 4, 280).

Iridium, oxychloride of. An oxychloride of Ir is said by Berzelius (*P.* 13, 484) to be formed as a yellowish-brown pp. by adding a small quantity of $HgNO_3Aq$ to $IrCl_4.2KClAq$; $HgCl_2$ goes into solution; addition of more $HgNO_3$ causes ppn. of HgCl.

Iridium, phosphide of. When Ir is very strongly heated with ½ its weight of P, the whole melts. By heating the product with CaO the P is removed. Ir and P probably combine when heated together, but no phosphide of Ir has been isolated.

Iridium, salts of. Very few salts of Ir are known other than the haloid compounds. Iridous sulphite, $IrSO_3.4H_2O$, and some double sulphites, irido-iridic sulphite, $Ir_2(SO_3)_3.6H_2O$, and several double and basic sulphites, and a few other salts (chiefly double and basic), corresponding with Ir_2O_3, have been isolated. None of these salts is obtained from the corresponding oxide; the sulphites, which are the best-known salts, are formed by reducing $IrO_2.2H_2O$, or chloriridates, by SO_2Aq.

Iridium, sulphides of. Three sulphides of Ir are known, IrS, Ir_2S_3, and IrS_2. Ir combines with S when heated with it.

IRIDOUS SULPHIDE IrS. (*Iridium monosulphide.*) A blue-black solid; by heating Ir_2S_3 or IrS_2 (Berzelius, *P.* 13, 487; Böttger, *J. pr.* 3, 227). The pp. obtained by passing H_2S into a solution of an iridous compound is probably IrS. Does not decompose by heating in absence of air; roasted in air gives SO_2 and a basic sulphate. The ppd. sulphide dissolves in KHSAq.

IRIDIC SULPHIDE IrS_2. (*Iridium disulphide.*) A black powder; obtained by strongly heating Ir black with S and Na_2CO_3, and washing with water (Fellenberg, *P.* 50, 66). Heated in air gives SO_2 and Ir. Berzelius (*l.c.*) obtained a dark brownish-yellow pp. by passing H_2S into $IrCl_4Aq$; heated, this gave IrS.

IRIDO-IRIDIC SULPHIDE Ir_2S_3. (*Iridium sesquisulphide.*) A brown-black pp. by passing H_2S into solution of an irido-iridic compound. Heated gives SO_2 and S, and leaves IrS (Berzelius, *l.c.*).

IRIDOLINE $C_{10}H_9N$. (252°–257°). S.G. $\frac{15}{}$ 1·072. A base occurring in coal-tar oil (G. Williams, *Tr. E.* 21, 377; *C. J.* 16, 375).

IRIDOSMIUM *v.* IRIDIUM, *Alloys of*, p. 47.

IRIS CAMPHOR $C_8H_{16}O_2$. Occurs in the root of *Iris florentina* (Dumas, *A.* 15, 158). Pearly plates; volatile with steam. Insol. water. Flückiger (*Ar. Ph.* [3] 8, 481) by distilling iris root with steam obtained crystals of myristic acid saturated with a fragrant oil.

IRISH PEARL MOSS *v.* CARAGHEEN MOSS.

IRISIN $6C_6H_{10}O_5$ aq. $[\alpha]_D = -51°$. A carbohydrate extracted from the rhizomes of the water lily (*Iris pseud-acorus*) with water and subsequently ppd. with lead acetate. Probably identical with graminin (Wallach, *A.* 234, 364; *B.* 21, 396).

Properties. — More strongly lævorotatory than inulin.—1. Does not reduce Fehling's solu-

tion. Is very easily converted into sugar (chiefly levulose) by weak acids. Gives no colouration with iodine. V. sol. strong HI solution from which solution NaOH separates iodoform. Also sol. HCl, and NaOH. Irisin is nearly 4 times as soluble as inulin in water at 22°. Under the microscope the globules of irisin resemble those of inulin, but do not exhibit double refraction.

IRON. Fe. At. w. 55·9. Mol. weight unknown. [1550°] (Pouillet); [1587°] (Daniell, *Tr.* 1830); [1600°] (Pictet, *P. M.* 1879. 446). S.G. determinations vary from 6·95 (Roberts a. Wrightson, *A. Ch.* [5] 30, 274) to c. 8·2. Almost pure Fe has S.G. c. 7·85 at 16° according to Caron (*C. R.* 70, 1263); 8·139 according to Chandler-Roberts (*C. N.* 31, 137). S.H. ·111641 at 0°; ·112359 at 50°, ·113795 at 100° (Byström, *Oefvers. k. Vetensk. Fördhandl.* [Stockholm, 1860] 17, 307; *v.* also Weinhold, *P.* 149, 214). C.E. ·00001233 at 13° to 100° (Kopp, *A.* 81, 1; *v.* also Fizeau, *A. Ch.* [4] 2, 143; *C. R.* 68, 1125). T.C. (Ag = 100) 11·9 (Wiedemann a. Franz, *P.* 89, 497). E.C. (Hg at 0° = 1) 9·68 at 0°, 6·19 at 100° (Lorenz, *W.* 13, 422, 582). Crystallises in regular system (Fuchs, *A.* 84, 257). Emission-spectrum is very complex (Angström, *P.* 94, 141; Cornu, *Spectre Normal* [Paris, 1881]; Liveing a. Dewar, *Pr.* 29, 402; 32, 402). Some of the thermal data for Fe are presented in the following table (*Th.* 3, 293):—

$$X\ [Fe,X^2,Aq]$$
$$Cl = 99{,}950$$
$$Br = 78{,}070$$
$$I = 47{,}650$$

$[Fe,Cl^3,Aq] = 127{,}720$; $[Fe^2,O^3,3H^2O] = 191{,}150$; $[Fe^2O^6H^6,3H^2SO^4Aq] = 33{,}840$; $[Fe,H^2SO^4Aq] = 24{,}840$.

For further details regarding physical properties *v.* Rammelsberg's *Hand. der Kryst.-physikal. Chemie*, 1, 193. For the physical properties of different kinds of pig-iron, wrought-iron, and steel, *v.* DICTIONARY OF APPLIED CHEMISTRY.

Occurrence.—The metal itself is found in small quantities in rocks of volcanic origin and in lavas; it also occurs in meteorites. Compounds of iron are very widely distributed, and occur in immense quantities. The spectroscope shows the existence of iron (or iron compounds) in the sun and other stars. The chief ores of iron are *hæmatite*, Fe_2O_3; *brown iron ore*, $Fe_2O_3.H_2O$; *yellow ochre*, $Fe_2O_3.2H_2O$; *magnetic iron ore*, Fe_3O_4; *spathic ore*, $FeCO_3$; *pyrites*, FeS_2 (the formulæ express approximately the compositions of the ores).

Preparation.—Commercial iron, whether pig-iron, malleable iron, or steel, always contains more or less C and Si, and generally small quantities of P and S; sometimes also traces of Mn, Ti, Ni, Co, Cu, Sb, and As. 1. Wöhler (*A.* 94, 125; 95, 192) prepares Fe_2O_3 by heating $FeSO_4$ crystals with 2-3 parts NaCl in a crucible and washing with water, and reduces the Fe_2O_3 by heating in H (*cf.* G. de Claubry, *C. C.* 1859. 214; Luca, *C. R.* 1851. 332; 1852. 202). Moissan (*C. R.* 89, 176) says the reduction must be carried out at c. 700°.—2. By reducing $FeCl_2$ in a stream of H (Peligot, *C. R.* 19, 670); or in neutral solution at b.-point by Zn (Capitaine, *C. R.* 9, 757); or by Zn vapour at a high temperature (Poumarède, *C. R.* 29, 518).—3. Troost melts pig-iron in a lime-crucible by the O-H flame (*Bl.* [2] 9, 250).—4. A mixture of dry Na_2SO_4 and $FeSO_4$ is heated in a Pt crucible so long as SO_2 comes off, the residue is washed with cold water, and the crystalline Fe_2O_3 is reduced in H in a Pt crucible, and the Fe is melted in the O-H flame (Matthiessen a. Prus-Szczepanowski, *C. N.* 20, 501).—5. By electrolysing $FeSO_4Aq$ saturated with NH_4Cl; Fe appears at the negative pole (a large iron plate); it contains H and other gases, which may be removed by heating (Varrentrap, *D. P. J.* 187, 152; Lenz, *J. pr.* 108, 438).

Properties.—A lustrous, greyish-white metal. Crystallises in regular cubes or octahedra. Very tenacious; a wire 2 mm. diameter breaks with a weight of 249660 kilos. Mechanical treatment, hammering, or torsion, changes many of the physical properties. The physical properties which have been determined are for the most part those of iron containing small quantities of foreign substances. Iron is magnetic (*cf.* Faraday, *P.* 70, 24; Gore, *P. M.* [4] 40, 170). Pure, or almost pure, Fe is softer and more malleable, but less tenacious, than ordinary malleable iron. The iron obtained by reducing Fe_2O_3 in H at temperatures below c. 600° is pyrophoric; the powder obtained at c. 700° is non-pyrophoric (Moissan, *C. R.* 89, 176). By passing a weak electric current through $FeSO_4Aq$ mixed with $MgSO_4$, Lenz (*C. C.* 1870. 188) obtained a greyish, non-crystalline, very brittle mass, easily pulverised by the finger; this iron contained c. 200 times its volume of gases, chiefly H (*v. Iron, hydrides of*), mixed with CO, CO_2, N, and H_2O vapour; by heating *in vacuo* the gases were removed, and the iron then resembled Pt in appearance. Iron is unchanged in dry O, but in moist O or in ordinary air it is slowly oxidised to $Fe_2O_3.xH_2O$; heated in air or O a mixture of Fe_2O_3 and Fe_3O_4 is produced. Iron combines directly with the halogens, also with S, C, B, Si, P, As; it forms alloys with many metals. Iron dissolves in the common mineral acids with formation of salts. Finely divided Fe decomposes water at 100°.

The atomic weight of Fe has been determined (1) by analysing and determining V.D. of $FeCl_3$ and $FeCl_2$; (2) by determining S.H. of Fe; (3) by reducing Fe_2O_3 in H (Berzelius, *P.* 8, 185; Svanberg a. Norlin, *A.* 50, 432; Erdmann a. Marchand, *J. pr.* 33, 5; Rivot, *A. Ch.* [3] 30, 192); (4) by transforming Fe into Fe_2O_3 (B., *A.* 50, 432; S. a. N., *l.c.*; Maumené, *A. Ch.* [3] 30, 380); (5) by determining the Cl in $FeCl_2$ and in $FeCl_3$ (Dumas, *A. Ch.* [3] 55, 157). The atom of Fe is trivalent in the gaseous molecule $FeCl_3$, and divalent in the gaseous molecule $FeCl_2$ (*v. Iron, chlorides of*).

Iron is distinctly a metallic element; it replaces the H of most acids, forming two series of salts, the simplest formulæ for which are FeX_2 and FeX_3 respectively, X = Cl, NO_3, $\frac{SO_4}{2}$, $\frac{PO_4}{3}$ &c. The ferrous salts, FeX_2, are easily oxidised to ferric salts, FeX_3; very many salts, both normal and basic, of both series have been isolated; numerous double salts are also known. Fe_2O_3 forms compounds with several oxides more basic than itself, *e.g.* with K_2O, BaO, CaO, MgO; these compounds may be

regarded as *ferrites* derived from the hydroxide $Fe_2O_4H_2(=Fe_2O_3.H_2O)$. There are also some salts known as *ferrates*, *e.g.* K_2FeO_4 and $BaFeO_4$, which may be looked on as derived from the hypothetical *ferric acid* H_2FeO_4, but neither this acid nor its anhydride, FeO_3, has been isolated (*v.* FERRATES and FERRITES, vol. ii. pp. 546–7). Fe_2S_3, like Fe_2O_3, forms some double compounds with more basic sulphides; these double compounds may be regarded as *thioferrites* (*v. Iron, sulphides of*). Fe is closely related to Co and Ni; these three metals show some marked analogies with the Pt metals; Fe is also related to Cr and Mn, and it shows some resemblance to Al and the other earth-metals (*v.* IRON GROUP OF ELEMENTS, also NOBLE METALS; and *cf.* CHROMIUM GROUP OF ELEMENTS, and EARTHS, METALS OF THE).

Reactions and Combinations.—1. Heated in *air* or *oxygen* Fe is oxidised to Fe_2O_3 and Fe_3O_4. 2. Unchanged in *dry air* at ordinary temperature, but rusts in moist air to $Fe_2O_3.xH_2O$.—3. Finely-divided Fe decomposes *water* at 100° (*v.* Ramann, *B.* 14, 1433), and rapidly decomposes steam. Compact Fe decomposes steam at red-heat; Fe_3O_4 is produced. Iron slowly rusts in contact with water and ordinary air; the formation of $Fe_2O_3.xH_2O$ proceeds slowly at first, and then more rapidly, probably because the Fe and Fe_2O_3 exert an electrolytic action on the water; presence of ammoniacal salts increases the rate of rusting; alkalis and alkaline carbonates hinder the rusting. According to Calvert (*C. N.* 23, 98) Fe does not rust in water if CO_2 is absent. For an account of the retarding or hastening action of various salts on the rusting of Fe *v.* Wagner, *D. P. J.* 218, 70. Various processes have been used for preventing iron-rusting; covering the iron with Zn is frequently done; Barff a. Bower heat the iron to c. 650° in water-vapour, whereby a hard protecting film of Fe_3O_4 is formed on the surface of the iron.—4. Fe decomposes solution of *hydrogen peroxide*, forming $Fe_2O_6H_6$; the Fe becomes covered with bubbles of O (Weltzien, *A.* 138, 129).—5. Iron dissolves in *dilute sulphuric* or *hydrochloric acid* with evolution of H. Cold *conc. sulphuric acid* is almost without action on Fe; when heated, SO_2 is evolved, and $Fe_2(SO_4)_3$ formed. Dilute *nitric acid* dissolves Fe, forming $Fe(NO_3)_2$ and NH_4NO_3 with evolution of N oxides. *Conc. nitric acid* is almost without action on Fe; *v. infra, Passivity of iron.*—6. Heated repeatedly with *caustic soda* solution Fe forms crystals of $Fe_2O_3.H_2O$ (Brunck a. Graebe, *B.* 13, 725).—7. When Fe is heated to redness in a stream of *ammonia* a nitride of Fe is formed, Fe_4N_2 according to Stahlschmidt (*P.* 125, 37).—8. Fe heated in a closed tube with *solution of sulphur dioxide* to 200° forms solution of $FeSO_3$ and FeS_2O_3, and crystals of FeS_2 (Geitner, *A.* 129, 350).—9. Fe is oxidised to Fe_2O_3, or K_2FeO_4 (*v.* vol. ii. p. 547) by fusion with *potassium nitrate.*—10. Fe combines with the *halogens*, with *arsenic*, *boron*, *carbon*, *hydrogen*, *nitrogen*, *phosphorus*, and *sulphur* (*v. Iron, chlorides of, borides of, carbides of,* &c.); it also forms *alloys* with several *metals* (*v. Iron, alloys of*).

Passivity of iron. Iron is not acted on by conc. nitric acid; iron which has been immersed in conc. nitric acid does not dissolve in dilute nitric acid, nor does it ppt. Cu from $CuSO_4Aq$; such Fe is said to be *passive*. Co and Ni, and perhaps Bi, also show passivity. According to Varenne (*A. Ch.* [5] 19, 251; 20, 240) immersion of iron in acid of 100 p.c. HNO_3 is not accompanied by evolution of any gas; if the acid has S.G. 1·382 (c. 63 p.c. HNO_3) NO is evolved copiously for 3 to 20 seconds and then ceases; in both cases the Fe becomes passive. Acid of less S.G. than 1·299 (c. 47 p.c. HNO_3) does not produce passivity. If part of a rod of Fe is dipped into conc. acid, and then the whole is carefully immersed in a dilute acid, the whole rod is passive. These facts are explained by Varenne by supposing that a gaseous film is deposited on the surface of the iron, and protects the iron from the action of the acid; the gas dissolves in the more dilute acid; in the case of the partly-immersed rod the gas-bubbles are removed from one part and then adhere to the other part of the rod. This view was also upheld by Mousson (*P.* 39, 330), but was controverted by Faraday and Schönbein (*P.* 39, 342), and Beetz (*P.* 67, 286, 365). Ramann (*B.* 14, 1430) considers the passivity to be due to a layer of Fe_3O_4, which is soluble in dilute, but insoluble in conc., nitric acid. R. thinks that immersion in the acid produces $Fe(NO_3)_2$, and that this then reacts with the Fe to produce Fe_3O_4 and NH_4NO_3; iron-wire, according to R., becomes passive when partly heated, also by making it the positive electrode in an O-containing liquid. Various oxidising agents acting on Fe render it passive, *e.g.* $HClO_3$, CrO_3, H_2O_2 (Keir). The passivity of Fe is removed by strongly rubbing the iron, or heating it in reducing gases, also by bringing it into contact with Zn. According to Saint-Edme (*C. R.* 106, 1079) commercial sheet Ni is passive in ordinary HNO_3Aq; Fe in contact with Ni becomes passive in the acid; passive Ni remains passive when heated to bright redness in H, whereas Fe loses its passivity.

Detection and Estimation.—Fe compounds are detected by giving a reddish-green colour to the hot borax bead in the oxidising flame, which becomes bottle-green to nearly colourless when cold; also by the ppn. of brown-red $Fe_2O_3.xH_2O$ by alkalis from ferric compounds; K_3FeCy_6Aq gives a deep blue pp. with ferrous salts, and no pp. but a brownish colour with ferric salts. Fe is estimated, *gravimetrically*, by ppn. as $Fe_2O_3.xH_2O$ and weighing as Fe_2O_3; *volumetrically*, by titration with $KMnO_4Aq$ or $K_2Cr_2O_7Aq$. For details and for other methods *v.* MANUALS OF ANALYSIS.

Metallurgy of iron. Pure iron is too soft and has too little tenacity for use in making machinery, &c. Ordinary iron is divided into three kinds: *pig* or *cast iron* containing from 2 to 5·75 p.c. C, besides small quantities of Si, P, S, and traces of metals other than Fe (chiefly As, Ti, V, Cr, Mn, Cu); *malleable* or *wrought iron* containing less than ·5 p.c. C; and *steel* containing about 1 p.c. C. Pig iron is obtained by very strongly heating Fe ores with lime and coal in large furnaces, and blowing in air at the bottom of the furnaces; the C of the coal is burnt chiefly to CO, and this reacting with oxides of Fe produces Fe, which then combines with, or it may be only dissolves, carbon; the C seems to be produced by a reaction between the partly reduced Fe_2O_3

and CO (*v.* Bell, *C. J.* [2] 7, 203). The reduction of Fe_2O_3 is probably aided by cyanides present in the furnace. The greater part of the foreign matter of the iron ores is removed in the form of a fusible slag consisting of silicate of Fe, Ca, Mg, Al, Mn, &c. Wrought iron is obtained by *puddling* cast iron; in this process the cast iron is strongly heated along with lumps of Fe_2O_3 in a reverberatory furnace; the Fe_2O_3 is partially deoxidised, and the O is used in burning the C, Si, S, and P, the C being thus almost entirely removed as CO or CO_2. Steel is obtained by completely removing the C from wrought iron by blowing in air, and then adding a sufficient quantity of Fe containing a known quantity of C. Steel is also sometimes made by causing wrought iron to take up C by strongly heating the iron with charcoal. Cast iron is more fusible, harder, and more brittle than wrought iron, which is more ductile and malleable than cast iron. Steel combines the malleability and ductility of wrought iron with the fusibility of cast iron; it is also very hard and elastic. Cast iron is divided into two kinds: *grey cast iron*; granular, with low malleability, S.G. c. 7·1, melting at c. 1600°; this variety contains C partly in combination with Fe and partly uncombined as graphite; *white cast iron*, harder but not so strong as grey, S.G. c. 7·5, melts at a lower temperature than grey; this variety contains only combined C. By melting grey, and cooling rapidly, white, cast iron is obtained; by melting white, and cooling slowly, grey, cast iron is produced. For details of the metallurgy of iron *v.* DICTIONARY OF APPLIED CHEMISTRY.

Iron, alloys of. Iron alloys with many metals; the softer metals—Ag, Sn, Zn, &c.—become harder and more tenacious when alloyed with a few parts of iron per thousand; the alloys may generally be prepared by fusing the various metals with iron-wire, a little Fe_2O_3 being added to remove C from the iron.

Alloys with *aluminium* have been described; approximately Al_2Fe (Wöhler, *A.* 115, 102), approximately Al_2Fe_3 and $AlFe_4$ (Calvert a. Johnson, *J.* 1855. 326). Sonnenschein (*J. pr.* 66, 168) described an alloy with *lead* having a composition approximating to Pb_2Fe. An *amalgam* of iron is formed by mixing finely-divided Fe with Na amalgam, adding a little water, and squeezing out excess of Hg; the crystals correspond in composition to Hg_3Fe_2; they slowly undergo decomposition, rapidly when much compressed (Ramann, *B.* 14, 1433). Alloys with the following metals have been described:—Sb; Cu (Musket, *P. M.* [3] 6, 81); Mn (M., *l.c.*); Mo (Heine, *J. pr.* 9, 176; Stromeyer, *P.* 28, 551; Wiggens, *P.* 28, 565; Steinberg, *J. pr.* 18, 379); Ni; Pd (Faraday a. Stodart, *Tr.* 1822. 254); Pt (Schönbein, *P.* 42, 17; Boussingault, *A. Ch.* [2] 53, 441); K (Calvert, *P. M.* 1855); Rh (F. a. S., *l.c.*); Sn (Lassaigne, *J. Chim. méd.* 6, 609); Ti (Riley, *C. J.* 16, 387); W (Bernouilli, *P.* 21, 573); Zn (Percy, *Metallurgy*, 2, 153).

Iron, arsenides of. The minerals *arsenical pyrites* and *mispickel* are compounds of Fe with As and with As and S respectively; their compositions approximate to the formulæ $FeAs_2$ and FeAsS. Brittle masses are obtained by fusing together As and Fe out of contact with air, but they have not been much examined.

Iron, borides of. When Fe is heated in a stream of BCl_3 vapour, a hard, white substance is obtained, which is decomposed by boiling water forming H_3BO_3 (? and Fe_2O_3), and evolving H (Fremy, Wurtz's *Dict. de chim.* 1, 1417); by heating ferric borate in H, Lassaigne (*J. Chim. méd.* 3, 535) obtained a similar compound; no analyses are given.

Iron, bromides of. Two exist, $FeBr_2$ and $FeBr_3$; both are produced by the direct union of their elements. Neither has been gasified; the formulæ are given because of the analogies between these salts and $FeCl_2$ and $FeCl_3$ (*v. Iron, chlorides of*).

FERROUS BROMIDE. (*Protobromide of iron.*) $FeBr_2$. A yellow solid; obtained by heating excess of Fe in Br vapour; soluble in water; solution deposits crystals $FeBr_2.6H_2O$; decomposed by heating in air to $FeBr_3$ and Fe_2O_3 (Scheufelen, *A.* 231, 156). Thomsen gives $[Fe,Br^2,Aq] = 78,070$ (*Th.* 3, 294).

FERRIC BROMIDE. (*Sesquibromide of iron.*) $FeBr_3$. Dark-red crystals; obtained by heating Fe in excess of Br vapour; may be sublimed, with partial decomposition, out of contact with air; deliquescent. Aqueous solution very easily partially reduced by heating to $FeBr_2$ (L. de Koninck, *Zeit. anorgan. Chemie*, 1889. 149).

Iron, carbides of. Whether pig-iron is a carbide of iron, or a mixture of carbides and free C, cannot yet be regarded as finally settled. The presence of a few per cents. of C in iron very much modifies the properties of the whole, by making it more fusible; if from ·2 to 1·5 p.c. C is present, the mass is only fusible with difficulty, but is very hard and tough, it has the properties of wrought iron or steel, according to the quantity of C. Iron takes up C directly, and by so doing has its properties changed. On the temperatures at which carburation of Fe occurs with amorphous C, diamond, and graphite, *v.* Hempel, *B.* 18, 998.

The following carbides of Fe have been described, but the investigation of none of these bodies is complete:—(1) Fe_4C, a brittle, fusible mass, by melting together an intimate mixture of equal parts of Fe and C (Faraday a. Stodart, *G. A.* 66, 183); (2) FeC_2, a black pyrophoric powder, by heating H_4FeCy_6, or $(NH_4)_4FeCy_6$, out of contact with air (Berzelius), or by fusing K_4FeCy_6, and washing away the KCN produced (Rammelsberg); (3) FeC_3 was obtained by Karsten by the action of dilute acids on grey pig-iron (*S.* 68, 182); (4) FeC, by the action of Br or I on pig-iron (Berthier, *J.* 1862. 127).

Iron, chlorides of. Two chlorides of iron, $FeCl_2$ and $FeCl_3$, have been isolated; and a third, Fe_4Cl_8, perhaps exists. When Fe is heated in a stream of Cl, both $FeCl_2$ and $FeCl_3$ are produced.

FERROUS CHLORIDE $FeCl_2$. (*Iron dichloride* or *protochloride.*) Mol. w. 126·64 (*v. infra*). S.G. 2·528 (Filhol, *A.Ch.* [3] 21, 415); 2·988 at 17·9° (Clarke's *Specific Gravity Tables* [new ed.] 24). V.D. 62·79 at 1300°–1400°; 61·55 at 1400°–1500° (Nilson a. Pettersson, *C. J.* 53, 828). V.D. at yellow-heat 94·4 (V. Meyer, *B.* 17, 1335); calc. for $FeCl_2$ 63·32, for Fe_2Cl_4 126·64 (*v. infra*). H.F. $[Fe,Cl^2] = 82,050$; $[Fe,Cl^2,Aq] = 99,950$; $[FeCl^2,4H^2O] = 15,150$ (*Th.* 3, 293).

Formation.—1. By heating excess of Fe filings

or wire in Cl.—2. By partially reducing $FeCl_3$ in H (Wöhler, *A.* 4, 255).—3. By dissolving Fe in HClAq out of contact with air, evaporating, and drying in a stream of H.—4. By heating Fe filings with NH_4Cl out of contact with air.

Preparation.—Fe wire is heated in a stream of dry HCl, and the product sublimed in the same gas (Wöhler a. Liebig, *P.* 21, 258).

Properties and Reactions.—White, lustrous, six-sided, deliquescent, tablets. Heated very strongly in N forms $FeCl_3$ and Fe (V. Meyer, *B.* 17, 1335). Heated in O, forms Fe_2O_3 with evolution of Cl. Oxidises readily in air to a mixture of $FeCl_3$ and Fe_2O_3. Heated to redness in steam forms Fe_3O_4, HCl, and H. Heated to redness in a stream of NH_3, Fe_5N_2 is produced (Fremy, *C. R.* 52, 321). Heated with PH_3 forms HCl and Fe phosphide. A mixture of $FeCl_2$ and C is reduced by Zn vapour with separation of Fe in crystals (Poumarède, *C. R.* 29, 520). S. c. 50 at 80°; less sol. in HClAq.

Molecular weight of gaseous ferrous chloride. By volatilising in HCl at a yellow heat, V. Meyer got values for V.D. which were about the mean between those calculated for $FeCl_2$ and Fe_2Cl_4 (*B.* 17, 1335); calculated for $FeCl_2 = 63{\cdot}32$, for $Fe_2Cl_4 = 126{\cdot}64$; observed 92·32 and 96·51. Meyer concluded that molecules of Fe_2Cl_4 probably exist at lower temperatures and molecules of $FeCl_2$ at a very high temperature. Nilson a. Pettersson (*C. J.* 53, 827) obtained values for V.D. at c. 1400° agreeing with that calculated for $FeCl_2$; calculated = 63·32, observed at 1300°–1400° = 62·79, at 1400°–1500° = 61·55. There can be no doubt then that molecules of the composition $FeCl_2$ exist at c. 1300°–1500°.

Combinations.—1. With *water* to form the hydrates $FeCl_2.2H_2O$ and $FeCl_2.4H_2O$. The former is obtained by saturating warm conc. HClAq with $FeCl_2$, or by passing HCl into saturated $FeCl_2Aq$; the latter is produced by dissolving Fe in HClAq and concentrating out of contact with air. $FeCl_2.4H_2O$ forms blue-green, monoclinic, deliquescent, transparent crystals; S.G. 1·93.—2. With *nitric oxide*; solution of $FeCl_2$, especially an alkaline solution, absorbs NO forming a green-brown liquid which contains $FeCl_2.NO$; NO is removed by warming.—3. With *ammonia* to form $FeCl_2.6NH_3$ and $3FeCl_2.2NH_3$ (Rogstadius, *J. pr.* 86, 310). The former is a white powder, produced by passing NH_3 over $FeCl_2$ at the ordinary temperature; the latter is formed by slowly heating $FeCl_2.6NH_3$ to melting. By strongly heating $3FeCl_2.2NH_3$ in NH_3 the nitride Fe_5N_2 is formed (Fremy, *C. R.* 52, 321).—4. With *ammonium chloride* to form $FeCl_2.2NH_4Cl$; obtained by crystallising mixed solutions of $FeCl_2$ and NH_4Cl, or, according to Hisinger a. Berzelius (*G. A.* 27, 273) (with evolution of NH_3 and H), by boiling Fe filings with NH_4ClAq (*cf.* Winkler, *R. P.* 59, 171; Vogel, *J. pr.* 2, 192). A compound $FeCl_2 2KCl.2H_2O$ is also known (Schabus, *W. A. B.* 1850. 475). Compounds with $CdCl_2$ and $HgCl_2$, viz. $FeCl_2.2CdCl_2.12H_2O$ and $FeCl_2.HgCl_2.4H_2O$ are also described (*v.* Hauer, *W. A. B.* 17, 331).

FERRIC CHLORIDE. (*Iron sesquichloride* or *perchloride.*) $FeCl_3$. Mol. w. 162·01, and probably also 324·02 (*v. infra*). (280°–285°) (Friedel a. Crafts, *C. R.* 107, 301). S.G. 2·804 at 10·8° (Clarke's *Tables of Specific Gravity* [new ed.], 24). V.D. varies from c. 165 at 320° to c. 80 at 1000°–1300° (*v. infra*). Crystallises in hexagonal forms $a:c = 1:1{\cdot}235$, Nordenskiöld (*v.* Rammelsberg's *Hand. der Krystal.-physikal. Chemie*, 1, 260). H.F. $[Fe,Cl^3] = 96{,}040$; $[FeCl^2,Cl] = 13{,}990$; $[Fe,Cl^3,Aq] = 127{,}720$; $[FeCl^2Aq,Cl] = 27{,}770$ (*Th.* 3, 293).

Occurrence.—In the craters of volcanoes.

Formation.—1. By heating Fe in a stream of Cl.—2. By heating $FeCl_2$ in Cl.—3. By strongly heating $FeCl_2$ in a wide-mouthed vessel; Fe_2O_3 remains and $FeCl_3$ sublimes.—4. By passing HCl over strongly heated amorphous Fe_2O_3 (Deville a. Troost, *C. R.* 45, 821).—5. By heating a mixture of calcined $FeSO_4$ with $CaCl_2$ or NaCl. The product obtained by boiling down a solution of Fe_2O_3 in HCl always contains oxychloride.

Preparation.—Fine iron-wire is strongly heated in a hard-glass tube in a stream of dry Cl, and the product is sublimed in the same gas.

To prepare a solution of $FeCl_3$, hydrated Fe_2O_3 is dissolved in hot HClAq, the solution is decanted, Cl is passed in until K_3FeCy_6 ceases to give any trace of blue colour, and excess of Cl is removed by warming; or 2 parts warm HClAq are saturated with Fe (filings or wire), to the clear decanted liquid 1 part HClAq is added, the liquid is warmed and HNO_3Aq is added little by little until all $FeCl_2$ is oxidised to $FeCl_3$; excess of HNO_3 is removed by evaporation with a little HClAq. Geissler (*Ar. Ph.* [2] 58, 159) recommends to evaporate the ferrous solution to S.G. 1·3 at 17° and then to add HNO_3Aq to the *cold* solution, when oxidation proceeds rapidly.

Properties.—By slowly cooling the vapour, $FeCl_3$ condenses in hexagonal crystals which appear very dark red by transmitted, and greenish by reflected, light (Deville a. Troost, *C. R.* 45, 821). As ordinarily prepared $FeCl_3$ forms a brownish-black crystalline mass. Volatilises at somewhat over 100°. Melts at 306°–307° in a sealed tube (Carnelley a. Williams, *C. J.* 37, 126). Deliquescent; conc. solution in water is dark brown and somewhat viscid; it becomes limpid and yellow on dilution; a very dilute solution is colourless when cold (*v. Reactions*, No. 4).

Franz (*J. pr.* [2] 5, 283) gives the following table showing S.G. and percentage composition of $FeCl_3Aq$ at 17·5°:—

S.G.	p.c. $FeCl_3$	S.G.	p.c. $FeCl_3$	S.G.	p.c. $FeCl_3$
1·0146	2	1·1746	22	1·3870	42
1·0292	4	1·1950	24	1·4118	44
1·0439	6	1·2155	26	1·4367	46
1·0578	8	1·2365	28	1·4617	48
1·0734	10	1·2568	30	1·4876	50
1·0894	12	1·2778	32	1·5153	52
1·1054	14	1·2988	34	1·5439	54
1·1215	16	1·3199	36	1·5729	56
1·1378	18	1·3411	38	1·6023	58
1·1542	20	1·3622	40	1·6317	60

Schult (*Forh. skand. Naturf.* 1868. 452) obtained the following results at 14·6°:—

S.G. $FeCl_3Aq$	p.c. $FeCl_3$	S.G. $FeCl_3Aq$	p.c. $FeCl_3$
1·0382	4·65	1·339	33·25
1·0918	10·45	1·3824	36·95
1·1517	16·80	1·4361	41·0
1·2107	22·54	1·554	49·61
1·2318	24·60		

$FeCl_3$ is soluble in alcohol or ether; the solution

easily decomposes in sunlight with formation of $FeCl_2$.

Molecular weight of gaseous ferric chloride.—Deville a. Troost (*C. R.* 45, 821) found the V.D. of ferric chloride at 440° to be 162·7; this corresponds to the formula Fe_2Cl_6. Grünewald a. V. Meyer (*B.* 21, 687) made a series of determinations of V.D., in an atmosphere of N, with the following results: 151·75 at 448° (mean of 4), 138·5 at 518° (mean of 3), 121·3 at 606° (mean of 6), 78·66 at 750° (mean of 2), 71·2 at 1036°, 77·6 at 1077°, 74·3 at 1300°. These numbers seem to indicate a gradual resolution of molecules of Fe_2Cl_6 into $FeCl_3$; none of the results, however, agrees exactly with the value calculated for $FeCl_3$ (81·005), but this was to be expected, as G. a. M. showed that even at 518° ferric chloride is partially resolved into $FeCl_2$ and Cl in an atmosphere of N. According to Friedel a. Crafts (*C. R.* 107, 301) ferric chloride is not dissociated at 440° in an atmosphere of Cl; F. a. C. made a series of determinations of V.D. in Cl, using a modification of Dumas' method; the results are appended:—165·1 at 321·6°, 180·4 at 325·2°, 174·2 at 356·9°, 171·5 at 357°, 168·7 and 163·5 at 442·2°. These values are all somewhat greater than 162·1, the value required by the formula Fe_2Cl_6. The most probable conclusion from all the results seems to be that at high temperatures, c. 700° and upwards, the vapour of ferric chloride consists of molecules of $FeCl_3$, but that as temperature falls these molecules are mixed with more complex molecules, some of which at any rate have the composition Fe_2Cl_6 (*cf.* Young, *N.* 39, 198).

Reactions.—1. When $FeCl_3$ is heated in *oxygen*, Fe_2O_3 and Cl are produced (*cf.* Schulze, *J. pr.* [2] 21, 407).—2. Heated in *hydrogen*, $FeCl_2$ is formed (Wöhler, *A. Suppl.* 4, 255).—3. Heated in *water-vapour*, Fe_2O_3 and HCl are formed.—4. $FeCl_3$ dissolves in *water*; the conc. solution is a syrupy dark-brown liquid, becoming yellow on dilution, and colourless when very dilute and cold. By heating $FeCl_3Aq$, colloidal soluble $Fe_2O_3.xH_2O$ and HCl are produced; fairly conc. $FeCl_3Aq$ forms oxychlorides, $Fe_2O_3.xFeCl_3$, at c. 100°, and at higher temperatures Fe_2O_3 is formed. The amount of decomposition and the composition of the products depend on the concentration of the solution and the temperature; very dilute solutions, c. 30,000 water to 1 $FeCl_3$, are decomposed with formation of colloidal soluble ferric hydrate even without warming (*cf. Iron, hydrated oxides or hydroxides of*, p. 59). Krecke (*J. pr.* [2] 3, 286) gives the following table (*cf.* Tichborne, *C. N.* 24, 123, 199, 209, 230; 25, 133; Müller, *J.* 1873. 40; Foussereau, *C. R.* 103, 42):—

$FeCl_3Aq$ containing $\frac{1}{16}$ p.c. $FeCl_3$ or less is decomposed by light at 5°–6° (Krecke, *l.c.*). When $FeCl_3Aq$ is heated in a sealed tube to 250°–300° it decomposes to Fe_2O_3 and HCl (Senarmont, *C. R.* 32, 762). From a very dilute cold colourless solution of $FeCl_3$, K_4FeCy_6Aq ppts. a pure blue pp., and NaCl produces no change. If the solution is heated it becomes yellow, and contains soluble ferric hydrate and HCl. From this solution K_4FeCy_6Aq ppts. greenish-blue solid, and on addition of NaCl a soluble ferric hydrate separates, which, after long contact with NaClAq, becomes insol. in water (Debray, *C. R.* 68, 913). Evaporation of $FeCl_3Aq$ is accompanied by evolution of some HCl; the residue contains oxychloride or hydrated oxide. $FeCl_3$ is not volatilised from violently boiling $FeCl_3Aq$ containing HCl (Fresenius, *Fr.* 6, 92). G. Wiedemann connects the decomposition of $FeCl_3Aq$, and also of other ferric salts, with the different magnetic behaviour of colloidal soluble $Fe_2O_3.xH_2O$, and that hydrate which remains in combination with the acid (*W.* 5, 45).—5. $FeCl_3$ dissolves in *alcohol* or *ether*. An ethereal solution mixed with alcohol and allowed to stand in sunlight loses its yellow colour, and $FeCl_2$ and chlorinated derivatives of alcohol and ether are formed.—6. An aqueous solution of $FeCl_3$ is *readily reduced* to $FeCl_2$, *e.g.* by As, Sb, Bi, Fe, Pb, or Zn; also by finely-divided Pt, more slowly by Pd and Au (*cf.* Béchamp, *C. R.* 52, 757; Saint-Pierre, *C. R.* 54, 1077). Also reduced by *stannous chloride*, *sulphurous acid*, or *sulphuretted hydrogen*; *hydriodic acid* reduces dilute $FeCl_3Aq$ slowly (*v.* Mohr, *A.* 105, 53). Many *organic compounds* also reduce $FeCl_3Aq$, especially in sunlight, *e.g.* alcohol and ether, or tartaric acid (*v.* Schoras, *B.* 3, 11; Poitevin, *C. R.* 52, 94).—7. A very little $FeCl_2$ is said to be formed by passing *hydrogen* for 48 hours through $FeCl_3Aq$ (Brunner, *J.* 1864. 125).—8. $FeCl_3$ dissolves freshly ppd. *ferric hydrate* forming oxychlorides (*q. v.*).—9. When $FeCl_3Aq$ is dropped into solution of *potassium nitrite*, in an atmosphere of CO_2, brisk evolution of NO proceeds, and a pp. of soluble ferric metahydroxide, $Fe_2O_3.H_2O$, separates (Pesci, *G.* 18, 183).—10. $FeCl_3Aq$ reacts with *potassium iodide* to form $FeCl_2$, I, and KCl; probably FeI_3 is at first produced, and is then resolved into FeI_2 and I, and then the FeI_2 reacting with unchanged $FeCl_3$ forms $FeCl_2$ and I (*v.* Carnegie, *C. N.* 60, 87).—11. When *electrolysed*, conc. $FeCl_3Aq$ gives $FeCl_2$ at the negative, and Cl with a little O at the positive, electrode.

Combinations.—1. With *water* to form various hydrates: (1) $FeCl_3.6H_2O$; yellow solid, formed by dissolving 100 parts $FeCl_3$ in 63·5 parts H_2O (S.G. of solution 1·67 at 25°); or by slowly eva-

P.c. $FeCl_3$ in solution. p.c.	Formation of Graham's colloidal hydrate °		Formation of colloidal hydrate of P. de Saint-Gilles °	Formation of oxychlorides °	Formation of Fe_2O_3 °
32	100–130	$FeCl_3$ re-formed on cooling	—	over 100	140
16	100–120		—	,,	120
8	100–110		—	,,	110
4	90–100		—	90	
2	87		—	87	
1	83	$FeCl_3$ not re-formed on cooling	100–130		
·5	75		,,		
·25	64		,,		
·125	54		,,		
·0625	36		,,		

porating $FeCl_3Aq$ on the water-bath, and allowing to crystallise; or by exposing $FeCl_3$ to the air (Mohr, *A.* 29, 173); or by passing HCl over commercial ferric chloride, filtering the liquid which forms through glass wool, and evaporating over KOH *in vacuo* (Engel, *C. R.* 104, 1708); melts at 35·5°, and solidifies again at 28° (Ordway, *Z.* 1866. 23). (2) $2FeCl_3.5H_2O$; reddish tablets, melting at 31°, formed by melting the hexahydrate, warming to 100°, for some hours, and cooling slowly (Engel, *l.c.*); or by evaporating $FeCl_3Aq$ to a syrup (S.G. c. 1·5), with addition of a little HClAq, and crystallising (Fritzsche, *J. pr.* 18, 479; Gobley, *J. Ph.* [3] 5, 301; 25, 259). According to Wittstein (*R. P.* [2] 36, 30) and Ordway (*Z.* 1866. 23), the hydrate thus obtained is $FeCl_3.3H_2O$. The hydrate $2FeCl_3.5H_2O$ is said to be formed by placing $FeCl_3.6H_2O$ over H_2SO_4; the hexahydrate at first liquefies and then loses water.—2. With *hydrogen chloride and water*, to form $FeCl_3.HCl.2H_2O$; thin, transparent, amber-yellow laminæ, formed by passing dry HCl gas over $2FeCl_3.5H_2O$, saturating the liquid thus produced with HCl at 25°, and cooling to 0° (Engel, *C. R.* 104, 1708; Sabatier, *Bl.* 1881. 197).—3. With *ammonia*, to form $FeCl_3.NH_3$. When heated, this compound partly sublimes, and is partly decomposed, giving $FeCl_2$.—4. With *phosphoric chloride*, to form a brown fusible compound, $FeCl_3.PCl_5$ (Weber, *J. pr.* 76, 410).—5. With *hydrocyanic acid*, to form a brown liquid, which then crystallises to $FeCl_3.2HCN$ (Klein, *A.* 74, 87).—6. With *cyanogen chloride*, but the compound has not been obtained pure (*v.* Klein, *l.c.*).—7. With *nitrosyl chloride*, to form $FeCl_3.NOCl$; a dark-coloured, very deliquescent mass, obtained by placing dry $FeCl_3$ in the fumes of *aqua regia* placed over $CaCl_2$ (Weber, *J. pr.* 89, 152).—8. With *alkali chlorides*, to form $FeCl_3.2MCl.H_2O$; M = K, Na, Rb, NH_4. The NH_4 compound forms garnet-red crystals; by evaporating mixed solutions of the constituent salts. The crystals are rhombic according to Fritzsche (*J. pr.* 18, 484), dimorphous according to Genth (*J. pr.* 71, 164). The double compounds $FeCl_3.2MCl.H_2O$ are all decomposed by water. The K salt is described by Fritzsche (*J. pr.* 18, 483), the Na salt by Deville (*C. R.* 43, 970), the Rb salt, said to be $FeCl_3.3RbCl$, by Godeffroy (*Ar. Ph.* [3] 9, 343). According to Kremers (*J. pr.* 55, 191), a compound of the form $FeCl_3.2MCl.H_2O$, in which M is partly K (12·1 p.c.), partly Na (·16 p.c.), and partly NH_4 (6·2 p.c.), is found in certain volcanic craters.—9. With *thallium chloride*, to form $FeCl_3.3TlCl$ (Wöhler a. Ahrens, *A.* 144, 250).—10. With *magnesium* and *beryllium chlorides*, to form $FeCl_3.MCl_2.H_2O$; formed by adding $MgCl_2$ or $BeCl_2$ to a conc. hot solution of $FeCl_3$ in HClAq (Neumann, *A.* 244, 328).

FERROSO-FERRIC CHLORIDE $Fe_3Cl_8(FeCl_2.2FeCl_3)$. When $Fe_3O_4.H_2O$ is treated with a little HClAq, $FeCl_2$ goes into solution, and Fe_2O_3 remains; but $Fe_3O_4.H_2O$ dissolves wholly in considerable excess of conc. HClAq. When the solution is cooled and placed *in vacuo* over H_2SO_4, yellow crystals of $Fe_3Cl_8.18H_2O$ are said to separate (Lefort, *C. R.* 69, 179). The crystals are deliquescent; at 50° they lose water; heated to 90° HCl is given off and O absorbed; by warming an aqueous solution of the crystals, $FeCl_2$ and $FeCl_3$ are formed.

Iron, cyanides of. No cyanides of iron have been isolated, but *ferri-* and *ferro-cyanides* are numerous; *v.* vol. ii. pp. 332, 334, 338.

Iron, ferricyanide and ferrocyanide of, *v.* vol. ii. pp. 334 a. 338.

Iron, fluorides of. Two fluorides of Fe are known, FeF_2 and FeF_3. The former is produced by dissolving Fe in HFAq, the latter by dissolving $Fe_2O_3.xH_2O$ in HFAq.

FERROUS FLUORIDE FeF_2. Small green crystals of this composition separate from a solution of Fe in HFAq (Scheurer-Kestner, *A. Ch.* [3] 68, 472). By careful heating, FeF_2 is obtained as a white solid. FeF_2 is unchanged by heat; the hydrate is partly decomposed to HF and Fe_2O_3. Slightly sol. in water, more easily on addition of HF. The double salt $FeF_2.2KF$ is a green pp., obtained by adding KFAq to $FeSO_4Aq$; the salts $FeF_2.KF.2H_2O$, $FeF_2.2NH_4F$, and $FeF_2.NH_4F.2H_2O$ are described by Wagner (*B.* 19, 896). The *Silicofluoride* $FeF_2.SiF_4(=FeSiF_6)$ is said to be formed as blue-green crystals by dissolving Fe in H_2SiF_6Aq and crystallising (Wurtz, *Dictionnaire*, i. 1408).

FERRIC FLUORIDE FeF_3. Crystals of the hydrate $2FeF_3.9H_2O$ are obtained by dissolving $Fe_2O_3.xH_2O$ in HFAq and evaporating, or by oxidising FeF_2 in HFAq by HNO_3. The crystals are yellowish according to Berzelius, colourless according to Scheurer-Kestner (*A. Ch.* [3] 68, 472). At 100° $3H_2O$ is removed; at higher temperatures H_2O and HF escape. By heating the salt dried at 100° in a Pt crucible colourless crystals of FeF_3 are formed on the surface of the mass, isomorphous with AlF_3 (Deville, *C. R.* 43, 970). Slowly dissolved by water; addition of NH_3Aq ppts. the *oxyfluoride* $3Fe_2O_3.2FeF_3.4H_2O$. FeF_3 forms double salts with K, Na, and NH_4; these are obtained by adding FeF_3Aq to solutions of the alkali fluorides; the salts described are $FeF_3.3KF$ (Berzelius; Wagner, *B.* 19, 896); $2FeF_3.4KF.H_2O$ (Nicklés, *Z.* 7, 480); $FeF_3.3NaF$ (B.; W., *l.c.*); $FeF_3.2NaF$ (Nicklés, *J.* 1869. 268); $FeF_3.2NH_4F$ (N., *l.c.*), to this salt Marignac gives the formula $FeF_3.3NH_4F$ (*A. Ch.* [3] 60, 306).

Iron, haloid compounds of. Iron readily combines with the halogens. With each halogen, two compounds are formed, ferrous FeX_2 and ferric FeX_3; ferric iodide, however, has not been isolated with certainty; the compound Fe_3Cl_8, corresponding to Fe_3O_4, also perhaps exists. The only compounds that have been gasified are ferrous and ferric chloride. The former has the molecular formula $FeCl_2$ at 1300°–1500°; but there are indications of the possible existence of molecules of Fe_2Cl_4 at lower temperatures; the latter appears to exist as a gas both as Fe_2Cl_6 and $FeCl_3$. The haloid compounds of Fe are soluble in water; solutions of $FeBr_3$ and $FeCl_3$ are decomposed by much water; the compounds all form several double compounds with the chlorides &c. of the more positive metals.

Iron, hydrides of. No definite hydride of Fe has been certainly isolated, but there are several indications of the existence of a compound or compounds of Fe and H. Fe heated to redness absorbs about ·46 vols. H (Deville a. Troost, *C. R.* 57, 965; 59, 102). Electrolytically deposited Fe contains H along with N, CO, and CO_2 (Lenz, *P. Ergänzbd.* 5, 252; *cf.* Meidinger,

D. P. J. 163, 283; Chandler-Roberts, *C. N.* 31, 137). Iron wire takes up H when immersed in dilute H_2SO_4Aq (Johnson, *Pr.* 23, 168; Reynolds, *C. N.* 29, 118). According to Cailletet (*C. R.* 80, 319) Fe ppd. electrolytically from neutral $FeCl_2Aq$ containing NH_4Cl gives off 235–238 vols. H when heated *in vacuo*. Observations on the supposed existence of a gaseous hydride of Fe were made by Thomson, Dupasquier (*C. R.* 14, 511), and Reinsch (*J.* 1858. 190). The non-existence of such a gas was proved by Fresenius a. Schlossberger (*A.* 51, 415) and by Erlenmeyer (*N. J. P.* 9, 97). Thoma has investigated the conditions under which H is absorbed by Fe (*Z. P. C.* 3, 91). He finds that when Fe is made the negative electrode in a voltameter, or when it is placed in dilute H_2SO_4Aq, it absorbs much H, but that Fe placed in an atmosphere of H does not absorb any of that gas; a certain portion of the H absorbed is given off again on exposure to air or immersion in water, the rest of the H is more firmly retained by the Fe. According to Wanklyn a. Carius (*A.* 120, 69) when FeI_2 reacts with $ZnEt_2$ in presence of ether, various gases including C_2H_4, C_2H_6, C_4H_{10}, and H are evolved, and a metal-like powder remains, which, after washing with ether, is decomposed by H_2O giving H and a mixture of H and FeO. They regard this powder as a hydride of Fe, perhaps FeH_2, but no analyses are given.

Iron, hydrated oxides or hydroxides of. Compounds with water of each of the three oxides of iron are known. The compositions of the various hydrated oxides are differently represented by different chemists; they appear to vary with small changes of conditions, so that it is impossible to say whether all the bodies described are true hydrates or not. The readiness with which most of the hydrated oxides undergo change of composition points to their being hydrates, *i.e.* compounds of water, rather than hydroxides, *i.e.* compounds of OH. Thomsen (*Th.* 3, 293) gives the thermal data:—$[Fe^2, O^3, 3H^2O] = 191,150$; $[2FeO^2H^2, O, H^2O] = 54,590$; $[Fe, O, H^2O] = 68,280$; $[FeO^2H^2, H^2SO^4Aq] = 24,920$; $[Fe^2O^6H^6, 3H^2SO^4Aq] = 33,840$.

Only one hydrate of *ferrous oxide*, $FeO.H_2O$, appears to exist; but it is doubtful whether any hydrate of this oxide has been obtained free from hydrates of Fe_2O_3. Descriptions are given of two hydrates of *ferroso-ferric oxide*, viz. $Fe_3O_4.H_2O$ and $Fe_3O_4.4H_2O$; but here again there is great doubt as to the composition of the substances described as definite hydrates. Many hydrates of *ferric oxide* have been obtained; the following are known as minerals ($M = Fe_2O_3$): $M.H_2O$, $M.2H_2O$, $M.3H_2O$, $2M.H_2O$, $2M.3H_2O$, $3M.5H_2O$; the following are said to have been obtained artificially: $M.H_2O$, $M.2H_2O$, $M.3H_2O$, $2M.H_2O$, $2M.3H_2O$; many of these appear to exist in different modifications each distinguished by special properties; broadly they fall into two classes, those which are insoluble in water, and those which dissolve in water.

Hydrate of ferrous oxide $FeO.H_2O$. The white pp. obtained by adding air-free KOHAq to an air-free solution of a ferrous salt, and washing out of contact with air, is probably $FeO.H_2O$. To obtain the pp. nearly free from ferric oxide Schmidt (*A.* 36, 101) ppts. in a closed flask, allows pp. to settle, draws off water by a syphon, carefully pours warm water which has been boiled for some time on to the surface of the cold water in the flask, withdraws water by a syphon, &c.; he then quickly transfers the moist pp. by a syphon to a retort containing ether, and having attached to it a long glass tube dipping under Hg, the ether covers the pp. and drives the air out of the retort; on warming, the water-vapour and condensed water escape through the Hg. When the ether is removed and the retort is cold, dry air-free H (not CO_2, as the hydrate combines with this gas) is passed through the apparatus, and portions of the solid are transferred in an atmosphere of H to small wide-mouthed stoppered tubes. Dried in this way, the hydrate is a pale-greenish, friable solid, which rapidly oxidises and glows in the air.

A. de Schulten (*C. R.* 109, 266) states that $FeO.H_2O$ may be obtained in green six-sided flat prisms, which almost instantly become red in air, by mixing 5 grams $FeCl_2$ dissolved in 100 c.c. air-free water, and 200 c.c. NaOHAq, containing 20 grams NaOH, in a flask filled with coal gas, heating, and allowing to stand for 24 hours.

According to Bineau (*C. R.* 41, 509) ferrous hydrate is soluble in c. 150,000 parts water. Ferrous hydrate is very easily oxidised; it is therefore an energetic reducer, *e.g.* it reduces salts of Au, Ag, and Pt, and also HIO_3Aq. It dissolves in acids to form ferrous salts FeX_2; $X = NO_3, \frac{SO_4}{2}, \frac{PO_4}{3}$, &c. (*cf. Ferrous oxide*, under *Iron, oxides of*).

Hydrates of ferroso-ferric oxide $Fe_3O_4.H_2O$ and $Fe_3O_4.4H_2O$; composition of both doubtful. Hydrates of Fe_3O_4 are produced by ppg. a mixture of equivalent quantities of a ferrous and ferric salt by alkali, and also by digesting ppd. $Fe_2O_3.xH_2O$ with Fe. The black powder obtained by Wöhler (*A.* 28, 92), by ppg. a mixture of equivalent parts of ferrous and ferric sulphates by slight excess of NH_3Aq, boiling, washing by decantation, and drying under 100° is said by Lefort (*C. R.* 69, 179) to be $Fe_3O_4.4H_2O$. By ppg. a mixture of equivalent quantities of a ferrous and ferric salt by hot conc. KOHAq, Lefort (*l.c.*) obtained a hydrate more stable than that got by using NH_3Aq; to this hydrate he gives the formula $Fe_3O_4.H_2O$. The black hydrate obtained by digesting $Fe_2O_3.xH_2O$ with Fe under water does not seem to have been analysed (*v.* Preuss, *A.* 26, 96). Ferroso-ferric hydrates are described as brown-black, magnetic, brittle, powders; when heated out of contact with air they give Fe_3O_4; heated in air, Fe_2O_3 is produced. Ferroso-ferric hydrates dissolve in acids to produce mixtures of ferrous and ferric salts; in some cases definite salts of the form Fe_3X_4, $X = SO_4$, &c., are formed, according to Lefort (*C. R.* 69, 179) (*cf. Ferroso-ferric oxide*, under *Iron, oxides of*).

Hydrates of ferric oxide. A great many supposed hydrates of Fe_2O_3 have been described, but there is much doubt as to the composition and properties of definite hydrates of the form $Fe_2O_3.xH_2O$. The following occur as minerals, the compositions of which more or less accurately agree with the formulæ:—*limonite* $Fe_2O_3.2H_2O$, $Fe_2O_3.3H_2O$, and $2Fe_2O_3.3H_2O$;

göthite $Fe_2O_3.H_2O$; *turgite* $2Fe_2O_3.H_2O$ and $3Fe_2O_3.5H_2O$. According to Ramsay (*C. J.* 32, 395), and Brescius (*J. pr.* [2] 3, 272), the pp. obtained by adding alkali to a ferric salt, either hot or cold, washing, and drying at 100°, is $Fe_2O_3.H_2O$; by ppg. $FeCl_3Aq$ with NH_3Aq, washing first with water and then with alcohol and ether, and drying at 100° the hydrate $Fe_2O_3.2H_2O$ is obtained, according to Brescius (*l.c.*). Wittstein (*C. C.* 1853. 367) says that the hydrate obtained by ppg. a ferric salt by NH_3Aq, washing with cold water, and drying at a gentle heat, or at 100° for a short time, is $Fe_2O_3.3H_2O$. The experiments of Carnelley a. Walker (*C. J.* 53, 89) on the dehydration of ppd. $Fe_2O_3.xH_2O$ through a range of temperature showed that the pp. after drying at 15° for 18 days contained more water than is required by $Fe_2O_3.5H_2O$, that when heated to 55° the residue had the composition $Fe_2O_3.3H_2O$, but that water was gradually and continuously given off from 15° upwards until Fe_2O_3 was formed at 500°; the composition, however, remained constant from 385° to 415°, and corresponded with the formula $10Fe_2O_3.H_2O$. Van Bemmelen (*R. T. C.* 7, 106) has examined the composition of the colloidal pp. by adding NH_3Aq to $FeCl_3Aq$; his experiments, which were very extended, showed the great readiness with which the ratio of Fe_2O_3 to H_2O varies; *e.g.* exposed to air for a year the composition became constant with the ratio Fe_2O_3:4 or $4{\cdot}1H_2O$; after 4 months in dry air the ratio was $Fe_2O_3:1{\cdot}6H_2O$; heated to 100° in dry air the ratio was $Fe_2O_3: {\cdot}96H_2O$; the same sample kept for 6 years in a closed flask and then heated to 15° until constant gave $Fe_2O_3:H_2O$; at 100° $Fe_2O_3: {\cdot}45H_2O$; between 100° and 300° the final state was $Fe_2O_3: {\cdot}25H_2O$; and so on. Besides the papers referred to above on the composition of ppd. $Fe_2O_3.xH_2O$, the following are of importance:—Lefort (*J. pr.* 54, 305); P. de Saint-Gilles (*J. pr.* 66, 137); Schaffner (*A.* 51, 177); Muck (*Z.* [2] 4, 41); Davies (*C. J.* [2] 4, 69); Tommasi (*B.* 12, 1929, 2334).

The *monohydrate* $Fe_2O_3.H_2O$ is said to be obtained: (1) by adding NaOHAq and KClOAq to *boiling* $FeSO_4Aq$, washing, and drying at 100° (Muck, *Z.* [2] 4, 41); (2) by keeping ppd. $Fe_2O_3.xH_2O$ in contact with boiling water for 6–8 hours (P. de Saint-Gilles, *A. Ch.* [3] 46, 47); (3) by repeatedly melting NaOH in a cast-iron vessel and washing (Brunck a. Græbe, *B.* 13, 725); (4) by keeping ppd. $Fe_2O_3.xH_2O$ under water for many years at the ordinary temperature (Schiff, *C. C.* 1860. 1768). This hydrate also occurs native as *göthite*. $Fe_2O_3.H_2O$ is described as a dark-red powder; slowly dissolved by dilute warm HClAq, H_2SO_4Aq, or HNO_3; insol. in cold conc. acids. The monohydrate obtained by Brunck a. Græbe was in the form of small tabular, brownish-violet, hexagonal crystals; S.G. 2·91. Göthite forms rhombic crystals, S.G. 3·8 to 4·2. The monohydrate obtained by Péan de Saint-Gilles, by keeping $Fe_2O_3.xH_2O$ in contact with boiling water for 6–8 hours, is described as a brick-red powder, scarcely acted on by conc. boiling HNO_3Aq, slowly dissolved by conc. hot HClAq; it dissolves in dilute HNO_3Aq, HClAq, or acetic acid, forming a red liquid which appears clear by transmitted, but turbid by reflected, light, and is ppd. by a very small quantity of an alkali salt; on addition of conc. HNO_3Aq or HClAq, this solution gives a red pp. which dissolves on adding water. This modification of $Fe_2O_3.H_2O$ does not form Prussian blue with K_4FeCy_6 and acetic acid.

The *dihydrate* $Fe_2O_3.2H_2O$ is said to be obtained by ppg. *cold* $FeSO_4Aq$ by NaOHAq and KClOAq or H_2O_2Aq, washing, and drying at 100° (Weltzien, *A.* 138, 129; Muck, *l.c.*). This hydrate also occurs native as *limonite*.

The *hydrates* $2Fe_2O_3.H_2O$ and $2Fe_2O_3.3H_2O$ are said to be formed by the action of water on ppd. $Fe_2O_3.xH_2O$; the first by boiling for 100 to 1,000 hours, Davies (*C. J.* [2] 4, 66); the second by long-continued action of water at the ordinary temperature (Wittstein, *Ar. Ph.* 74, 158), or, crystalline, by freezing $Fe_2O_3.xH_2O$ suspended in water (Limberger, *C. C.* 1853. 783). By heating any of the hydrates in sealed tubes Fe_2O_3 is eventually produced (Sénarmont, *C. R.* 32, 762).

Muck (*Z.* 1868. 41) thinks that the ferric hydrates obtained by oxidising ferrous hydrate or carbonate in air differ essentially in properties from the ferric hydrates obtained directly from ferric salts. Tommasi (*Bl.* [2] 38, 152; T. a. Pellizzari, *Bl.* [2] 37, 196) arranges the ferric hydrates in two classes: the red hydrates obtained by ppg. ferric salts by alkali, and the yellow hydrates obtained by oxidising hydrates of FeO or Fe_3O_4, or by oxidising $FeCO_3$.

Ferric hydrates give up O to readily oxidised compounds such as SO_2Aq, $SnCl_2Aq$; in contact with decaying organic bodies the hydrates part with O, but again take it up if exposed to air; they absorb gases *e.g.* NH_3 and CO_2 (*v.* Reinhart, *Fr.* 7, 187). They dissolve in acids to form ferric salts FeX_3, $X = NO_3, \frac{SO_4}{2}, \frac{PO_4}{3}$ &c. These hydrates when freshly ppd. also dissolve in $FeCl_3Aq$ forming oxychlorides (*q. v.*) (*v. Ferric oxide*, under *Iron, oxides of*, p. 62).

Soluble ferric hydrates. A modification of $Fe_2O_3.H_2O$ soluble in water was prepared by P. de Saint-Gilles in 1855 (*A. Ch.* [3] 46, 47). Ordinary ppd. $Fe_2O_3.xH_2O$ is dissolved in acetic acid, the solution is heated to 100° for a long time in a closed vessel; the blood-red colour of the liquid changes to brick red, the liquid appears opalescent in reflected light, and the taste is no longer metallic but merely that of acetic acid; on now adding conc. HClAq or HNO_3Aq, or the merest trace of H_2SO_4Aq or an alkali salt, the whole of the Fe is thrown down as a brown-red curdy pp., which, when dried on a porous tile, appears as a brown, lustrous, varnish-like solid, having the composition $Fe_2O_3.H_2O$. This modification of ferric hydrate, sometimes called *ferric metahydrate*, is insol. in conc. acids, but dissolves easily in water, forming a deep-yellow, opalescent, tasteless liquid, unchanged by K_4FeCy_6 or KCNS. Traces of H_2SO_4 or alkali salts, and also conc. HClAq or HNO_3Aq, ppt. the hydrate from its aqueous solution. The same hydrate has been obtained by Scheurer-Kestner by prolonged heating an aqueous solution of basic ferric nitrate in a sealed tube at 100° (*C. R.* 48, 1160); also by Debray by heating dilute $FeCl_3Aq$ to 100° (*C. R.* 68, 913; *cf. Ferric chloride, Reactions*,

No. 4, p. 55). Another soluble modification of ferric hydrate, sometimes called *dialysed* or *colloidal ferric hydrate*, is obtained by dialysing a solution of $FeCl_3$ containing $Fe_2O_3.xH_2O$ so long as the dialysate contains HCl (Graham, *Tr.* 1861. 183). The solution is prepared by digesting $FeCl_3Aq$ with ppd. $Fe_2O_3.xH_2O$, or by adding $(NH_4)_2CO_3Aq$ to $FeCl_3Aq$ so long as the pp. dissolves on stirring; the solution should contain 4–5 p.c. of solid matter, and have 5–6 equivalents of ferric hydrate in it. After dialysis a deep-red liquid is left on the dialyser; this liquid gelatinises by exposure to the air for some days, or by traces of H_2SO_4, alkalis, alkaline salts, but not by HCl, HNO_3, or acetic acid; the jelly-like mass thus obtained slowly becomes insol. in water, and is then sol. in dilute acids; it appears to be changed to the ordinary $Fe_2O_3.xH_2O$ (Graham, *l.c.*; *cf.* Shuttleworth, *Ph.* [3] 8, 545; Becquerel, *A.* 126, 208).

Krecke (*J. pr.* [2] 3, 286) has examined the formation of soluble ferric hydrates from $FeCl_3Aq$. Formation of the colloidal hydrate occurs in $FeCl_3Aq$ containing $\frac{1}{16}$ to $\frac{1}{8}$ p.c. $FeCl_3$ at ordinary temperatures; solutions containing 8 to 32 p.c. must be heated to above 100° in closed tubes; on cooling the more conc. solutions (if not heated too long and too highly) re-formation of $FeCl_3$ occurs, but in solutions of less than 1 p.c. the base and acid remain uncombined on cooling. If a solution containing less than 1 p.c. is boiled for some time formation of ferric metahydrate begins, and after a time the hydrate is ppd. as an orange-yellow powder. A table showing the various products obtained by heating solutions of $FeCl_3Aq$ of different concentrations to different temperatures is given under *Ferric chloride*, *Reactions*, No. 4 (p. 55).

Iron, iodides of. Only one iodide of iron, FeI_2, has been isolated with certainty.

Ferrous iodide. (*Proto-iodide of iron.*) FeI_2. H.F. $[Fe,I^2,Aq] = 47,650$ (*Th.* 3, 294). Fe and I combine by rubbing together with or without water; Fe and I heated together form a crystalline grey mass which melts at 177° (Carius a. Wanklyn, *A.* 120, 69). According to De Luca, FeI_2 is white, but goes green on addition of water (*C. R.* 55, 615). Green deliquescent crystals of $FeI_2.5H_2O$, S.G. 2·873, are obtained by digesting 1 part Fe filings with 3–4 parts I in presence of water, adding Fe filings, evaporating out of contact with air, and filtering. FeI_2, especially FeI_2Aq, rapidly absorbs O with formation of oxyiodide (*q. v.*). Addition of sugar-syrup to FeI_2 renders the solution more stable. H_2O_2Aq decomposes FeI_2 with formation of $Fe_2O_3.xH_2O$ and separation of all the I. FeI_2Aq dissolves I; addition of K_2CO_3 to a solution containing $3FeI_2{:}2I$ forms KI and $Fe_3O_4.xH_2O$; the solution may contain Fe_3I_8.

Ferric iodide. (?FeI_3.) This iodide has not been isolated; it is probably contained in a solution of FeI_2 to which I is added in the ratio $FeI_2{:}I$. FeI_2Aq containing I is separated by heating to FeI_2 and free I. Fleury (*J. Ph.* [5] 16, 529) says that the action of I on Fe in presence of water soon ceases if the temperature is kept down to 15°; on filtering, only Fe is obtained; if, however, the mixture is boiled the red colour of the liquid disappears and a considerable quantity of Fe_2O_3 is found in the residue. A large excess of I is required to dissolve all the Fe, and a large excess of Fe is required to convert all the I into FeI_2. F. supposes that FeI_3 is at first formed and is then decomposed by the heat to Fe_2O_3 and HI, and the HI then acts on the free Fe forming FeI_2. Mohr observed that a very dilute solution of $FeCl_3$ (1 in 12,300) gives a blue colour on addition of starch and KI only after a considerable time (*A.* 105, 53). Nicklès found that a solution of $Fe_2O_3.xH_2O$ in HIAq in presence of ether did not at once give a blue pp. with K_3FeCy_6 (*A. Ch.* [4] 5, 161; *cf.* Ordway, *Am. S.* [2] 26, 197). A solution made by digesting 126 parts I with sufficient iron, filtering, and adding 63 parts I, gives an apple-green pp. on addition of 201 parts citric acid previously neutralised by alkali carbonate (Creuse, *Ph.* [3] 3, 953). According to Carius a. Wanklyn (*A.* 120, 70) if Fe is heated with excess of I until a little I is vaporised, and the mass is allowed to cool in a covered crucible, I is suddenly evolved, and the residue consists of FeI_2.

Iron, nitrides of. A nitride of Fe, Fe_5N_2, is found as a silver-like lustrous deposit in the lavas of Etna (Silvestri, *P.* 157, 165); heated in H it yields Fe and NH_3. Finely-divided Fe, prepared by heating ferrous oxalate or reducing Fe_2O_3 by H, takes up about 2 p.c. N when heated in N (Geuther a. Brieglet, *A.* 133, 228; Rogstadius, *J. pr.* 86, 307; Remsen, *Am.* 3, 134). By heating Fe in NH_3 the Fe increases in weight 12–13 p.c. and becomes brittle (Berthollet, *G. A.* 30, 378). By electrolysing a mixture of NH_4Cl and a ferrous salt a lustrous deposit is obtained, supposed by Krämer to be a nitride of Fe with 1·5 p.c. N (*Ar. Ph.* [2] 105, 284), but said by Meidinger (*D. P. J.* 163, 283) to be an Fe-NH_4 amalgam. A nitride (or nitrides) of iron seems to be produced by heating $FeCl_2$ or $FeCl_3$ in NH_3. The product is a brittle, grey-white, solid; heated alone it gives N and Fe; heated in H it gives NH_3 and Fe; it is slowly and partially decomposed by boiling water; sol. in acids with formation of H, ferrous and NH_4 salts; not acted on by Cl, Br, or I in presence of H_2O at ordinary temperatures, but when heated ferric and NH_4 salts are formed, and H, and probably also N, are evolved. The formula Fe_5N_2 agrees with most of the analyses; the formula Fe_4N_2 was given by Stahlschmidt (*P.* 125, 37; *cf.* Rogstadius, *J. pr.* 86, 307; Fremy, *C. R.* 52, 321).

Iron, nitroprusside of, *v.* vol. ii. p. 340.

Iron, nitrosulphides or nitrososulphides of. In 1858 Roussin obtained a salt by the reaction of NH_4HS and KNO_2 on $FeCl_3Aq$, which contained Fe, but in which Fe could not be detected by the ordinary tests (*A. Ch.* [3] 52, 285). Proczinsky (*A.* 125, 302) obtained the same compound by adding NH_4HS to a solution of a ferrous salt saturated with NO. A similar salt was obtained by Pavel by using K_2S in place of NH_4HS (*B.* 12, 1407). By treating these salts with alkali others were obtained more or less closely related to the original salts. The compounds thus obtained were analysed and examined by Roussin (*l.c.*), Proczinsky (*l.c.*), Rosenberg (*B.* 3, 312; 12, 1715), Demel (*B.* 12, 461), and Pavel (*B.* 12, 1407, 1949; 15, 2600). Roussin's analyses of the compound formed by using

NH_4HS led to the formula $Fe_3S_5H_2(NO)_4$; to the same compound Proczinsky gave the formula $Fe_3S_3(NO)_4.2H_2O$; and Rosenberg assigned the composition $Fe_6S_5(NO)_{10}.4H_2O$. In his second paper R. showed that the compound prepared by using K_2S contained K; this was confirmed by Pavel. All the observers admitted the presence of the NO group in these compounds.

Pavel (*B.* 15, 2600) has given an account of the compounds of which Roussin's salt is the type, and has indicated what appear to be their relations to other compounds of iron. As the compounds contain the group NO in addition to S they are better called nitroso- than nitro-sulphides. Pavel regards the nitroso-sulphides of Fe as salts of acids, the acidic radicles of which are composed of Fe, NO, and S; the salts may be formulated generally as derived from the acids $H_wFe_x(NO)_yS_z$. P. compares the *ferronitroso-sulphides* with the *ferronitrosocyanides* or *nitro-prussides*, which are salts of $H_2Fe(NO)Cy_5$ (*v. Nitroprussides*, vol. ii. p. 340). According to P. there are two series of ferronitroso-sulphides derived from the two acids $HFe_4(NO)_7S_3$ (or $H_2Fe_8(NO)_{14}S_6$), and $HFe(NO)_2S$ (or $H_2Fe_2(NO)_4S_2$). The former acid has been isolated, the latter is not as yet known in the free state. The two series may perhaps be called *ferrinitroso-* and *ferronitroso-sulphides*. In the following account of the salts Pavel's formulæ are adopted:—

Series I. *Ferrinitrososulphides* $M^IFe_4(NO)_7S_3$.

Potassium ferrinitrososulphide $KFe_4(NO)_7S_3$. A solution of KHS, made from 44 grams KOH in 400 c.c. water, is added to a boiling solution of 35 grams pure $NaNO_2$ in 400 c.c. water, the mixture is heated just to boiling, and a solution of 159 grams ferrous sulphate in 1200 c.c. water, to which a drop of dilute H_2SO_4Aq has been added, is allowed to flow into it with constant stirring; the liquid is kept warm on a water-bath, and is shaken from time to time until a greenish-red pp. (of Fe_2O_3, FeO, and S) forms on the sides of the flask, when the liquid is rapidly filtered, a little dilute KOHAq is added to it when cold, and it is allowed to stand for 48 hours. The salt which separates is dissolved in water at 70°, a little KOHAq is added as the liquid cools, and the crystals thus obtained are recrystallised in the same way, after standing 48 hours; the crystals are then dried over H_2SO_4 *in vacuo* protected from the light. About 30 grams of the pure salt are thus obtained (Pavel, *B.* 15, 2601). If more KHS is used than directed above double sulphides of Fe and K are obtained and no nitrososulphide.

$KFe_4(NO)_7S_3$ crystallises in large, nearly black, lustrous, rhombic prisms; it is fairly stable in the air; decomposition begins at c. 115° with evolution of NO; at c. 130° S, $(NH_4)_2SO_3$, NH_4NO_3, &c., sublime; heated in air H_2O, NO, N, SO_2 are evolved, and the residue consists of FeS, Fe_3O_4, Fe_2O_3, and K_2SO_4; strong mineral acids evolve H_2S. Various metallic salts form metallic sulphides and NO, while Fe salts remain in solution; heated with alkali, crystalline Fe_2O_3 is ppd., NO evolved, and ferronitrososulphide $KFe(NO)_2S$ is formed (Pavel, *l.c.*). $KFe_4(NO)_7S_3$ is soluble in about 2 parts hot water, slightly sol. in cold water, very sol. with decomposition (Pavel, *B.* 12, 1410) in alcohol or ether; the salt is ppd. by NH_3Aq or KOHAq. The salts of this series do not react with K_3FeCy_6.

The following salts of this series have been isolated: NH_4X, BaX_2, CsX (the most stable salt of the series), CaX_2, FeX_2, LiX, MgX_2, RbX, TlX ($X = Fe_4(NO)_7S_3$). The Na salt is formed similarly to the K salt; also by the reaction of Na_2CS_3 with $NaNO_2$, the compound $Fe_4S(NO)_6.CS_2$ said by Löw (*C. C.* 1865. 948) to be formed in this reaction does not exist according to Pavel (*B.* 15, 2603). For other reactions of the salts of the series *v.* Pavel, *B.* 15, 2604.

Ferrinitrososulphydric acid $HFe_4(NO)_7S_3$ seems to be obtained by adding a slight excess of dilute H_2SO_4Aq to a dilute solution of the Na salt; it is insol. in water, alcohol, and ether; sol. in $CHCl_3$ or CS_2. The acid has not been obtained pure (P., *l.c.*).

Series II. *Ferronitrososulphides* $M^IFe(NO)_2S$. These salts are formed by the action of dilute alkali solutions on the salts of Series I.; in these reactions NO is evolved and Fe_2O_3 ppd., but NH_3 is not evolved except from the salt $NH_4Fe_4(NO)_7S_3$. The salts of Series II. are very unstable; they easily pass into Series I.; the Cs salt is the most unstable of all; these salts are insol. in ether (except the Fe salt), CS_2 and $CHCl_3$; they decompose in the air with separation of S and Fe_2O_3 and evolution of a little H_2S, the solutions then have an alkaline reaction, and contain salts of Series I. along with alkaline nitrite and thiosulphate. If CO_2 is passed into a solution of K_3FeCy_6 and the K salt of Series II. is then added, NO is evolved, S and Prussian blue are ppd., and the filtrate contains K_4FeCy_6 and some KNO_2.

Potassium ferronitrososulphide $KFe(NO)_2S.2H_2O$ is obtained by warming $KFe_4(NO)_7S_3$ on the water-bath with dilute KOHAq, washing, and drying *in vacuo* over H_2SO_4 and CaO in the dark; it is very unstable, and can be obtained approximately pure only with difficulty (P., *B.* 15, 2606). By warming an alcoholic solution of $KFe(NO)_2S$ with considerable excess of EtI, quickly distilling, washing the residue first with water and then with aqueous alcohol, and crystallising from benzene, *ethyl ferronitrososulphide* $(C_2H_5)Fe(NO)_2S$ is obtained in black, lustrous, monoclinic crystals (P., *l.c.*). For a discussion of the probable constitution of these nitrososulphides and a comparison of them with the nitroprussides *v.* Pavel, *B.* 15, 2613.

Iron, oxides of. Three oxides of iron have been isolated, FeO, Fe_3O_4, and Fe_2O_3. The molecular weight of none is known with certainty, as none has been gasified. FeO and Fe_2O_3 are basic oxides; they produce salts by reactions with acids, of the forms FeX_2 and FeX_3, X = Cl, NO_3, $\frac{SO_4}{2}$, $\frac{PO_4}{3}$, &c.; Fe_2O_3 also combines with some more positive metallic oxides to form compounds $Fe_2O_3.xM^{II}O$, which are usually called *ferrites* (*v.* vol. ii. p. 547). Fe_3O_4 reacts with acids to form both ferrous and ferric salts, FeX_2 and FeX_3; according to Lefort a few salts corresponding with Fe_3O_4 are known, *e.g.* Fe_3Cl_8, $Fe_3(SO_4)_4.2SO_3.15H_2O$ (*v. Ferroso-ferric oxide*, p. 61). Besides the ferrites a series of *ferrates* is known (*v.* vol. ii. p. 546); these salts are of

the form $M^I{}_2FeO_4$; they may be regarded as salts of the hypothetical ferric acid H_2FeO_4; the anhydride of this acid would be FeO_3, this oxide of iron has not been isolated, but the corresponding oxide of Mn, MnO_3, is known. All the oxides of Fe form hydrates (*v. Iron, hydrated oxides of*, p. 57). FeO very readily and rapidly absorbs O and changes to Fe_2O_3; at a very high temperature Fe_2O_3 parts with O, and is reduced to Fe_3O_4.

FERROUS OXIDE. (*Protoxide of iron.*) FeO. This oxide cannot be obtained free from Fe_2O_3 by ppn. from ferrous salts and dehydrating the pp.

Preparation.—1. Pure Fe_2O_3 is heated to c. 300° in a stream of pure H (Wackenroder a. Stromeyer, *Ar. Ph.* 36, 27).—2. By heating ferrous oxalate out of contact with air (Liebig, *A.* 95, 116; Moissan, *A. Ch.* [5] 21, 199).—3. By heating Fe_2O_3 for 20 minutes to c. 500° in H or CO, or in CO at 440° for 6 hours (Moissan, *l.c.*). 4. By heating Fe in CO_2 to c. 1000° (Moissan, *l.c.*).—5. By adding ferrous oxalate to boiling KOHAq (Böttger, *J. pr.* 76, 239).

Properties and Reactions.—An ivory-black powder. According to Moissan (*l.c.*) FeO obtained by heating ferrous oxalate, or reducing Fe_2O_3 in CO at 500°, is pyrophoric, burns to Fe_2O_3, and decomposes water at ordinary temperatures; while the FeO obtained by heating Fe in CO_2 at c. 1000° is non-pyrophoric, burns to Fe_3O_4, and does not decompose water at 100°. Siewert (*J.* 1864. 266) says that pyrophoric FeO, produced by reduction of Fe_2O_3 in H, becomes non-pyrophoric by remaining in an atmosphere of H for 12 hours after cooling. FeO is readily oxidised to Fe_2O_3 (*cf.* Moissan, *supra*). It dissolves in acids to form ferrous salts FeX_2, X = Cl, NO_3, $\frac{SO_4}{2}$, &c.

Combinations.—The compound $FeO.Al_2O_3$ occurs native as *hercynite*, and $FeO.Cr_2O_3$ as *chrome-ironstone*; magnetic oxide of iron may be regarded as $FeO.Fe_2O_3$. The hydrate $FeO.H_2O$ has been isolated (*v. Hydrate of ferrous oxide*, p. 57).

FERROSO-FERRIC OXIDE. (*Black* or *magnetic oxide of iron.*) Fe_3O_4. This oxide occurs native in large quantities as *magnetite*. According to Spring (*Bl.* [2] 50, 215) it is produced on the surface of iron which has been subjected to great pressure; the formation of a film of this oxide on iron rails is the reason why the surfaces of the rails of railroads do not rust (Spring, *l.c.*). When iron is strongly heated in air a film (*hammer-scale*) is produced consisting of Fe_3O_4, mixed with, or combined with, Fe_2O_3; the outer layer of this film contains a large quantity of Fe_2O_3, the inner layer, which is blackish-grey and magnetic, is approximately $6FeO.Fe_2O_3$ (Mosander, *P.* 6, 35; *cf.* Berthier, *A. Ch.* [2] 27, 19; Beaujen a. Mène, *C. R.* 61, 1135; Maumené, *Bl.* 16, 25; Völcker, *W. A. B.* 66, 193; Glasson, *A.* 62, 89). S.G. 5·453 (Playfair a. Joule, *C. S. Mem.* 3, 81); 5·3 at 16·5° (Herapath, *P. M.* 64, 321). S.G. of *magnetite* 5·1 to 5·18 (Kopp; Rammelsberg). According to Moissan (*A. Ch.* [5] 21, 223) two varieties of Fe_3O_4 exist, one having S.G. 4·86 obtained by reducing Fe_2O_3 at 500°, the other having S.G. 5·18 obtained by reducing Fe_2O_3 at a higher temperature. Berthelot (*A. Ch.* [5] 23, 118) describes two varieties, one with S.G. 4·86 obtained by heating $FeCO_3$ to 350°, the other with S.G 5–5·9 obtained by highly heating the first in N. *Magnetite* crystallises in regular octahedra, isomorphous with Mn_3O_4 (Rammelsberg). C.E. ·000029 (Kopp). S.H. 24°–99° ·16779 (Regnault, *A. Ch.* [3] 1, 129). H.F. $[Fe^3,O^4] = 26,900$; $[FeO,Fe^2O^3] = 8,800$ (Berthelot, *A. Ch.* [5] 23, 118).

Preparation.—1. By heating $FeCO_3$ to c. 350° in a current of CO_2 (Berthelot, *A. Ch.* [5] 23, 118).—2. By heating $FeCl_2.2NH_4Cl$ in air (Hauer, *W. A. B.* 13, 456).—3. By heating FeO in a gentle stream of HCl (Deville, *C. R.* 53, 199).—4. By melting ferric phosphate with 3–4 pts. Na_2SO_4 (Debray, *C. R.* 52, 985).—5. By melting $CaCl_2$ with ferrous sulphate in a closed crucible (Kuhlmann, *C. R.* 52, 1283).—6. By the action of FeF_3 on boric acid at a high temperature in absence of air (Deville a. Caron, *A.* 108, 56).—7. By heating $FeCl_2$ with excess of Na_2CO_3 to low redness and washing with water (Liebig a. Wöhler, *P.* 21, 582).—8. By heating Fe in steam. 9. By long-continued heating Fe_2O_3 to white-heat (Sidot, *C. R.* 69, 201).—10. By reducing Fe_2O_3 in CO at 350° for about an hour (Moissan, *A. Ch.* [5] 21, 223; *cf.* Birnie, *R. T. C.* 2, 273; Ackermann a. Särnström, *B.* 16, 783).—11. By dehydrating $Fe_3O_4.xH_2O$ at as low a temperature as possible (*v. Hydrates of ferroso-ferric oxide*, p. 57).

Properties and Reactions.—A black, magnetic powder; the crystals obtained by methods 4–7 (*supra*) are black octahedra. According to Moissan (*A. Ch.* [5] 21, 223) and Berthelot (*A. Ch.* [5] 23, 118), Fe_3O_4 obtained by heating $FeCO_3$ in CO_2 at 350°, or by reducing Fe_2O_3 by CO at 350°, or by heating reduced Fe in H saturated with H_2O, or in CO_2 at 440°, has a lower S.G. than Fe_3O_4 produced by reductions at higher temperatures, or by strongly heating the first variety in N; the first variety is said to be easily soluble in conc. HNO_3Aq, and to give Fe_2O_3 when heated on Pt foil; the second variety is described as almost unacted on by boiling conc. HNO_3Aq and as unchanged to Fe_2O_3 by heat. Fo_3O_4 is reduced to Fe by heating with C, or by strongly heating in H. With a little HClAq it gives $FeCl_2Aq$ and Fe_2O_3; with more HClAq it gives a solution showing the reactions of both ferrous and ferric chloride. According to Lefort (*C. R.* 69, 179) Fe_3Cl_8 is obtained by cooling a solution of $Fe_3O_4.xH_2O$ in excess of conc. HClAq and evaporating *in vacuo* over H_2SO_4 (*v. Ferroso-ferric chloride*, p. 56). Lefort (*l.c.*) also describes a ferroso-ferric sulphate—$Fe_3O_4.6SO_3.15H_2O$—obtained by evaporating, over H_2SO_4, solutions of Fe_3O_4 in H_2SO_4; he says that arsenates and phosphates of Fe_3O_4 also exist; the solutions of these salts are decomposed to a mixture of ferrous and ferric salts by warming to 60°–70° (for hyrates of Fe_3O_4 *v. Hydrates of ferroso-ferric oxide*, p. 57).

FERRIC OXIDE. (*Peroxide, sesquioxide, or brown oxide, of iron.*) Fe_2O_3. Occurs native in large quantities widely distributed as *red hæmatite*, *specular iron ore*, and *martite*. S.G. *native* 5·2 to 5·28 (Rammelsberg; Kopp); *calcined*, 5·135 (Playfair a. Joule, *C. S. Mem.* 3, 80); *ppd.* 5·959 at 16·5° (Herapath, *P. M.* 64, 321). S.H.

15°–98° ·16695 (Regnault, *A. Ch.* [3] 1, 129). C.E. ·00004 (Kopp). Crystallises in hexagonal forms, $a:c = 1:1·36557$ (Rammelsberg).

Preparation.—1. By ppg. a ferric salt by NH_3Aq, thoroughly washing, and strongly heating the pp.—2. By strongly heating ferrous oxalate in air; Vogel (*J. pr.* 63, 187) says this method gives a very pure product.—3. By heating ferrous carbonate in air.—4. By strongly heating ferrous sulphate in air; the product seems always to contain a little basic sulphate unless the temperature is kept very high for a long time.

The oxide is obtained in crystals by the following methods:—5. By heating a mixture of equal parts ferrous sulphate and NaCl, and washing with water; the temperature must not be too high, else some Fe_3O_4 is produced.—6. By heating Fe_2O_3 in a *slow* stream of HCl gas (Deville, *C. R.* 52, 1364); in a rapid current of HCl, $FeCl_3$ is produced.—7. By melting Fe_2O_3 with $CaCl_2$ (Kuhlmann, *C. R.* 52, 1283).—8. By the action of $FeCl_3$ vapour on strongly-heated lime (Daubré, *C. R.* 49, 143).—9. By melting Fe_2O_3 with borax and treating the fused mass with warm dilute HClAq (Hauer, *W. A. B.* 13, 456).

Properties.—A reddish-brown, very hard, non-magnetic powder; extremely hygroscopic; slightly volatile at c. 3000° (Elsner, *J. pr.* 99, 257). According to Malaguti a magnetic variety of Fe_2O_3 exists (*A. Ch.* [3] 69, 214; *cf.* Lallemand, *A. Ch.* [3] 69, 233; Lawrence Smith, *B.* 8, 183).

Reactions.—1. *Heated* to a very high temperature Fe_2O_3 is partially deoxidised to Fe_3O_4 (Sidot, *C. R.* 69, 201).—2. Reduced by heating in *hydrogen*; according to Moissan (*C. R.* 74, 1296) Fe_2O_3 (prepared from ferrous oxalate) is reduced to Fe_3O_4 by heating to 350° for an hour in H, reduced to FeO by heating to 500° for 20 minutes in H, and to Fe when heated in H at 700° (*cf.* Siewert, *J.* 1864. 265). Wright a. Luff (*C. J.* 33, 1) found that the temperature at which reduction of Fe_2O_3 by H begins varies from 195° to 260° according to the physical state of the Fe_2O_3 used.—3. Reduced by heating in *carbon monoxide*; to Fe_3O_4 at 350°, to FeO at 500°, and to Fe at 700°–800° (M., *l.c.*; *cf.* Gruner, *C. R.* 73, 28). Temperature at which reduction begins varies from 90° to 220° according to physical state of Fe_2O_3 used (W. a. L., *l.c.*).—4. Reduced by heating with *carbon* to Fe_3O_4, and then to Fe which combines with part of the C (*v. Iron, carbides of*, p. 53). Reduction begins at 430°–450° (W. a. L., *l.c.*). According to Parry (*C. N.* 27, 313) reduction of Fe_2O_3 by C in a vacuum begins at above 400°; at 1200° c. $\frac{3}{4}$ of the oxide is reduced.—5. Reduced to FeO by heating in a mixture of equal volumes of *carbon monoxide and dioxide* (Debray, *C. R.* 45, 1018).—6. A mixture of *carbon dioxide and cyanogen* (6 vols. : 1 vol.) partially reduces Fe_2O_3 to Fe at c. 600°–700° (Bell, *J.* 1874. 266).—7. Heated in *ammonia* Fe_5N_2 is produced (*v. Iron, nitrides of*, p. 59). 8. *Chlorine* forms $FeCl_3$ slowly at full red-heat (Weber, *P.* 112, 619).—9. Heated with *sulphur* SO_2 and FeS are produced (Brescius, *D. P. J.* 192, 125).—10. Heated strongly in a *rapid stream of hydrogen chloride* $FeCl_3$ and H_2O are formed (Deville, *C. R.* 52, 1264).—11. *Sulphuretted hydrogen* does not act on dry Fe_2O_3; with moist Fe_2O_3 ($Fe_2O_3.xH_2O$) FeS, S, and H_2O are formed (Wright, *C. J.* 43, 156; Brescius, *D. P. J.* 192, 125).—12. *Phosphoric chloride* produces $FeCl_3$ which then combines with part of the PCl_5 forming $FeCl_3.PCl_5$ (Weber, *J. pr.* 76, 410).—13. Fe_2O_3 is slowly dissolved by *acids*, the more slowly the denser the specimen of Fe_2O_3; most easily dissolved by 16 times its weight of a boiling mixture of 8 pts. H_2SO_4 and 3 pts. H_2O (Mitscherlich, *J. pr.* 81, 108). After strongly heating with alkalis, alkaline carbonates, or acid sulphates, Fe_2O_3 is readily dissolved by acids.—14. Fe_2O_3 readily parts with O when heated with *oxidisable organic compounds*, on exposure to air O is again taken up (Robin, *C. R.* 49, 500; Gräger, *A.* 111, 124). Moist Fe_2O_3 ($Fe_2O_3.xH_2O$) in presence of ordinary air serves as an oxidiser of various vegetable matters, *e.g.* wood (Kuhlmann, *D. P. J.* 155, 31; *cf.* P. Thénard, *C. R.* 49, 289).

Combinations.—1. Fe_2O_3 is extremely hygroscopic; it forms several hydrates by combining with *water*. For conditions of formation, composition, and properties *v. Hydrates of ferric oxide*, p. 57.—2. With some more *positive metallic oxides* to form *ferrites* (*q.v.* in vol. ii. p. 547).

Hypothetical ferric anhydride. (?FeO_3). This oxide has not been isolated, but a number of salts are known, which are best regarded as derived from the hypothetical acid H_2FeO_4, of which FeO_3 would be the anhydride. These salts are described under the heading Ferrates (vol. ii. p. 546). In addition to the descriptions there given it is to be noted that when air is blown into hot conc. NaOHAq containing c. 34 p.c. NaOH, a perceptible quantity of Fe is dissolved to form a colourless liquid, from which $Fe_2O_3.xH_2O$ slowly separates (Zirnité, *Chem. Zeitung*, 12, 355); possibly the solution contains a ferrate of Na, or, according to the suggestion of Z., a perferrate $NaFeO_4$ (?).

Iron, oxybromides of. Oxybromides of Fe are said to be formed by evaporating $FeBr_3$Aq, and by the action of $Fe_2O_3.xH_2O$ on $FeBr_3$Aq or HBrAq (Ordway, *J. pr.* 76, 19; Béchamp, *A. Ch.* [3] 57, 296; Scheufelen, *A.* 231, 157).

Iron, oxychlorides of. The oxychlorides of Fe are numerous and of complex composition; they belong to the form $xFeCl_3.yFe_2O_3.zH_2O$. They are divided into two classes, those which are soluble in water, and those which are insoluble.

Soluble oxychlorides. Prepared by digesting freshly ppd. $Fe_2O_3.xH_2O$ in $FeCl_3$Aq; also by digesting excess of $Fe_2O_3.xH_2O$ in HClAq. By the former method Ordway obtained $2FeCl_3.23Fe_2O_3$ (*J. pr.* 76, 19). By the second method Béchamp (*A. Ch.* [3] 51, 296) obtained liquids containing $FeCl_3$ and Fe_2O_3 in ratio 2:5, 1:3, 1:4, and 1:5. All these solutions evaporated at c. 40° give residues soluble in water; solutions containing more Fe_2O_3 than the foregoing (up to $10Fe_2O_3$) give residues on evaporation which are insol. in water. Solutions of soluble oxychlorides are not decomposed by dilution or heating, but addition of various acids and salts causes ppn. of $Fe_2O_3.xH_2O$, mixed with oxychlorides, which are soluble in water. From solutions of soluble oxychlorides NH_3Aq ppts. $Fe_2O_3.xH_2O$ free from chloride, whereas the pp. obtained from the insol. oxychlorides contains chloride.

Insoluble oxychlorides. Prepared by oxidation of $FeCl_2Aq$, by exposure to air or by HNO_3 in presence of a little HCl (Béchamp, *l.c.*). To saturated $FeCl_2Aq$, HCl is added in less proportion than 3HCl to $FeCl_2$; the solution is heated to 100°, and HNO_3Aq is gradually added; a violent reaction occurs, the nearly black liquid becomes yellow, and oxychlorides separate which are insol. in water. The composition of these oxychlorides varies according to the temperature and the proportion of HCl used. Insol. oxychlorides are also formed by adding alkali to $FeCl_3Aq$ in quantity insufficient for complete ppn. These oxychlorides vary in colour from yellow to brown; they are slowly soluble in HClAq; when heated they lose H_2O and HCl.

Iron, oxyfluoride of. By adding NH_3Aq to a solution of FeF_3 a yellow salt of the composition $2FeF_3.3Fe_2O_3.4H_2O$ is obtained (Deville, *A. Ch.* [3] 49, 85).

Iron, oxysulphide of. According to Rammelsberg (*P.* 121, 339) the product obtained by heating Fe_2O_3 in H_2S gas to near redness is $3Fe_2S_3.Fe_2O_3$.

Iron, reduced. *Ferrum redactum.* Very finely divided Fe is obtained by reducing Fe_2O_3 in a stream of pure H. Reduced iron is very readily oxidised; commercial specimens generally contain 40 p.c. or more of oxide.

Iron, phosphides of. Meyer in 1780, and Bergmann somewhat later, obtained a phosphide of Fe; supposing it to be a new metal they called it *Hydrosiderum* (*Berl. Ges. d. naturforsch. Freunde* [1781] 2, 334; Bergmann's *Opusc.* 3, 109). Several Fe phosphides have been described. According to Freese (*P.* 132, 225) only three exist, Fe_3P_4, FeP, and Fe_2P. They are non-magnetic and almost infusible; unchanged by cold HClAq, slowly acted on by boiling HClAq giving $\frac{3}{8}$ of their P as phosphoric acid and $\frac{5}{8}$ as PH_3; oxidised at ordinary temperature by HNO_3 and *aqua regia*.

Fe_3P_4. By heating FeS_2 in PH_3 gas (H. Rose, *P.* 6, 212; 24, 333); also by heating reduced Fe or $FeCl_2$ in PH_3 (Freese, *l.c.*). A blue-grey powder, S.G. 5·04; loses P by heating in H or CO, probably forming FeP.

FeP. By heating FeS in PH_3 for a long time (Freese, *l.c.*); also by passing a mixture of H and P vapour over strongly-heated Fe_2O_3, and by the action of PH_3 on $FeCl_3$ (H. Rose, *l.c.*). A black crystalline mass; not acted on by HNO_3 or HClAq, nor by I.

Fe_2P. 7 parts dry $FePO_4$ with 1 part lampblack are covered with a layer of NaCl and heated to whiteness, and the fused mass is treated with HClAq; Fe_2P remains as a grey crystalline solid; S.G. 5·74; unchanged by heating in H, CO, or CO_2 (Freese, *l.c.*).

The following phosphides have been described in addition to those mentioned; according to Freese they are not definite compounds:—Fe_3P (Hvoslef, *A.* 100, 99); Fe_3P_2 (Schenk, *C. J.* [2] 11, 826); Fe_4P_3 (Struve, *J. pr.* 79, 321); FeP_8 (Sidot, *C. R.* 74, 1425).

Iron, salts of. Two series of Fe salts, obtained by replacing H of acids by Fe, are known; *ferrous* salts FeX_2, and *ferric* salts FeX_3 (X = Cl, &c., NO_3, &c., $\frac{SO_4}{2}$, &c., $\frac{PO_4}{3}$, &c.). The ferric salts are the more stable; as a class ferrous salts are readily oxidised to FeX_3. Both series contain many well-marked and very definite compounds. Lefort (*C. R.* 69, 179) asserts the existence of a few salts, *e.g.* chloride, sulphate, phosphate, corresponding to Fe_3O_4 (*v. Ferroso-ferric oxide*, p. 61). Ferrous salts are usually obtained by dissolving Fe in various acids, or in the cases of the insol. salts by double decomposition from $FeSO_4$; they are for the most part sol. in water; a few basic ferrous salts are known, but the greater number are normal salts. Many double ferrous salts, especially with the alkali sulphates, have been isolated; many ferrous salts are isomorphous with the corresponding salts of Co, Ni, Mn, Zn, and Mg. A double ferrous-aluminium sulphate, $FeSO_4, Al_23SO_4.24H_2O$, is said to exist and to be isomorphous with the alums. Ferric salts are generally prepared by dissolving $Fe_2O_3.xH_2O$ in the different acids; many basic, and numerous double, ferric salts are known; the double salt $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$ belongs to the class of alums. The ferric salts are generally analogous to the persalts of Al, Cr, Co, Ni, and Mn (*cf.* IRON GROUP OF ELEMENTS). The following list comprises the more important salts of Fe derived from oxyacids; for details *v.* CARBONATES, NITRATES, SULPHATES, &c.: *antimonates*, *arsenates* and *-ites*, *borates*, *bromates*, *carbonates*, *chlorates*, *chromates*, *hypophosphite*, *iodates*, *molybdates*, *niobates*, *nitrates*, *perchlorates*, *periodates*, *phosphates* and *-ites*, *selenates* and *-ites*, *silicates*, *sulphates* and *-ites*, *tantalates*, *tellurates* and *-ites*, *thiosulphates*, *titanates*, *tungstates*, *vanadates*.

Iron, selenides of. Selenides of Fe seem to be obtained (1) by passing Se vapour over strongly-heated Fe; (2) by heating the product obtained in (1) with Se (Berzelius); (3) by method (2) covering the mass with borax, Little (*A.* 112, 211) obtained Fe_2Se_3 thus, S.G. 6·38; (4) by ppg. Fe salts by H_2Se (Reeb, *J. Ph.* [4] 9, 173). By heating Fe filings with Se to redness Divers a. Shimidzu (*C. J.* 47, 441) obtained FeSe, resembling FeS in appearance; with acids yields H_2Se.

Iron, selenocyanides of. None has been isolated; Crookes (*C. J.* 4, 12) mentions various reactions which do not yield a definite salt.

Iron, silicide of. It is doubtful whether any definite compound has been isolated. Silicides are apparently formed (1) by heating Fe with Si (Deville a. Caron, *C. R.* 45, 163); (2) by the action of molten Fe on silicates. Hahn (*A.* 129, 57) obtained a body approximately Fe_4Si by fusing 60 parts Na_2SiF_6, 20 parts Na, 60 parts Zn, and 22 parts steel, under NaCl. Other bodies, approximately Fe_2Si and $Fe_{10}Si_9$, are described by Deville a. Caron (*l.c.*) and Hahn (*l.c.*; *cf.* Boussingault, *A. Ch.* [3] 16, 15).

Iron, silicofluoride of, $FeSiF_6$; *v. Ferrous fluoride*, p. 56.

Iron, sulphocyanides of, *v.* vol. ii. p. 350.

Iron, telluride of. Produced by reducing ferrous tellurite in H (Berzelius).

Iron, sulphides of. Four are known, FeS, Fe_3S_4, Fe_2S_3, and FeS_2; a subsulphide, Fe_2S, also probably exists. According to Gautier a. Hallopeau (*C. R.* 108, 806) a yellow-grey lustrous body, Fe_4S_3, is formed by heating Fe in CS_2 for several hours at 1300°–1400°.

IRON SUBSULPHIDE Fe_2S. Said by Arfvedson

(*P.* 1, 72) to be produced, as a greyish-black powder, by heating dry $FeSO_4$ in H.

Ferrous sulphide FeS. (*Iron monosulphide* or *protosulphide.*) Occurs sometimes in meteorites; also in combination with NiS.

Formation.—1. By heating FeS_2 with Fe until the mass is thoroughly molten.—2. By reducing FeS_2 in H.—3. By the reduction of Fe_2O_3 or ferric salts by decomposing organic matter in presence of sulphates (Chevreul, *C. R.* 43, 218). 4. By gently heating a mixture 1 part S with $1\frac{3}{4}$ parts Fe filings moistened with water; if a considerable quantity of such a mixture is made into a paste with water and covered with earth, the mass after a time becomes red hot and evolves much steam which throws up the earth with some violence.—5. By strongly heating Fe_2O_3 or a ferric salt in H_2S (Sidot, *C. R.* 66, 1257; *cf.* Carnot, *Bl.* [2] 32, 162).—6. By heating a mixture of Fe_2O_3 and S in H (Rose, *P.* 110, 120).—7. By heating to redness a mixture of Fe_2O_3 and excess of $Na_2S_2O_3$ (Gibbs, *Am. S.* [2] 37, 346).

Preparation.—1. A mixture of 3 parts Fe filings and 2 parts S is strongly heated in a covered crucible until the whole mass is thoroughly melted; if the temperature is not high enough some Fe remains and some Fe_2S_3 is formed.—2. A white-hot rod of iron is plunged into molten S; the FeS formed flows off; the operation is repeated as long as any S remains (Gahn; Rammelsberg, *B. B.* 1862. 681).—3. By ppg. a ferrous salt by an alkali sulphide, preferably NH_4 sulphide.

Properties.—FeS prepared in the dry way is yellow-brown, lustrous, metal-like solid, crystallising in hexagonal prisms, S.G. 4·69. Non-magnetic; not changed by heating out of contact with air or in H. FeS prepared in the wet way is an amorphous, greenish-black powder, which on gently heating in air is partly changed to $FeSO_4$; it is slightly soluble in water. By ppg. FeS in a very dilute solution, and then dialysing away the other products of the reaction, Winssinger (*Bl.* [2] 49, 452) obtained a very dilute solution of colloidal FeS; the solution was greenish-brown, oxidised and coagulated very readily.

Reactions.—FeS prepared in dry way: 1. Heated in *hydrogen*, or *out of contact with air*, is unchanged.—2. Heated in *steam* evolves H and H_2S, and leaves a black magnetic mass containing Fe_3O_4 (Regnault, *A. Ch.* [3] 62, 379).—3. Heated strongly in *air* forms Fe_2O_3 and SO_2.—4. With dilute *hydrochloric* or *sulphuric acid* evolves H_2S, and forms $FeCl_2$ or $FeSO_4$.—5. Oxidised by *nitric acid.*—6. Heated with *chlorine* from S_2Cl_2 and $FeCl_3$.

FeS prepared in the wet way: 7. Oxidises in *air* at ordinary temperature, forming $Fe_2O_3.xH_2O$, S, and a little basic Fe sulphate (Wagner, *D. P. J.* 192, 131).—8. Slightly soluble in *water*; re-ppd. by NH_4HS.—9. Soluble in *sulphurous acid* solution, also in *potassium cyanide* solution (Goueront, *C. R.* 75, 1276).—10. Slightly soluble in solutions of *alkaline sulphides.*—11. Very easily decomposed by *acids*, with evolution of H_2S.

Ferroso-ferric sulphide Fe_3S_4. (*Magnetic sulphide of iron.*) Occurs native as *magnetic pyrites* in hexagonal crystals, S.G. 4·51 to 4·64; the composition may be expressed as $xFeS.Fe_2S_3$, x is very seldom = 1, generally = 5 and 6. The first product of the action of H_2S on strongly heated Fe_3O_4 is Fe_3S_4, but this decomposes to FeS (Sidot, *C. R.* 66, 1257).

Ferric sulphide Fe_2S_3. (*Sesquisulphide of iron.*) By heating a mixture of powdered FeS and S to redness, or by passing H_2S over Fe_2O_3 at 100° (Berzelius, *P.* 7, 393). A greenish-yellow mass; magnetic according to Proust (*Scher. J.* 10, 54); non-magnetic according to Berzelius (*l.c.*). When heated, gives Fe_3S_4; when moist soon changes to a mixture of S and Fe_2O_3; decomposed by dilute acids forming ferrous salts, H_2S, and $H_2S.xS$.

Combines with Fe_2O_3 when heated with it. The product of the reaction of H_2S on Fe_2O_3 at somewhat above 100° is $Fe_2O_3.3Fe_2S_3$ according to Rammelsberg (*P.* 121, 337). Combines with CuS to form $CuS.Fe_2S_3$; also with K_2S, Na_2S, Ag_2S. These compounds may be regarded as *sulphoferrites*; they belong to the form $M^I_2Fe_2S_4$, and are produced by fusing 1 part Fe filings with 5–6 parts S and 5–6 parts alkaline carbonate; the Ag salt is obtained by adding $AgNO_3$ to the K salt suspended in water (*v.* Schneider, *P.* 136, 460; Preis, *J. pr.* 107, 10). Fe_2S_3 is said to form a hydrate, $Fe_2S_3.3H_2O$, a greenish-black pp. obtained by adding NH_4HSAq to a ferric solution containing an oxidiser such as Cl or a hypochlorite (Phipson, *C. N.* 30, 139).

Iron disulphide FeS_2. (*Iron pyrites.*)

Occurrence.—In large quantities; in regular crystals as *yellow pyrites*, and in rhombic crystals as *white pyrites.*

Formation.—1. By slowly heating a mixture of Fe_2O_3, S, and NH_4Cl (Wöhler, *P.* 37, 238).—2. By the action of CS_2 on Fe_2O_3 (Schlagdenhauffen, *J. Ph.* [3] 34, 175).—3. By heating Fe, or Fe_2O_3, with SO_2Aq in a sealed tube to 200° (Geitner, *A.* 129, 350).—4. By passing H_2S over an oxide or chloride of Fe at a temperature above 100° but below redness.—5. By the action of organic matter on water containing Fe and sulphates in solution.—6. Glatzel (*B.* 23, 37) obtained crystals of FeS_2 by strongly heating $FeCl_3$ with P_2S_5.

Preparation.—1. An intimate mixture of 2 parts FeS and 1 part S, or of 1 part Fe with $1\frac{1}{4}$ parts S, is heated in a retort to a temperature somewhat under red heat, and the product is treated with dilute HClAq (Berzelius); below 100° the chief product is Fe_2S_3, and at red heat Fe_3S_4 is formed.—2. By mixing an alkaline persulphide solution with $FeCl_2Aq$ at 180° or with $FeSO_4Aq$ at 165° (Senarmont, *A. Ch.* [3] 30, 129).

Properties.—A bulky dark-yellow powder, or crystallised in small brass-yellow cubes and octahedra. Not magnetic. The rhombic form of FeS_2 oxidises in moist air forming $FeSO_4$, S, and H_2SO_4.

Reactions.—1. White iron pyrites, finely-divided yellow pyrites, or FeS_2 prepared in the wet way, oxidise in *air*, forming chiefly $FeSO_4$, and at higher temperatures SO_2 and Fe_2O_3.—2. Calcined with *carbon*, gives CS_2.—3. Not acted on by *dilute acids*; but decomposed by *conc. hydrochloric acid*, giving H_2S and S.—4. Oxidised by heating with *conc. nitric acid.*

M. M. P. M.

IRON ALUMS

K_2[or $(NH_4)_2$]$SO_4.Fe_2(SO_4)_3.24H_2O$, *v.* Alums, vol. i. p. 148; and Sulphates. M. M. P. M.

IRON GROUP OF ELEMENTS. The four elements, IRON, NICKEL, COBALT, and MANGANESE, are more or less closely connected. Fe, Ni, and Co occur in meteorites, some of which also contain minute quantities of Mn. The chief ores of Fe and Mn are oxides, carbonates, and sulphides, of Ni and Co sulphides and arsenides. Fe has been known and used for ages; Ni, Co, and Mn have been known from about the middle of the eighteenth century. The name *iron* is probably a form of the Sanscrit word *ayas* (=metal); the names *nickel* and *cobalt* are derived from terms used by miners in the Middle Ages to express false or spurious metals, or minerals from which no useful metals could be obtained; *manganese* is said to be a corruption from *magnesia nigra*, a name long given to the mineral pyrolusite. Compounds of Fe occur in large quantities, widely distributed; compounds of Mn are not so common, nor so widely distributed; and compounds of Ni and Co occur only sparingly. Fe, Ni, Co, and Mn are obtained by reducing the oxides with charcoal at high temperatures. The metals are all hard, lustrous, fairly malleable and ductile; they crystallise in the regular system; they are more or less magnetic; they are unacted on by dry air, but oxidise slowly in moist air; they decompose steam, and react with acids to form salts. The following table presents some of the characteristic properties of the four metals:—

	MANGANESE	IRON	NICKEL	COBALT
Atomic weights.	55	55·9	58·6	58·8
	One compound of Mn ($MnCl_2$), and two of Fe ($FeCl_2$ and $FeCl_3$) have been gasified; no Ni or Co compounds have been gasified; specific heats of the four metals have been directly determined. Molecular weights unknown.			
Melting-points (approx.)	1800°–1900°	1600°	1500°	1500°
Spec. gravs. (approx.)	8	7·8	8·9	8·6
Atom. weight. / *Spec. grav.* (approx.)	6·9	7·2	6·6	6·8
Occurrence and Preparation.	Occurs chiefly as MnO_2. Obtained by reducing the oxides by C at a high temperature; Also by reducing the chloride or fluoride by Na.	Chiefly as Fe_2O_3, Fe_3O_4, and $FeCO_3$. Obtained by reducing Fe_2O_3 by C, or CO, at a high temperature; also by reducing Fe_2O_3 or Fe_3O_4 in H, and by electrolysis of $FeSO_4Aq$.	Chiefly as NiAs and NiAsS. Obtained by reducing Ni_2O_3 by C at a high temperature, or by heating in H.	Chiefly as $CoAs_2$, and CoAsS. Obtained by reducing Co_3O_4 by heating with C or in H.
Physical properties.	Greyish - white, brittle, very hard, lustrous, magnetic. Melts above M.P. of Fe.	Lustrous, greyish-white, very tenacious; crystallises in regular cubes and octahedra; magnetic. Ordinary iron, containing from ·2 to ·5 p.c. C, is very hard, malleable, and fairly ductile. Fe obtained by reduction of Fe_3O_4 in H below 600° is pyrophoric. By electrolysis of $FeSO_4Aq$ a soft, amorphous, brittle mass is obtained.	Silver-white, very tenacious, hard, ductile, malleable; magnetic up to c. 250°; crystallises in regular cubes and octahedra.	Steel-grey, lustrous, hard, very ductile at red heat and upwards; somewhat malleable; magnetic; crystallises in regular cubes and octahedra.
Chemical properties.	Oxidises easily in air; Mn obtained by reducing chloride by Na is said not to tarnish in ordinary air. Oxidised by heating in air. Decomposes steam; said to decompose	Unchanged in dry air; in moist air forms $Fe_2O_3.xH_2O$; heated in air or O, burns to Fe_3O_4 and Fe_2O_3. Decomposes steam, forming Fe_3O_4 and H. Dissolves in dilute acids, almost in-	Unchanged in ordinary air; heated in air or O burns to NiO or Ni_2O_3 according to the temperature. Decomposes steam at red heat. Dissolves in dilute acids, but is unacted on by	Unchanged in ordinary air; heated in air or O burns to Co_3O_4. Decomposes steam at red heat; decomposes NH_3 to N and H. Dissolves in dilute acids, but is unacted on by

TABLE—*continued.*

	MANGANESE	IRON	NICKEL	COBALT
	cold water slowly. Dissolves in dilute acids; hardly acted on by cold conc. H_2SO_4. Combines directly with Cl and Br. No simple cyanide of Mn is known; but the acid H_4MnCy_6 and salts derived from it, and also salts of the hypothetical acid H_3MnCy_6, have been isolated. With acids forms two series of salts, MnX_2 and MnX_3, of which the manganous salts ($X = Cl, \frac{SO_4}{2}$, &c.) are the more stable. Besides the oxides corresponding to the salts (MnO and Mn_2O_3) other acidic oxides, MnO_3 and Mn_2O_7, have been isolated; the acid $HMnO_4$, and numerous salts of this acid, are known; salts of the hypothetical acid H_2MnO_4 are also numerous. Atom of Mn is divalent in the gaseous molecule $MnCl_2$.	sol. in cold conc. H_2SO_4; unacted on by cold conc. HNO_3. Combines directly with Cl, Br, and I; also with C, and probably with H and N. No simple cyanide is known, but a large nnmber of ferro- and ferri-cyanides, and also the acids H_4FeCy_6 and H_3FeCy_6, have been isolated. Some ammonio-compounds are known. Reacts with acids to form two series of salts, FeX_2 and FeX_3, of which the ferric salts ($X = Cl, \frac{SO_4}{2}$, &c.) are the more stable. Ferrates, $M^I_2FeO_4$, are also known, but neither the corresponding acid nor anhydride has been isolated. Atom of Fe appears to be divalent and trivalent in gaseous molecules ($FeCl_2$ and $FeCl_3$); perhaps also tetravalent (Fe_2Cl_4 and Fe_2Cl_6).	cold conc. HNO_3. Combines directly with Cl, Br, and I. Probably forms a nitride by heating NiO in NH_3. $NiCy_2$ and many double cyanides are known, but no acids or salts corresponding with ferro-, ferri-, mangano-, and mangani-cyanides have been isolated. Some ammonio-compounds are known. With acids forms two series of salts, NiX_2 and NiX_3, of which the nickelous salts ($X = Cl, \frac{SO_4}{2}$, &c.) are much the more stable. No salts in which Ni forms part of the acidic radicle have yet been certainly isolated.	cold conc. HNO_3. Combines directly with Cl, Br, and I; also probably with C. $CoCy_2$ is known; also the acids H_4CoCy_6 and H_3CoCy_6, and many salts derived therefrom. Very many ammonio-compounds are known. With acids forms two series of salts, CoX_2 and CoX_3, of which the cobaltous salts ($X = Cl, \frac{SO_4}{2}$, &c.) are much the more stable. By the action of molten KOH on CoO a salt is obtained in which Co seems to form part of the negative radicle.

General formulæ and character of compounds.—Oxides.—MO, M_3O_4, M_2O_3; also MnO_2, MnO_3, Mn_2O_7. Sulphides.—MS, M_3S_4, M_2S_3, MS_2. Haloid compounds.—MX_2 or M_2X_4; also FeX_3 or Fe_2X_6; ? $MnCl_3$, ? $MnCl_4$. Salts.—MX_2 and MX_3, $X = NO_3, \frac{SO_4}{2}, \frac{PO_4}{3}$, &c. Salts containing M in the acidic radicle.—$M^I_2MO_4$, where M = Mn or Fe; also M^IMnO_4 (? $NaFeO_4$); also $xMO.yFe_2O_3$, where M = decidedly positive metal. Acids.—$HMnO_4$.

The *oxides* MO are basic. They react with acids to form salts MX_2. MnO and FeO are readily oxidised by standing in air, FeO very rapidly. NiO and CoO, on the other hand, are obtained by heating the higher oxides in air. The oxides M_2O_3 are basic, forming salts MX_3. In the case of Mn only a few salts corresponding to M_2O_3 are known, *e.g.* $Mn_2(SO_4)_3$. In the cases of Ni and Co the salts of M_2O_3 are hardly known; the oxides dissolve in cold conc. acids, probably forming salts; but on warming salts of MO are obtained. Both Fe_2O_3 and Mn_2O_3 show feebly acidic properties, as they combine with some more basic oxides, *e.g.* CaO, BaO, ZnO. The oxides M_3O_4 react with acids, for the most part, as compounds of MO with M_2O_3. Fe_3O_4, however, is said to produce a few corresponding salts, *e.g.* Fe_3Cl_8 and $Fe_3(SO_4)_4$. It is doubtful whether MnO_2 form any corresponding salts; with acids it usually evolves O, and forms manganous salts MnX_2. It combines with several more positive oxides, *e.g.* CaO or BaO, to form compounds $xM^{II}O.yMnO_2$. MnO_3 and Mn_2O_7 are extremely unstable acidic oxides. The acid of Mn_2O_7, *viz.* $HMnO_4$ or $H_2Mn_2O_8$, is known, and from it a large series of salts has been obtained. The acid of MnO_3 (H_2MnO_4) has not been isolated; but the manganates $M^I_2MnO_4$ are well-known salts. Ferrates, $M^I_2FeO_4$, corresponding to the manganates, are known, although neither the acid H_2FeO_4 nor the anhydride FeO_3 has been isolated.

The *sulphides* MS are basic; but MnS shows slightly acidic properties. MnS forms a compound with the very positive K_2S ($K_2S.3MnS$); CoS, on the other hand, combines with the slightly negative As_2S_3 ($2CoS.As_2S_3$). Fe_2S_3 forms compounds with Ag_2S, CuS, &c., which may be regarded as sulphoferrites.

The *haloid compounds* MX_2 or M_2X_4 are generally formed by direct union of the elements, also by dissolving the oxides MO in the haloid acids HX and evaporating. Fe is the only member of the group which certainly forms haloid compounds containing more halogen than MX_2. There are, however, indications of the existence of $MnCl_3$, and $MnCl_4$. The haloid compounds which have been gasified are $MnCl_2$, $FeCl_2$, and $FeCl_3$. There are no indications of the existence of gaseous molecules Mn_2Cl_4; but the V.D.s of ferrous and ferric chlorides point to the existence of the gaseous molecules $FeCl_2$ and $FeCl_3$ at high temperatures, and Fe_2Cl_4 and Fe_2Cl_6 at lower temperatures.

The *salts* of the metals of the iron group belong to the series MX_2 and MX_3, where $X = NO_3$, ClO_3, $\frac{1}{2}SO_4$, $\frac{1}{2}CO_3$, $\frac{1}{3}PO_4$, &c. Fe forms many salts of both series; Mn forms chiefly manganous salts MnX_2, but a few manganic salts are known, *e.g.* $Mn_2(SO_4)_3$; Ni forms only nickelous salts NiX_2. The cobaltic salts are represented by a few double salts, *e.g.* $Co(NO_2)_3.3KNO_2$; but the cobaltous salts are numerous. Ferrous salts are perfectly definite, but are fairly easily oxidised to ferric. Ferric and manganic sulphates form alums, $K_2SO_4.Fe_2(\text{or } Mn_2)(SO_4)_3.24H_2O$. Many of the salts MX_2 are isomorphous with the corresponding salts of Cu, Zn, Mg, and Cd.

The only member of the series which forms *acidic oxides* that have been isolated is Mn (*v. supra*). Permanganic acid, $HMnO_4$, has also been isolated, but no oxyacid of Fe, Ni, or Co.

The iron elements exhibit analogies with several other families of elements. Their relations with the elements of Group III., especially with Al, Ga, and In, are shown in the composition of the salts MX_3; in the existence of alums, *e.g.* $K_2SO_4.M_2(SO_4)_3.24H_2O$, where M = Al, Ga, In, Fe, or Mn; also in the existence and dissociation of the gaseous molecules Fe_2Cl_6, Al_2Cl_6, and Ga_2Cl_6. The analogies shown by Ni and Co to the Al family are very slight.

The iron family is distantly connected with the halogens. This is shown in the existence of the salts M^IMO_4, where M = Mn (? Fe), Cl, or I.

The relations between the iron family and the chromium family of Group VI are fairly well marked; the MX_3 salts are similar to the CrX_3 salts; MnO_3 resembles CrO_3 in being acidic and forming salts $M^I_2MnO_4$, analogous to and isomorphous with the chromates. Ferrates, $M^I_2FeO_4$, are also known, although neither FeO_3 nor H_2FeO_4 has been isolated. MnO_2 is not unlike CrO_2 in some of its reactions. The sulpho-ferrites, *e.g.* $CuFe_2S_4$, resemble the sulpho-chromites, *e.g.* $ZnCr_2S_4$. The relations of Ni and Co to the Cr family are chiefly shown in the formulæ of the nickelous, cobaltous, and chromous salts, MX_2; in the existence of many ammonio-cobalt and ammonio-chromium compounds. The formation of the cyanogen acid H_4MCy_6, and of salts of H_3MCy_6, where M = Mn, Fe, Co, or Cr, is a point of similarity between Cr and the iron family.

The composition of the salts MX_2 is similar to that of the salts of Group II.; so far as properties go these salts most resemble those of the odd series members of Group II., Mg, Zn, and Cd; the ammonio-compounds of Co also recall the ammonio-compounds of Hg which is an odd-series member of Group II.

There are some resemblances between Cu which belongs to Group I. and the iron elements; thus the salts MX_2 resemble in many respects the cupric salts CuX_2; there are many ammonio-copper compounds; numerous double cyanides of Cu exist and some of those are probably derived from a cyanogen acid $H_2Cu_2Cy_4$.

Finally some of the physical properties of the iron family resemble the properties of the two other families of Group VIII., viz. Rh, Ru, Pd, and Os, Ir, Pt; this resemblance is carried out in the formulæ of some of the salts, and in the existence, and in some cases the composition and properties, of numerous complex cyanides; these complex cyanides are indicated in the following table:—

H_4MCy_6 and salts.	H_3MCy_6 and salts.
M = Mn, Fe, Co; Os, Ru	M = Fe, Co; Ir

Salts of H_3MCy_6 (acid not isolated).
M = Mn, Rh.

The acid H_2PtCy_4 and salts of this acid exist; salts of H_2PdCy_4 are known. It should be noted that Ni does not form nickelo- or nickeli-cyanides analogous to any of the complex cyanides formulated above, but only ordinary double cyanides.

The position of the iron family of elements in the classification based on the periodic law is somewhat peculiar (*v.* Table on p. 204 of vol. ii.) Mn is placed in the even series of Group VII.; the only other members of this group as yet known are the halogens. Fe, Ni, and Co form a division, or family, of Group VIII.; the other families of this group are (1) Rh, Ru, Pd, and (2) Os, Ir, Pt. The iron family should therefore, strictly, include only Fe, Ni, and Co; Mn has been included in this family because of its close relations to Fe; but because of its position in Group VII., Mn has also been included in the halogen family (*v.* HALOGEN ELEMENTS, vol. ii. p. 664). Each of the three families which together constitute Group VIII. is separated from the others by many elements; the analogies between these families cannot be very close. The iron family is preceded in order of atomic weights by a series of elements, which begins with the very positive element K and ends with the element Cr which is both metallic and non-metallic; the iron family is succeeded by series 5 which begins with the undoubtedly metallic Cu and ends with the no less undoubted non-metal Br. The iron family forms one of the turning-points in the swing of properties from very positive to very negative; the next similar turning-point is marked by the second family of Group VIII., Rh, Ru, Pd; and the third turning-point is marked by the last family of Group VIII., Os, Ir, Pt. Recent researches show that Co and Ni are probably separable each into two other elements, *v.* NICKEL in this volume. In connection with this article *v.* CHROMIUM GROUP OF ELEMENTS, vol. ii. p. 168; COPPER GROUP OF ELEMENTS, vol. ii. p. 250; EARTHS, METALS OF THE, vol. ii. p. 424; HALOGEN ELEMENTS, vol. ii. p. 664; NOBLE METALS, in this vol. For detailed properties of the members of the iron group *v.* COBALT, vol. ii. p. 217; IRON, this vol. p. 51; MANGANESE and NICKEL, in this vol.

M. M. P. M.

ISAMIC ACID *v.* Isatin.

ISATANE *v.* Isatyde.

ISATIC ACID $C_8H_7NO_3$ *i.e.* $C_6H_4(NH_2).CO.CO_2H$. *o-Amido-phenyl-glyoxylic acid.* Formed, as potassium salt, by boiling isatin with conc. KOHAq (Laurent, *A. Ch.* [3] 3, 371; Erdmann, *J. pr.* 24, 13). Obtained synthetically by reduction of an alkaline solution of o-nitro-phenyl-glyoxylic acid with ferrous sulphate (Claisen a. Shadwell, *B.* 12, 353). By decomposing the lead salt with H_2S and evaporating at atmospheric temperature *in vacuo* isatic acid may be obtained as an amorphous white powder, soluble in cold water. The acidified solution deposits, after a while, crystals of isatin, which is its anhydride, and the separation may be hastened by warming. With acetone in alkaline solution isatic acid forms (*Py.* 3)-methyl-quinoline (*Py.* 1)-carboxylic acid [241°]. Its silver salt forms microscopic needles (W. Pfitzinger, *J. pr.* [2] 33, 100; Beyer, *J. pr.* [2] 33, 416). Acetophenone gives, in like manner, phenyl-quinoline carboxylic acid.

Salts.—KA′: faint yellow crystals, which dissolve in conc. KOHAq, forming a deep violet-red solution, turned yellow on dilution with water. Its solution gives a yellow flocculent pp. with lead acetate, and, when concentrated, it is also ppd. by $BaCl_2$.—BaA'_2 (at 150°): scales.—AgA′: beautiful yellow prisms, sol. water.

Acetyl derivative $C_6H_4(NHAc).CO.CO_2H$. [160°]. Obtained from acetyl-isatin by dissolving in cold dilute NaOHAq and ppg. with dilute H_2SO_4 (Suida, *B.* 11, 586). Needles (from alcohol). Sl. sol. cold water, m. sol. alcohol, ether, and benzene. Boiling HClAq converts it into isatin. Sodium-amalgam reduces it to the acetyl derivative of α-oxy-o-amido-phenyl-acetic acid $C_6H_4(NHAc).CH(OH).CO_2H$, which forms colourless needles [142°] converted by HI into oxindole.

Chloro-isatic acid $C_6H_3Cl(NH_2).CO.CO_2H$. From chloro-isatin by warming with KOHAq (Erdmann, *J. pr.* 19, 339; 24, 5; *A.* 33, 129; Laurent, *A. Ch.* [3] 3, 378). Not known in the free state, since, when its salts are acidified, chloro-isatin is formed. — KA′: light-yellow flattened needles (from alcohol); v. sol. water.—BaA'_2aq: pale yellow needles.—BaA'_2 3aq: brilliant deep-yellow laminæ.—PbA'_2 2aq: brilliant yellow gelatinous pp., which in a few minutes changes to scarlet PbA'_2aq.—AgA′: light-yellow pp.; sol. boiling water.—The *cupric salt* is ppd. as a brownish-red powder, which changes to blood-red.

Di-chloro-isatic acid $C_6H_2Cl_2(NH_2).CO.CO_2H$. Formed by dissolving di-chloro-isatin in hot KOHAq. Separates on addition of HCl as a yellow pp., which, even when exposed over sulphuric acid *in vacuo* in the cold, splits up into water and di-chloro-isatin. It dissolves in water forming a light-yellow solution, which becomes turbid at 60° and deposits di-chloro-isatin.—KA′aq: yellow laminæ. — BaA'_2 2aq: golden needles. — CuA'_2: reddish-brown pp. changing to greenish-yellow and crimson. — AgA′: small yellowish needles (from hot water).

Bromo-isatic acid $C_6H_3Br(NH_2).CO.CO_2H$. Formed by warming bromo-isatin with aqueous caustic potash (Gericke, *J. pr.* 95, 176, 257). The free acid splits up at once into water and bromo-isatin.—KA′: easily soluble cauliflower-like crystals.—NaA′: warty crystals.—BaA'_2 3aq: yellow prisms.—CuA'_2 2aq: red granular pp.—PbA'_2 2aq: yellow pp., changing to a scarlet crystalline powder.—ZnA'_2 2aq: brownish pp., changing to red granular powder.—AgA′: light-yellow needles (from hot water).

Di-bromo-isatic acid $C_6H_2Br_2(NH_2)CO_2H$. From di-bromo-isatin and hot KOHAq (Erdmann, *J. pr.* 19, 360). The free acid is ppd. by adding HCl to a conc. solution of the K salt as a light-yellow powder, soluble in a large quantity of water. By desiccation, even at 15° *in vacuo*, it is decomposed into di-bromo-isatin and water.—KA′aq: pale yellow needles, v. sl. sol. water.

Ethyl ether EtA′. [105°]. From the silver salt and EtI (Baeyer a. Oekonomides, *B.* 15, 2099). V. sol. ordinary solvents. At 110° it gives di-bromo-isatin.

Sulpho-isatic acid $C_6H_3(SO_3H)(NH_2).CO.CO_2H$. From isatin sulphonic acid and excess of alkali (G. a. A. Schlieper, *A.* 120, 12). Only known in its salts, which are converted by mineral acids into isatin sulphonic acid.—K_2A''aq: waxy-yellow prisms, v. sol. water.—BaA'' 3aq: long silky lemon-yellow needles; v. sol. boiling water, insol. alcohol.—PbA'' $1\frac{1}{2}$aq: yellow needles, v. sol. water. — Ag_2A'' $1\frac{1}{2}$aq: pale yellow needles, sl. sol. water.

Isomeride of isatic acid *v.* *m*-Amido-phenyl-glyoxylic acid.

***p*-Methyl-isatic acid.** *Acetyl derivative* $C_6H_3(CH_3)(NHAc)CO.CO_2H$. [172°]. Small white needles, soluble in alcohol and hot water, very sparingly in ether, benzene, ligroïn, and CS_2. Formed by the action of cold aqueous alkalis upon acetyl-*p*-methyl-pseudo-isatin.

Ethyl ether of the acetyl derivative $C_6H_3(CH_3)(NHAc)CO.CO_2Et$. [79°]. White glistening plates; insol. water. Formed by boiling acetyl-*p*-methyl-pseudo-isatin with dilute alcohol (Duisberg, *B.* 18, 198).

Amide of the acetyl derivative $C_6H_3(CH_3)(NHAc).CO.CONH_2$. [141°]. Formed by the action of alcoholic NH_3 on the acetyl derivative of methyl-ψ-isatin (Panaotović, *J. pr.* [2] 33, 72). Trimetric prisms (from alcohol), insol. water.

ISATILIM *v.* Isatin.

ISATIMIDE *v.* Isatin.

ISATIN $C_8H_5NO_2$ *i.e.* $C_6H_4{<}{}^{CO}_{N}{>}C.OH$ (stable form) or $C_6H_4{<}{}^{CO}_{NH}{>}CO$ (transition form or pseudo-isatin. *Anhydride of isatic acid. o-Amido-phenyl-glyoxylic lactim.* [201°].

Formation.—1. Discovered simultaneously by Laurent (*A. Ch.* [3] 3, 371) and by Erdmann (*J. pr.* 24, 11) as a product of the oxidation of indigo by nitric acid (L.) or chromic acid (E.).—2. By oxidising amido-oxindole with $FeCl_3$, nitrous acid, or $CuCl_2$ (Baeyer, *B.* 11, 1228). The oxindole may be obtained from phenyl-acetic acid by nitration and reduction (Baeyer, *B.* 11, 583), and converted successively into nitroso-oxindole and amido-oxindole.—3. Prepared by boiling o-nitro-phenyl-propiolic acid with alkalis (Baeyer, *B.* 13, 2259). The reaction possibly takes place as follows:

$$C_6H_4\Big<\begin{matrix}NO_2\\C.C.CO_2H\end{matrix} + 4H_2O$$
$$= C_6H_4\Big<\begin{matrix}N(O_2H_4)\\C(OH)_2.C(OH)_2.CO_2H\end{matrix}$$
$$= C_6H_4\Big<\begin{matrix}N\\COCO.CO_2H\end{matrix} + 4H_2O$$
$$= C_6H_4\Big<\begin{matrix}N\\CO.CHO\end{matrix} + CO_2 + 4H_2O$$
$$= C_6H_4\Big<\begin{matrix}NH_2\\CO.COOH\end{matrix} + CO_2 + 3H_2O$$
$$= C_6H_4\Big<\begin{matrix}N\\CO\end{matrix}\Big>COH + CO_2 + 4H_2O$$

(Michael, *J. pr.* [2] 35, 255).—4. Together with $N_2(C_6H_4.CO_2H)_2$, by dissolving isatogenic ether in aqueous Na_2CO_3 (Baeyer, *B.* 15, 55).—5. From isatogenic acid by dissolving in H_2SO_4 and adding water (Baeyer, *B.* 14, 1742).—6. By oxidising carbostyril with alkaline $KMnO_4$ (Friedländer a. Ostermaier, *B.* 14, 1921).—7. By boiling nitroso-(γ)-oxy-carbostyril with conc. HClAq (Baeyer a. Homolka, *B.* 16, 2217).—8. By heating anthroxanic acid with $FeSO_4$ and dilute ammonia (Schillinger a. Wleügel, *B.* 16, 2224).

Preparation.—1. Finely-powdered indigo (50g. of 65 p.c.) is made into a thin paste with boiling water, and a dilute solution of CrO_3 (30 g.) is added. The liquid is boiled till it begins to froth strongly, and is then filtered hot, when isatin separates on cooling. The yield is moderate (9 g.) (Sommaruga, *A.* 190, 369).—2. A mixture of indigo (100 pts.), boiling water (300 pts.), and nitric acid (70 pts. of S.G. 1·35) is boiled for two minutes, diluted with boiling water (2000 pts.), boiled for five minutes more and filtered. The isatin separates on cooling. It may be purified by dissolving in aqueous KOH, adding HCl as long as it forms a black or brown pp., filtering, adding more HCl to the clear yellow filtrate, and washing the red pp. of isatin (Forrer, *B.* 17, 976; Hofmann, *A.* 53, 11).

Properties. — Yellowish - red monoclinic prisms; $a{:}b{:}c = \cdot425{:}1{:}\cdot503$; $\beta = 85°\,18'$ (Bodewig, *Z. K.* 4, 65). Has no odour, but a bitter taste. Sl. sol. cold, m. sol. boiling, water, forming a reddish-yellow solution. V. e. sol. alcohol, sl. sol. ether. The alcoholic solution imparts an unpleasant odour to the skin.

Reactions.—1. It is not attacked by dilute *nitric acid*, but a stronger acid forms nitro-*o*-oxy-benzoic acid, while conc. HNO_3 forms oxalic acid.—2. *Nitrous acid*, acting upon isatin suspended in water, forms nitro-*o*-oxy-benzoic acid (Hofmann, *A.* 115, 280); while, in presence of alcohol, nitrous acid forms benzoic acid (Baeyer, a. Knop, *A.* 140, 4).—3. *Chromic acid* in presence of acetic acid forms isatoic acid

$$C_6H_4\Big<\begin{matrix}CO\\N\end{matrix}\Big>C.OH + O = C_6H_4\Big<\begin{matrix}CO\\|\\N.CO_2H\end{matrix}.$$

On the other hand, acetyl-isatin $C_6H_4\Big<\begin{matrix}CO\\NAc\end{matrix}\Big>CO$, being a derivative of pseudo-isatin, yields acetyl-*o*-amido-benzoic acid $C_6H_4(NHAc).CO_2H$ on similar treatment (E. v. Meyer a. J. Bellmann, *J. pr.* [2] 33, 30).—4. *Chlorine* and *bromine* form products of substitution.—5. Cold aqueous *caustic potash* forms a red solution, which on boiling immediately becomes yellow, and then contains potassium isatate. If the solution be concentrated by distillation, decomposition suddenly takes place, aniline and hydrogen being given off.—6. Aqueous *ammonia* forms isamic acid. Alcoholic NH_3 gives a variety of products, called by Laurent imesatin, imasatin, amisatin, isatimide, and isatilim. By heating isatin with alcoholic NH_3 in sealed tubes Sommaruga (*A.* 190, 371) obtained di-imido-isatin, oxy-di-imido-isatin, and deoxy-imido-isatin.—7. Isatin combines with *alkaline bisulphites.*—8. SO_2 has no action.—9. H_2S gives di-thio-isatyde.—10. *Sodium-amalgam* reduces it to isatyde $C_{16}H_{12}N_2O_4$ and dioxindole $C_8H_7NO_2$.—11. *Ammonium sulphide* reduces it to isatyde.—12. *Zinc* and dilute H_2SO_4 form isatyde.—13. *Zinc-dust* and a little dilute HCl form isatyde and dioxindole (Baeyer, *B.* 12, 1309).—14. *Zinc-dust* added to a cold solution of isatin in HOAc forms a colourless solution (? of isatin hydride) which becomes coloured again on exposure to the air, isatin being reproduced.—15. Aqueous HI (S.G. 1·4) at 100° forms isatyde. At 140° it forms a dark-green insoluble mass, whence boiling alcohol leaves a dark-grey residue, isatochlorin ($C_{32}H_{24}N_4O_5$?), whilst the alcoholic solution, mixed with water, gives a pp., whence ether extracts red isatopurpurin ($C_{32}H_{28}N_4O_3$?), while white isatone ($C_{32}H_{24}N_4O_3$?) remains undissolved (Schützenberger, *Bl.* [2] 4, 170).—16. PCl_5 forms 'isatin chloride' (Baeyer, *B.* 12, 456).—17. *Hydroxylamine* forms nitroso-oxindole or isatoxim.—18. Alcoholic KCy has no action.—19. A solution of isatin, warmed with phenyl-hydrazine, forms a pp. of the phenyl-hydrazide.—20. In presence of H_2SO_4 or $ZnCl_2$ isatin forms condensation products, with (2 mols. of) toluene, phenol, di-methyl-aniline, thiophene, &c., by elimination of water (1 mol.). Thus, phenol and H_2SO_4 give di-oxy-di-phenyl-oxindole $C_6H_4\Big<\begin{matrix}C(C_6H_4.OH)_2\\NH.CO\end{matrix}\Big>$; toluene gives di-tolyl-oxindole, while di-methyl-aniline gives tetra-methyl-di-amido-di-phenyl-oxindole [234°] (Baeyer, *B.* 18, 2642).—21. When heated with *phenyl cyanate*, for three hours at 130°, it forms the anilide of isatin ν-carboxylic acid, which crystallises from alcohol in needles [180°-185°] (Gumpert, *J. pr.* [2] 31, 120; 32, 283).—22. *Phenyl mercaptan*, added to a hot alcoholic solution of isatin, forms silky needles of a compound $(C_8H_5NO_2)(C_6H_5SH)$, insol. water, but decomposed by hot benzene into its components (Baumann, *B.* 18, 890).—23. By boiling with *m-amido-benzoic acid* and alcohol there is formed an acid which is termed isat-amido-benzoic acid $C_6H_4\Big<\begin{matrix}C{:}NC_6H_4.CO_2H\\—NH——\end{matrix}\Big>CO$ [253°]. *m-Amido-benzamide* gives, in like manner, the corresponding amide [c. 280°] (Schiff, *A.* 218, 192).—24. Heating with *tolylene-diamine* forms $C_{15}H_{11}N_3$ [290°], which is probably a quinoxaline (Hinsberg, *A.* 237, 344).

Metallic derivatives.—$C_8H_4AgNO_2$: obtained by mixing isatin with water at 0°, adding KOH (1 mol.) followed immediately by $AgNO_3$ (1 mol.) (Baeyer a. Oeconomides, *B.* 15, 2093). Red pp. $C_8H_4AgNO_2NH_3$. Formed in presence of ammonia (L.).—$Cu(C_8H_4NO_2NH_3)_2$. From cupric acetate and an ammoniacal solution of isatin (Laurent). Brown pp.—Potassium-isatin is present in the violet-red solution obtained by dissolving isatin in conc. KOHAq.

Indophenine reaction.—A solution of isatin

in conc. H_2SO_4, shaken with benzene containing thiophene, is coloured blue, through formation of indophenine (*q. v.*). A similar reaction is given by most derivatives of thiophene.

Combinations with bisulphites $C_8H_5NO_2KHSO_3 2aq$. Formed by boiling isatin with aqueous $KHSO_3$ or by saturating a solution of potassium isatate with SO_2 (Laurent). Large, pale-yellow tables; v. e. sol. water and boiling alcohol, sl. sol. cold alcohol. Gives with lead acetate a pp. of isatin and lead sulphite.—$C_8H_5NO_2(NH_4)HSO_3$: pale yellow tables, sl. sol. cold water.—$C_8H_5NO_2(NH_3C_5H_{11})HSO_3$ (Schiff, *A.* 144, 49).—$C_8H_5NO_2(NH_3Ph)HSO_3$. Crystals; v. sol. water (S.).

Acetyl-ψ-isatin $C_6H_4{<}{}^{CO}_{NAc}{<}CO$. [141°]. Prepared by heating isatin (1 pt.) with Ac_2O (2 pts.) for 4 hours (Suida, *B.* 11, 584). Yellow needles (from benzene). V. sol. benzene and alcohol, sl. sol. cold water. Resolved into isatin and acetic acid by boiling with water, or, more readily with HClAq. Cold NaOHAq dissolves it, forming $C_6H_4(NHAc).CO.CO_2Na$ and, on warming, isatic acid. Chromic acid in HOAc oxidises it to $NHAc.C_6H_4.CO_2H$.

Benzoyl-ψ-isatin $C_6H_4{<}{}^{CO}_{NBz}{>}CO$. From isatin and BzCl (Schwartz, *C. R.* 56, 1050).

Oxim $C_8H_6N_2O_2$ *i.e.* $C_6H_4{<}{}^{C(NOH)}_{N:C(OH)}{>}$. *Isatoxim. Nitroso-oxindole.* [c. 202°]. Formed by passing nitrous acid into a 1 p.c. aqueous solution of oxindole (Baeyer a. Knop, *A.* 140, 34). Formed also by boiling diazo-nitroso-oxindole chloride with alcohol and HCl (Gabriel a. R. Meyer, *B.* 14, 2332). Obtained by treating isatin with hydroxylamine (Gabriel, *B.* 16, 518; Baeyer a. Comstock, *B.* 16, 1706). Very slender golden needles. Decomposed by fusion. V. sl. sol. water, sl. sol. alcohol. Dissolves in KOHAq, forming a dark reddish-brown solution. Not decomposed by boiling aqueous KOH.—$C_8H_5AgN_2O_2$: orange pp., got by adding dilute NH_3 to an alcoholic solution of isatin and $AgNO_3$. Dries up to a brick-red powder.

Mono-ethyl-ether of the oxim $C_6H_4{<}{}^{C(NOEt)}_{N}{\geqslant}C(OH)$. *Isato-ethyl-oxim.* [138°]. Fine yellow needles, soluble in caustic alkalis; formed by the action of ethyl iodide on the silver salt of isatoxim. By successive treatment with zinc-dust and HOAc and with $FeCl_3$ it is converted into isatin.

Di-ethyl-ether of the oxim $C_6H_4{<}{}^{C(NOEt)}_{N}{\geqslant}C(OEt)$. *Ethyl-isato-ethyl-oxim.* Crystalline solid; formed by the action of ethyl iodide on the silver salt of the mono-ethyl-ether (Baeyer a. Comstock, *B.* 16, 1706).

Oxim of ψ-isatin $C_6H_4{<}{}^{CO}_{NH}{>}C{:}NOH$. *Isonitroso-ψ-indoxyl.* Formed by the action of nitrous acid on ethyl-indoxylic acid $C_6H_4{<}{}^{C(OEt)}_{NH}{\geqslant}C.CO_2H$. Flat yellow needles. Decomposes at about 200°. Sol. alkalis and reppd. by CO_2. With phenol and H_2SO_4 it does not give Liebermann's reaction. Reduction with zinc-dust followed by oxidation with Fe_2Cl_6 yields isatin.

Ethyl ether of the oxim of ψ-isatin $C_6H_4{<}{}^{CO}_{NH}{>}C(NOEt)$. From ψ-isatoxim, KOH, and EtI: yellow plates; dissolves in sodium ethylate with a blue colour; reduction with zinc-dust followed by oxidation with Fe_2Cl_6 yields isatin. Forms a violet solution when warmed with aqueous NaOH.

Di-ethyl-derivative of the oxim of ψ-isatin $C_6H_4{<}{}^{CO}_{NEt}{>}C(NOEt)$: [99°]; yellow needles, sublimable, easily soluble in alcohol and ether, sparingly in hot water, insol. alkalis. On reduction with zinc-dust and oxidation with Fe_2Cl_6 it yields ethyl-pseudo-isatin (Baeyer, *B.* 15, 782; 16, 2191).

Phenyl-hydrazide $C_{14}H_{11}N_3O$. [211°]. Fine yellowish-red needles. Formed as a yellow crystalline pp. by boiling a solution of isatin in 1,000 pts. of water with phenyl-hydrazine hydrochloride (*q. v.*); the pp. is quite distinct with a solution of 1 in 20,000 (E. Fischer, *B.* 17, 577).

Chloride C_8H_4ClNO *i.e.* $C_6H_4{<}{}^{CO}_{N}{\geqslant}CCl$. [c. 180°]. Formed by warming isatin (5 g.) with PCl_5 (7 g.) and benzene (9 g.) (Baeyer, *B.* 11, 1296; 12, 456). Brown needles. Decomposed on fusion. V. sol. ether, forming a blue solution. Decomposed by moist air. Potash converts it into isatin. HI gives indigo; zinc-dust and HOAc do the same.

Chloro-isatin $C_8H_4ClNO_2$. [243°]. S. ·1 at 0°; c. ·5 at 100°. Obtained by passing chlorine in sunlight into boiling water containing isatin in suspension. The mono- aud di-chloroisatin are separated by recrystallisation from alcohol, in which the former is much less soluble (Hofmann, *A.* 53, 12; Laurent, *A. Ch.* [3] 3, 462; Erdmann, *A.* 33, 129; Dorsch, *J. pr.* [2] 33, 49). Orange prisms (from alcohol). V. sl. sol. water and alcohol. Its solution imparts an unpleasant odour to the skin. Decomposed on fusion. Hot KOHAq forms potassium chloro-isatate. Distillation with NH_3 gives *p*-chloro-aniline. An ammoniacal solution of $AgNO_3$ added to an alcoholic solution of chloro-isatin ppts. $C_8H_3ClAgNO_2NH_3$.

Di-chloro-isatin $C_8H_3Cl_2NO_2$. [186°]. Obtained from the alcoholic mother-liquors that have yielded chloro-isatin. Small, reddish-yellow needles or short laminæ (from alcohol). M. sol. alcohol. When thrown upon solid potash, moistened with alcohol, a red solution is formed which solidifies to a violet-black magma of $C_8H_2KCl_2NO_2$, the solution of which gives a pp. with $AgNO_3$. Hot aqueous KOH forms potassium di-chloro-isatate. Distillation with KOH forms di-chloro-aniline. Chlorine does not act on its aqueous solution, but with its alcoholic solution it forms tetra-chloro-quinone and other bodies. $KHSO_3$ forms light-yellow needles of $C_8H_3Cl_2NO_2KHSO_3$, sl. sol. boiling water. Di-chloro-isatin (10 g.) oxidised by CrO_3 (15 g.) in glacial acetic acid (60 g.) as described under *Bromo-isatin* forms *di-chloro-*Isatoic acid (*q. v.*).

Bromo-isatin $C_8H_4BrNO_2$ *i. e.*

$$\begin{array}{l}CBr{:}CH.C.CO\diagdown \\ |\qquad\quad \| \qquad\quad {>}C.OH. \\ CH:CH.C.N\ /\!\!/\end{array}$$

[255°]. Formed, together with di-bromo-isatin, by the action of bromine and water on isatin (Erdmann, *J. pr.*

19, 358; Hofmann, *A.* 53, 40). The product is exhausted with boiling water and the crystals that separate on cooling are recrystallised from alcohol whence bromo-isatin crystallises first. Orange prisms. Aqueous KOH converts it, even in the cold, into potassium bromo-isatate. Distillation with KOH yields *p*-bromo-aniline. When mixed with alcoholic ammonium sulphide and exposed to the air it yields bromo-indigo. Bromo-isatin (10 g.) is oxidised by a mixture of glacial acetic acid (90 g.) and CrO_3 (15 g.) to bromo-isatoic acid. The mixture must first be kept ice-cold, but after 12 hours it may be slowly raised to 70°. The product, when cold, is poured into cold dilute H_2SO_4 and the yellow sandy powder crystallised from a mixture of alcohol and acetone (Dorsch, *J. pr.* [2] 33, 45).

Acetyl derivative $C_8H_3BrAcNO_2$. [172°]. Formed by boiling bromo-isatin (5 pts.) with Ac_2O (8 pts.) (Baeyer a. Oeconomides, *B.* 15, 2096). Long straw-yellow prisms (from benzene).

Chloride $C_8H_3BrClNO$. Formed by treating bromo-isatin with PCl_5 (Baeyer, *B.* 12, 1315). Reddish-brown needles; sol. hot benzene and ether. HI gives bromo-indigo.

Oxim $C_8H_4BrNO(NOH)$. From isatoxim and bromine-water in the cold (Baeyer a. Knop, *A.* 140, 35). Crystals, sl. sol. water.

Di-bromo-isatin $\left|\begin{array}{l}CBr{:}CH.C.CO\\ \qquad\quad\;\; \| \\ CBr{:}CH.C.N\end{array}\right\rangle C.OH.$ [250°]. Formed as above or by digesting bromo-isatin or isatin with bromine in sunshine. Formed also by heating bromo-isatin (1 mol.) with bromine (2 mols.) in HOAc for 20 hours (Baeyer a. Oeconomides, *B.* 15, 2098). Orange prisms (from alcohol). Gives di-bromo-aniline when distilled with KOH.—$C_8H_2Br_2KNO_2$: bluish-violet scales, sl. sol. water. Very stable but converted into di-bromo-isatate by warming with KOHAq.—AgA′: brownish-violet powder. —$C_8H_3Br_2NO_2KHSO_3$: yellow solid, v. sl. sol. water.

Oxim $C_8H_4Br_2O_2N_2$ or $C_6H_2Br_2\left\langle\begin{array}{c}C(NOH)\\ N\end{array}\right\rangle C(OH)$. Formed by the action of hydroxylamine on di-bromo-isatin (Baeyer a. Comstock, *B.* 16, 1708). Yellow pointed needles. Carbonises without melting at about 255°. Sol. caustic alkalis but precipitated by CO_2.

Mono-ethyl-ether of the oxim $C_6H_2Br_2\left\langle\begin{array}{c}C(NOEt)\\ N\end{array}\right\rangle C(OH)$. *Di-bromo-isato-ethyl-oxim.* [252°]. Yellow needles; formed by the action of ethyl-iodide on the silver salt of di-bromo-isatoxim.

Di-ethyl-ether of the oxim $C_6H_2Br_2\left\langle\begin{array}{c}C(NOEt)\\ N\end{array}\right\rangle C(OEt)$. *Di-bromo-ethyl-isato-ethyl-oxim.* [116°]. Long yellow, silky needles; formed by the action of ethyl iodide on the silver salt of the mono-ethyl-ether.

Tri-bromo-isatin. *Oxim* $C_8HBr_3\left\langle\begin{array}{c}C(NOH)\\ N{:}C(OH)\end{array}\right\rangle$. [162°]. From the oxim of isatin and bromine in excess (B. a. K.). Dirty violet needles (from alcohol). Insol. water, v. sol. boiling alcohol. At 190° it sublimes as red needles.

Nitro-isatin $C_8H_4NO_2(NO_2)$. [226°-230°]. Prepared by nitration of isatin dissolved in H_2SO_4 by addition of powdered KNO_3 (Baeyer, *B.* 12, 1312). Sparingly soluble in water, more easily in alcohol.

Bromo-nitro-isatin $C_6H_2(NO_2)Br\left\langle\begin{array}{c}CO\\ N\end{array}\right\rangle C.OH$. [237°]. From bromo-isatin, KNO_3 and H_2SO_4 (Dorsch). Clumps of orange crystals (from alcohol). Sol. acetone, glacial acetic acid and alcohol, sl. sol. benzene and chloroform, v. sl. sol. water and ether. Forms a dark-red solution in NaOH,Aq, whence an orange powder presently separates.

ALKYL DERIVATIVES.

Alkyl derivatives of isatin are either derived from the stable form $C_6H_4\left\langle\begin{array}{c}CO\\ N\end{array}\right\rangle C.OH$ or from the transition form $C_6H_4\left\langle\begin{array}{c}CO\\ NH\end{array}\right\rangle CO$ (pseudo-isatin). Alkyl iodides acting on silver-isatin form alkyl derivatives of stable isatin $C_6H_4\left\langle\begin{array}{c}CO\\ N\end{array}\right\rangle C.OR$.

Alkyl derivatives of pseudo-isatin $C_6H_4\left\langle\begin{array}{c}CO\\ NR\end{array}\right\rangle CO$ are formed by the action of an alkaline solution of bromine or chlorine followed by alcoholic NaOH on the methyl-, ethyl-, phenyl-, &c. -indole-carboxylic acids which are obtained by the action of HCl on phenyl-methyl-hydrazine-pyruvic acid, phenyl-ethyl-hydrazine-pyruvic acid, &c. (Fischer a. Hess, *B.* 17, 559).

Methyl derivative of isatin $C_8H_4O_2N(CH_3)$ *i.e.* $C_6H_4\left\langle\begin{array}{c}CO\\ N\end{array}\right\rangle COMe$. [102°]. Formed by the action of methyl iodide on the silver compound of isatin (Baeyer a. Oeconomides, *B.* 15, 2093). Red trimetric prisms. Sol. ether, acetone, benzene, and CS_2, less easily in alcohol, v. sl. sol. ligroïn. It changes on keeping into methyl-isatoid. Slowly dissolves in dilute KOHAq, forming a solution from which acids ppt. isatin. Its solution in alcoholic ammonium sulphide forms indigo when exposed to the air.

Methyl-isatoid $C_{17}H_{12}N_2O_4$ (?) [219°]. Formed by spontaneous change by keeping methyl-isatin (Baeyer a. Oeconomides, *B.* 15, 2094). Small yellow needles; sparingly soluble in all solvents. Dissolves in dilute NaOH on boiling, and on adding acid isatin is precipitated.

Methyl derivative of bromo-isatin $C_8H_3BrO_2NMe$. [147°]. Formed by the action of MeI on the silver compound of bromo-isatin (Baeyer a. Oeconomides, *B.* 15, 2095). Red needles.

Bromo-methyl-isatoid [231°]. Formed by spontaneous change of methyl-bromo-isatin by keeping (B. a. O.).

Methyl-pseudo-isatin $C_9H_7NO_2$ *i.e.* $C_6H_4\left\langle\begin{array}{c}CO\\ NMe\end{array}\right\rangle CO$. [134°]. Red needles.

Formation.—1. By the action of a cold alkaline solution of bromine or chlorine followed by hot alcoholic NaOH on methyl-indole-carboxylic acid [212°], which is obtained by heating phenyl-methyl-hydrazine-pyruvic acid with HCl (Fischer a. Hess, *B.* 17, 563).—2. By boiling di-

bromo-methyl-oxindole with water (Colman, *C. J.* 55, 5; *A.* 248, 118).

Reactions.—Dissolves in alkalis with a yellow colour. With H_2SO_4 and benzene containing thiophene it gives the indophenine reaction. Gives a crystalline compound with phenyl-hydrazine. Yields the same product on oxidation in alkaline solutions as in acid solution, viz. methyl-di-oxindole.

Oxim $C_6H_4<\begin{matrix}C(N.OH)\\N(CH_3)\end{matrix}>CO$. [180°–183°]. From methyl-pseudo-isatin and hydroxylamine sulphate in hot aqueous solution (Colman, *C. J.* 55, 6). Tufts of small pale-yellow needles; m. sol. hot water, sl. sol. cold water, v. sol. alcohol, acetone, ether, and benzene.

Phenyl hydrazide $C_6H_4<\begin{matrix}C{=}N_2H.Ph\\NMe\end{matrix}>CO$. [146°]. Formed by the action of phenyl-hydrazine hydrochloride and NaOAc on an aqueous solution of methyl-ψ-isatin. A less pure product is produced by the action of phenyl-hydrazine hydrochloride on dibromomethyloxindole (Colman). Fascicular group of small yellow needles; insol. water and petroleum ether, sl. sol. ether, v. sol. hot alcohol or benzene.

p-Methyl-isatin $C_9H_7NO_2$ *i.e.*

$C_6H_3Me<\begin{matrix}CO\\N\end{matrix}>COH$ (stable form) or

$C_6H_3Me<\begin{matrix}CO\\NH\end{matrix}>CO$ (transition form).

Tolisatin. Anhydride of amido-tolyl-glyoxylic acid. [184°] (P.); [187°] (M.).

Formation.—From *p*-toluidine and di-chloro-acetic acid by digestion in alcoholic solution, the resulting *p*-toluide (*p*-tolyl-methyl-imesatin) $C_6H_3Me<\begin{matrix}C{=}NC_6H_4Me\\NH\end{matrix}>CO$ being decomposed by HCl, and the crude product purified by boiling with aqueous KOH, ppg. with HCl, and crystallising from alcohol and afterwards from water (P. J. Meyer, *B.* 16, 2261; Fr. Baeyer a. Co., *B.* Ref. 17, 367; Panaotović, *J. pr.* [2] 33, 57).

Properties.—Red crystals or glistening red plates. Sol. hot water and alcohol, sl. sol. cold water, v. sol. hot HClAq. Dissolves in cold alkalis with a deep-violet colour, and on heating or standing it then takes up water, becoming yellow and forming methyl-isatic acid. Dissolves in conc. H_2SO_4 with a red colour. Gives the indophenine reaction. CrO_3 in acetic acid forms methyl-isatoic acid. Boiling with Ac_2O for three hours forms the acetyl derivative of methyl-ψ-isatin.

Acetyl derivative of methyl-ψ-isatin $C_6H_3Me<\begin{matrix}CO\\NAc\end{matrix}>CO$. [172°]. Formed by boiling *p*-methyl-ψ-isatin with Ac_2O for 3 hours (Panaotović, *J. pr.* [2] 33, 71). Formed also by the action of HCl upon the acetyl derivative of *p*-methyl-ψ-isatin *p*-toluide (Duisberg, *B.* 18, 197). Lemon-yellow needles (from benzene); sol. chloroform and benzene, sl. sol. water, alcohol, ether, ligroïn, and CS_2. Converted by cold dilute alkalis into acetyl-*p*-methyl-isatic acid. Alcoholic NH_3 converts it into the amide of acetyl-*p*-methyl-isatic acid $C_6H_3Me(NHAc).CO.CONH_2$, which crystallises from alcohol in trimetric columns [141°]. CrO_3 in HOAc oxidises it to methyl-isatoic acid, which crystallises from boiling alcohol in trimetric plates and, when heated, decomposes at 245° with great increase in bulk, finally melting at 300°.

Oxim $C_6H_3Me<\begin{matrix}C(NOH)\\N{:}C(OH)\end{matrix}>$. *Isonitroso-methyl-oxindole.* [226°]. Formed by the action of hydroxylamine (base) on *p*-methyl-isatin (P. J. Meyer, *B.* 16, 2268). Long yellow prisms; sol. alcohol and NaOH, sl. sol. water.

Phenyl-hydrazide of methyl-isatin $C_6H_3Me<\begin{matrix}C(N_2HPh)\\N\end{matrix}>C.OH$. From *p*-methyl-isatin and phenyl-hydrazine (P.). Golden needles (from chloroform). Nearly insol. water, sol. alcohol. May be sublimed at 240°, but melts above 300° with evolution of gas.

Di-phenyl-hydrazide of methyl-ψ-isatin $C_6H_3Me<\begin{matrix}C(N_2HPh)\\NH\end{matrix}>C(N_2HPh)$. [255°] Formed by warming the acetyl derivative of methyl-ψ-isatin with phenyl-hydrazine (P.). Yellow trimetric columns (from alcohol) decomposed by fusion. Nearly insol. water, sol. chloroform.

Imide $C_9H_8N_2O$ or $C_{18}H_{16}N_4O_2$. *p-Methyl-imesatin.* Formed by heating *p*-methyl-isatin-*p*-toluide with alcoholic NH_3 at 100° (P. J. Meyer, *B.* 16, 2264). Nearly colourless fine silky needles. V. sl. sol. hot alcohol and hot water. Insol. cold alcohol and water. Is not re-converted into *p*-methyl-isatin by acids or alkalis.

Phenyl-imide $C_{15}H_{12}N_2O$ *i.e.* $C_6H_3(CH_3)<\begin{matrix}C(NPh)\\N\end{matrix}>C.OH$. *Methyl-isatin anilide. Phenyl-methyl-imesatin.* [240°]. Formed by heating *p*-methyl-isatin with an absolute alcoholic solution of aniline (Meyer, *B.* 16, 2267). Thick yellowish-red tables or prisms. Sol. hot alcohol, sl. sol. cold alcohol and water. Heated with acids or caustic alkalis it is resolved into its constituents.

o-*Tolyl-imide* $C_{16}H_{14}N_2O$ *i.e.* $C_6H_3(CH_3)<\begin{matrix}C(NC_7H_7)\\N\end{matrix}>C.OH$. o-*Toluide of methyl-isatin.* o-*Tolyl-p-methyl-imesatin.* [191°]. Red prismatic crystals. Formed by heating *p*-methyl-isatin with an absolute alcoholic solution of o-toluidine. By HCl or hot NaOH it is resolved into its constituents (Meyer, *B.* 16, 2268).

p-Tolyl-imide $C_{16}H_{11}N_2O$ *i.e.* $C_6H_3(CH_3)<\begin{matrix}C(NC_7H_7)\\N\end{matrix}>C.OH$. *p-Toluide of methyl-isatin. p-Tolyl-p-methyl-imesatin.* [259°]. Formed by heating di-chloro-acetic acid (1 mol.) with *p*-toluidine (4 mols.) at 100° C., either alone or in aqueous or alcoholic solution; the yield is 70 p.c. *p*-Tolyl-amido-*p*-methyl-oxindole $C_6H_3Me<\begin{matrix}NH\\CH\end{matrix}>CO$ (with $CH—NH(C_7H_7)$) is first formed and then undergoes oxidation by absorption of oxygen from the air. Formed also by heating di-chloracetamide (1 mol.) with *p*-toluidine (3 mols.); and by heating *p*-methyl-isatin with an absolute alcoholic solution of *p*-toluidine (Meyer, *B.* 16, 2261). Glistening yellow needles or plates. Sol. ether and hot alcohol, sparingly sol. cold alcohol, insol. water. By cold

HCl it is resolved into *p*-toluidine and *p*-methyl-isatin. Hot HCl or hot NaOH gives *p*-methyl-isatic acid.—Sodium salt crystallises in red prisms, decomposed by water.

Acetyl derivative $C_6H_3Me{<}\substack{NAc\\ C=N(C_7H_7)}{>}CO$. [122°]. Glistening red needles; insol. water. By HCl it is split up into *p*-toluidine and the acetyl derivative of *p*-methyl-pseudo-isatin (Duisberg, *B.* 18, 190).

Bromo-p-toluide $C_{16}H_{13}BrN_2O$. [210°]. Red needles or prisms. By heating with acids or alkalis it is split up into its constituents (P. J. Meyer, *B.* 16, 2267).

ν o-Di-methyl-ψ-isatin $C_6H_3Me{<}\substack{CO\\ NMe}{>}CO$. *Methyl-ψ-o-tolisatin.* [157°]. Formed by adding pyruvic acid to a solution of methyl-*o*-tolyl-hydrazine in dilute HCl, and warming the resulting oil with a large quantity of phosphoric acid (S.G. 1·17). The resulting di-methyl-indole carboxylic acid is then warmed with NaOCl in slightly alkaline solution, when a product [152°] is obtained, which when warmed with water yields the di-methyl-isatin (Hegel, *A.* 232, 221). Brick-red needles (from water).

νp-Di-methyl-ψ-isatin $C_6H_3Me{<}\substack{CO\\ NMe}{>}CO$. [148°]. Formed in like manner from methyl-*p*-tolyl-hydrazine and pyruvic acid; the di-methyl-indole carboxylic acid giving with alkaline hypochlorite a chlorinated compound crystallising in yellow needles [135°] which yield the di-methyl-isatin on dissolving in water (H.). Red needles.

Ethyl-pseudo-isatin $C_6H_4{<}\substack{CO\\ NEt}{>}CO$. *Lactam of ethyl-isatic acid.* [95°].

Formation.—1. By the action of a cold alkaline solution of chlorine followed by hot alcoholic NaOH on ethyl-indole carboxylic acid [183°] which is obtained by the action of HCl on phenyl-ethyl-hydrazine-pyruvic acid (E. Fischer a. Hess, *B.* 17, 566).—2. By reduction of the di-ethyl derivative of pseudo-isatin-ω-oxim $C_6H_4{<}\substack{CO\\ NEt}{>}C(NOEt)$ with zinc-dust and oxidation of the product with Fe_2Cl_6 (Baeyer, *B.* 16, 2193). Large red plates, sol. hot water, alcohol and ether. With thiophene and H_2SO_4 it gives a blue colouring matter soluble in ether. It dissolves in alkalis with a yellow colour, at once forming a salt of ethyl-isatic acid $C_6H_4{<}\substack{CO.CO_2H\\ NHEt}$

Ethyl-pseudo-isatin α-oxim $C_6H_4{<}\substack{C(NOH)\\ NEt}{>}CO$. [162°]. Yellow four-sided prisms. Formed by the action of hydroxylamine on ethyl-pseudo-isatin. On reduction with zinc-dust followed by oxidation with Fe_2Cl_6 it yields ethyl-pseudo-isatin. It does not yield indigo on treatment with ammonium sulphide (Baeyer, *B.* 16, 2196).

Ethyl-pseudo-isatin ω-oxim. *Ethyl ether* $C_6H_4{<}\substack{CO\\ NEt}{>}C(NOEt)$. [99°]. From the ethyl ether of the ω-oxim of ψ-isatin by further ethylation (Baeyer, *B.* 16, 2191). Yellow needles, v. sol. alcohol and ether, sl. sol. hot water. May be sublimed. Insol. alkalis. After reduction with zinc-dust, on oxidation with $FeCl_3$ it yields ethyl-ψ-isatin.

Bromo-ethyl-isatin $C_8H_3BrO_2NEt$ *i.e.* $C_6H_3Br{<}\substack{CO\\ N}{>}COEt$. [109°]. From the silver compound of bromo-isatin and EtI (Baeyer a. Oeconomides, *B.* 15, 2095). Long red prismatic needles (from benzene). On keeping it slowly changes into bromo-ethyl-isatoid.

Bromo-ethyl-isatoid $C_{18}H_{12}Br_2N_2O_4$. [245°]. Fine needles. Sparingly soluble in all solvents, most easily in hot alcohol and acetone. Formed by spontaneous change of ethyl-bromo-isatin by keeping; also by the action of acetic anhydride on ethyl bromo-isatin (Baeyer a. Oeconomides, *B.* 15, 2095).

***p*-Ethyl-isatin** $C_{10}H_9NO_2$ *i.e.* $C_6H_3Et{<}\substack{CO\\ N}{>}C.OH$. [137°]. Long red needles (Paucksch, *B.* 17, 2805). Formed by heating with HClAq the product of the action of di-chloro-acetic acid on *p*-amido-phenyl-ethane $C_6H_4Et(NH_2)$ [1:4].

Di-bromo-ethyl-isatin $C_8H_2O_2NBr_2Et$ *i.e.* $C_6H_2Br_2{<}\substack{CO\\ N}{>}C.OEt$. [89°]. From silver di-bromo-isatin and EtI (B. a. O.). Red crystals.

***p*-Methyl-ν-ethyl-ψ-isatin** $C_6H_3Me{<}\substack{CO\\ NEt}{>}CO$. [110°]. *Ethyl-ψ-p-tolisatin.* Formed from the *p*-toluide by treatment with conc. HClAq (Duisberg, *B.* 18, 197). Formed also from methyl-ethyl-indole carboxylic acid by treatment with a weak alkaline solution of NaOCl, and warming the resulting pp. with water (Hegel, *A.* 232, 219). Red needles or prisms; v. sol. alcohol, ether, benzene, and CS_2, sl. sol. water and ligroïn. Sol. aqueous alkalis. Gives the indophenine reaction.

p-Tolylimide $C_6H_3Me{<}\substack{C(NC_6H_4Me)\\ NEt}{>}CO$. *p-Toluide* [152°]. Formed by boiling the *p*-tolylimide of *p*-methyl isatin with NaOEt and EtBr (Duisberg, *B.* 18, 198). Large orange-red prisms; v. sol. alcohol, acetic acid, benzene, and CS_2, sl. sol. ether, insol. water. Split up by HCl into *p*-toluidine and methyl-ethyl-ψ-isatin.

Isobutyl-bromo-isatin $C_6H_3Br{<}\substack{CO\\ N}{>}COC_4H_9$. Crystallises with difficulty. Is converted by Ac_2O into iso-butyl-bromo-isatoid $C_{20}H_{16}Br_2O_4$ [210°] which crystallises in slender needles, sl. sol. all solvents (Baeyer a. Oeconomides, *B.* 15, 2097).

Benzyl-ψ-isatin $C_6H_4{<}\substack{CO.CO\\ N(CH_2Ph)}{>}$. [131°]. Formed by adding a solution of sodium benzyl-indole carboxylate to one of NaOCl. The pp. is dissolved in alcoholic NaOH, warmed gently, diluted with water, freed from alcohol by distillation, and ppd. with water (Antrick, *A.* 227, 364). Long silky red needles (from water). Almost insol. cold water, v. sol. alcohol and ether.

Phenol-isatin *v.* Di-oxy-di-phenyl-oxindole.

Tolu-isatin *v.* Di-tolyl-oxindole.

(α)-Naphth-isatin $C_{10}H_6{<}\substack{NH\\ CO}{>}CO$ or

$C_{10}H_6<\genfrac{}{}{0pt}{}{N}{CO}>C.OH$. [255°]. Formed by dissolving (α)-naphthoxindole in alcohol and adding HOAc and $NaNO_2$. The isonitroso- derivative so obtained is reduced with Sn and HCl, and subsequently oxidised with Fe_2Cl_6 (Hinsberg, *B.* 21, 117). Red needles. Forms a compound with phenyl-hydrazine [270°].

(β)-Naphth-isatin $C_{10}H_6<\genfrac{}{}{0pt}{}{N}{CO}>C.OH$. [248°].

Formed by dissolving (β)-naphthoxindole in HOAc and adding sodium nitrite. The isonitroso-body formed yields on reduction with Sn and HCl, and subsequent oxidation with Fe_2Cl_6, the isatin (Hinsberg, *B.* 21, 115). Red needles, v. sol. ordinary solvents.

Ammoniacal Derivatives of Isatin.

Imesatin $C_8H_6N_2O$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{CO}{N}>C.NH_2$ or $C_6H_4<\genfrac{}{}{0pt}{}{CO}{NH}>C:NH$ (?) or $C_6H_4<\genfrac{}{}{0pt}{}{C(NH)}{N}>C.OH$. *Isatin-imide* (?) Obtained by Laurent (*J. pr.* 25, 457) by passing dry NH_3 into a boiling alcoholic solution of isatin containing a little isatin in suspension. Could not be obtained by Sommaruga (*B.* 10, 432). Rectangular prisms: insol. water, v. sl. sol. ether, m. sol. boiling alcohol. Readily decomposed by heating with alcohol and HClAq into isatin and NH_3. KOH acts in like manner.

Chloro-imesatin $C_8H_5ClN_2O$. From chloro-isatin and alcoholic NH_3 (Laurent). Yellow six-sided prismatic tables; v. sl. sol. boiling alcohol, insol. ether. Dissolves in KOH, giving a red liquid.

Bromo-imesatin $C_8H_5BrN_2O$. From bromo-isatin and boiling alcoholic NH_3 (Gericke, *Z.* 1865, 593). Yellowish-brown crystalline mass.

Iso-amyl-imesatin $C_8H_5(C_5H_{11})N_2O$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{CO}{N}>C.NHC_5H_{11}$ or $C_6H_4<\genfrac{}{}{0pt}{}{C(NC_5H_{11})}{N}>C.OH$ (?). Formed by heating isatin with isoamylamine (Schiff, *A.* 144, 53; *Z.* [2] 4, 13). Yellow laminæ; sl. sol. ether, v. sol. alcohol. Decomposed by dilute acids or by prolonged treatment with water into isatin and isoamylamine.

Phenyl-imesatin $C_8H_5(C_6H_5)N_2O$. *Anilide of isatin.* From isatin and aniline in boiling alcoholic solution (Engelhardt, *J.* 1855, 541). Formed also by heating the compound of isatin with bisulphite of aniline, and crystallising from ether-alcohol.

Chloro-phenyl-imesatin $C_8H_5(C_6H_4Cl)N_2O$. From isatin and chloro aniline (E.). Yellowish crystals.

Bromo-phenyl-imesatin $C_8H_5(C_6H_4Br)N_2O$. Resembles the preceding (E.).

Phenyl-chloro-imesatin $C_8H_4Cl(C_6H_5)N_2O$. Formed by adding aniline to a boiling solution of chloro-isatin in alcohol (Engelhardt, *J. pr.* 65, 260). Yellow needles; insol. water, v. sol. hot alcohol. Resolved by boiling dilute acids into chloro-isatin and aniline. Potash gives aniline and potassium chloro-isatate.

Phenyl-bromo-imesatin $C_8H_4Br(C_6H_5)N_2O$. Resembles the above (E.).

Di-phenyl-di-ethyl-di-amide of isatin $C_{24}H_{25}N_3O$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{CO}{NH}>C(NPhEt)_2$ or $C_6H_4<\genfrac{}{}{0pt}{}{C(NPhEt)_2}{N}>C.OH$ (?). So-called *phenyl-ethyl-imesatin.* From isatin by heating with ethyl-aniline (Schiff). Yellow laminæ; sl. sol. ether, v. sol. alkalis. Split up by acids, alkalis, or hot water into isatin and ethyl-aniline.

***p*-Methyl-imesatin** *v. Imide of p-Methyl-isatin* (*supra*).

Phenyl-*p*-methyl-imesatin *v. Anilide of p-methyl-isatin* (*supra*).

Imasatin $C_{16}H_{11}N_3O_3$. Formed by passing NH_3 into a boiling saturated solution of isatin in dilute alcohol (Laurent, *A. Ch.* [3] 3, 483). Greyish-yellow granules; insol. water and ether, v. sl. sol. boiling alcohol. Not attacked by boiling aqueous HCl. Caustic potash dissolves it, and the solution is ppd. by dilute HClAq.

Di-chloro-imasatin $C_{16}H_9Cl_2N_3O_3$. From chloro-isatin and alcoholic NH_3 (L.). Slightly reddish powder.

Di-bromo-imasatin $C_{16}H_9Br_2N_3O_3$. Formed by heating an alcoholic solution of bromo-isatin with ammonia (Gericke, *Z.* 1865, 593). Brownish-yellow crystalline granules.

Tetra-bromo-imasatin $C_{16}H_7Br_4N_3O_3$. From tetra-bromo-isatin and alcoholic NH_3. Reddish-yellow scales (L.).

Amasatin $C_{16}H_{14}N_4O_3$. *Isamide. Amide of Isamic acid?* One of the products of the action of ammonia on isatin. Prepared by heating ammonium isamate till water is given off, and washing the residue with water (Laurent, *A. Ch.* [3] 3, 488; *J. pr.* 35, 117). Yellow powder; insol. water, nearly insol. ether, v. sl. sol. alcohol, m. sol. boiling alcoholic NH_3. Cold KOHAq dissolves it, giving off NH_3, and forming a yellow liquid containing potassium isamate. HClAq forms a violet solution containing isamic acid.

Di-chloro-amasatin $C_{16}H_{12}Cl_2N_4O_3$. Yellow powder, formed by evaporating a solution of ammonium chloro-isatate (L.).

Tetra-chloro-amasatin $C_{16}H_{10}Cl_4N_4O_3$. Formed by heating ammonium di-chloro-isatate.

Di-bromo-amasatin $C_{16}H_{10}Br_2N_4O_3$(?). Formed by evaporating an aqueous solution of ammonium bromo-isatate and treating the pasty residue with water (Gericke). Orange-yellow substance, sl. sol. water, insol. alcohol and ether. Dissolves with violet colour in acids.

Amisatin $C_{48}H_{39}N_{11}O_9$. A product of the action of dilute alcoholic ammonia on isatin and ppd. by adding water to the solution after isatimide and isatilim have crystallised out (L.). Minute needles, insol. alcohol, sol. alcoholic potash.

Isamic acid $C_{16}H_{13}N_3O_4$. Produced by the action of warm ammonia on isatin; but is best prepared by dissolving isatin to saturation in aqueous KOH, evaporating the solution to dryness, dissolving in alcohol, adding a very concentrated solution of ammonium sulphate, filtering, and evaporating to dryness. The residue contains amasatin and ammonium isamate, and the latter may be dissolved in alcohol, whence, after addition of HCl, isamic acid crystallises (Laurent, *A. Ch.* [3] 3, 490). Ruby-coloured hexagonal tables or scarlet trimetric laminæ. Sl. sol. boiling water, forming a yel-

low solution; v. sol. hot alcohol, m. sol. ether. Aqueous HCl dissolves it with violet colour, and it separates again from the solution in violet crystals turned red by water. Boiling dilute acids split it up into isatin and ammonia. Bromine forms 'indelibrome,' a yellow substance $C_{16}H_9Br_4N_3O_3$ insol. water.

Salts.—NH_4A': small needles, or very acute minute rhombs. When strongly heated it gives off water and forms amasatin. Its solution does not ppt. salts of Ba, Ca, or Mg, but gives a yellow pp. with lead acetate and with $AgNO_3$, and a red pp. with $HgCl_2$.—The potassium salt may be boiled without decomposing.—AgA'.

Di-chloro-isamic acid $C_{16}H_{11}Cl_2N_3O_4$. Formed by adding HCl to a solution of di-chloro-amasatin in dilute KOH and crystallising the brick-red pp. from alcohol (L.). Bright-red elongated hexagonal laminæ. More sol. alcohol and ether than isamic acid. Forms yellow solutions. Decomposed by distillation. HClAq forms a violet solution, but on boiling it is split up into NH_3 and chloro-isatin.

Tetra-chloro-isamic acid $C_{16}H_9Cl_4N_3O_4$. By boiling tetra-chloro-amasatin with alcohol and adding silver nitrate a flocculent precipitate of $C_{16}H_8AgCl_4N_3O_4$ is formed (L.).

Di-bromo-isamic acid $C_{16}H_{11}Br_2N_3O_4$. Formed by dissolving di-bromo-amasatin in KOHAq and neutralising with dilute HCl (Gericke). Red powder, nearly insol. water, v. sol. alcohol and ether. HClAq gives a violet solution. Boiling KOHAq gives bromo-isatic acid.—KA': yellow needles, sl. sol. water.—BaA'_2.

Isatimide $C_{24}H_{17}N_5O_4$. Formed by passing dry NH_3 over isatin moistened with alcohol (86 to 100 p.c.). When absolute alcohol is used, imasatin first crystallises out, and the filtrate deposits isatimide as a yellow crystalline powder. Insol. water, scarcely sol. boiling alcohol or ether, v. sol. boiling alcoholic NH_3. Potash dissolves it with yellow colour and evolution of NH_3, the liquid then containing isatin.

Isatilim $C_{24}H_{16}N_4O_5$ (?). Sometimes formed when dry NH_3 is passed over isatin moistened with alcohol, separating from the alcoholic filtrate from which isatimide has separated (Laurent, *J. pr.* 35, 121). Yellow amorphous flocks, easily decomposed by KOH.

Di-isatin diamide $C_{16}H_{12}N_4O_2$. Formed by saturating an alcoholic solution of isatin with dry NH_3 and heating to 100° for 24 hours. The product is filtered boiling, the filtrate containing deoxy-imido-isatin, while the di-isatin diamide and oxydiamidoisatin diamide which remain on the filter are separated by treatment with water in which the di-isatin diamide is the less soluble (E. von Sommaruga, *A.* 190, 367; *B.* 11, 1082; 12, 980). Pale yellow crystals, sl. sol. alcohol and water. Nitrous acid forms some di-isatin amide.

Salts.—B'HCl: yellow crystalline powder, almost insol. cold water.—$B'HNO_3$: yellow needles.—$B'H_2SO_4$: yellow needles. Not decomposed by heating with water at 100°.—$B'H_2CrO_4$: orange powder.

Di-isatin amide $C_{16}H_{11}N_3O_3$. [252°]. Formed by warming di-isatin diamide with dilute KOH and ppg. with HCl (Sommaruga, *M.* 1, 579). Small yellowish needles (from alcohol). Scarcely sol. water, v. sol. alcohol.—$C_{16}H_{10}(NH_4)N_3O_3$: silvery scales.—$C_{16}H_{10}KN_3O_3$ $1\frac{1}{2}$aq: silvery plates or needles.

Dihydride $C_{16}H_{13}N_3O_3$. [213°]. Formed by treating di-isatin amide or di-isatin diamide with sodium-amalgam (Sommaruga, *A.* 194, 88). Slender needles (from alcohol); scarcely sol. water and ether. Oxidised by boiling with HgO or aqueous $FeCl_3$ to di-isatin amide. Not affected by aqueous KOH (S.G. 1·27) at 100°.—$NaC_{16}H_{12}N_3O_3$: long colourless needles, v. sol. hot water.—$KC_{16}H_{12}N_3O_3$: broad needles with silky lustre.

Oxy-diamido-di-isatin diamide $C_{16}H_{14}N_6O_3$. *Oxydiimidodiamidoisatin.* [295°–300°]. Formed as above (S.). Large colourless needles. Sol. water, v. e. sol. alcohol. Dissolves readily in acids, and is not reppd. from these solutions by NH_3. Boiling with water and sodium-amalgam converts it into di-amido-di-hydrindic acid. The solutions of its salts show intense red fluorescence.—$B'HNO_3$: granules, v. sol. hot water.—$B'H_2SO_4$: prisms.

Di-amido-di-hydrindic acid $C_{16}H_{16}N_4O_3$. [217°]. Formed as above. Crystalline granules. Decomposed on fusion. V. sol. hot water. Oxidised by chromic acid mixture to 'di-imido-di-hydrindin dicarboxylic' acid $C_{16}H_{12}N_4O_4$ which crystallises from hot water in needles.

Deoxyimido-diisatin $C_{16}H_{11}N_3O_2$. [210°]. Formed as mentioned under diisatin diamide (S.), and purified by solution in aqueous KOH and ppn. by an acid. Yellowish powder. Decomposed by fusion. V. sol. alcohol, hot water, and alkalis.

Oxy-amido-hydro-isatin, so called, $C_{16}H_{13}N_3O_3$. Formed by treating the preceding body with sodium-amalgam or by heating it with KOHAq in sealed tubes at 100° (S.). Yellowish amorphous powder, insol. water, v. sol. alcohol. Decomposes at 188° without fusion.

ISATIN CARBOXYLIC ACID. *Anilide.* $C_{15}H_{10}N_2O_3$ *i.e.* $C_8H_4NO.CONPhH$, probably $C_6H_4\left\langle\begin{matrix}CO\\N.CONHPh\end{matrix}\right\rangle CO$. *Carbanilido-isatin.* [180°–183°]. Formed by heating isatin for 3 hours at 130° with phenyl cyanate (Gumpert, *J. pr.* [2] 32, 283). Crystallises from benzene in canary-yellow needles. Sol. alcohol, ether, and glacial acetic acid.

Reactions.—1. When fused it forms isatin and phenyl cyanate (compare the formation of isatin from acetyl-isatin).—2. With H_2SO_4 and crude benzene it gives the indophenin reaction. 3. Dissolves in warm dilute KOH forming potassic carbanilo-isatate. HCl throws down sparingly soluble carbanilido-isatic acid, $NPhH.CO.NH.C_6H_4.CO.CO_2H$, [170°–180°, with decomposition]. The acid is very stable, but by heating at 110° for a long time it loses H_2O, changing back to carbanilido-isatin. Carbanilido-isatic acid, when heated with ethyl or methyl alcohol, splits off CO_2 and H_2O forming $C_{16}H_{16}N_2O_2$ [175°], and $C_{15}H_{14}N_2O_2$ [197°], respectively.—4. Converted by *amines* into amides of carbanilido-isatic acid, thus alcoholic NH_3 at 100° forms $NPhH.CO.NH.C_6H_4.CO.CO.NH_2$ [229°], crystallising from alcohol in needles. It dissolves in dilute NaOH, but is reppd. unaltered by HCl. When dissolved in glacial acetic acid it is converted by N_2O_3 into an indifferent body, $C_{14}H_{12}N_2O_2$, [270°].—5. $NEtH_2$

forms $NPhH.CO.NH.C_6H_4.CO.CO.NEtH$ [210°]. It forms needles (from alcohol) and is a weak acid. — 6. *Phenyl-hydrazine* forms $NPhH.CO.NH.C_6H_4.CO.CON(NH_2)Ph$ [193°].— 7. *Hydroxylamine* forms $NPhH.CO.NH.C_6H_4.CO.CO.NH.OH$ [225°].

ISATIN DIHYDRIDE *v.* DIOXINDOLE.

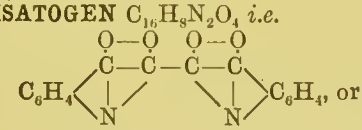
ISATIN INDOGENIDE *v.* INDIGO.

ISATIN SULPHONIC ACID $C_8H_5NSO_5$ *i.e.* $SO_3H.C_6H_3{<}\begin{matrix}CO\\N\end{matrix}{>}C.OH$. *Isatosulphuric acid.*

Preparation.—Commercial indigo-carmine (18 pts.) is stirred up into a thin paste with water (18 pts.), H_2SO_4 ($1\frac{1}{2}$ pts.) is added, and the mixture heated to boiling while $K_2Cr_2O_7$ (1 pt.) is gradually thrown in, as long as decolourisation ensues. The hot solution is filtered and KNO_3 added, which facilitates the deposition of potassium isatin sulphonate. The K salt is mixed with resinous matter, which can be got rid of by dissolving in hot baryta-water, ppg. excess of baryta by CO_2, and then ppg. by K_2SO_4 (G. a. A. Schlieper, *A.* 120, 1). Yellow radio-crystalline mass (containing 2aq). Insol. ether and benzene, m. sol. alcohol, v. sol. water. Powerful acid, separating HCl from its salts. Not decomposed by H_2SO_4 or HNO_3, even on boiling. Aqua regia slowly forms tetra-chloro-quinone. Alcoholic NH_3 forms dark-brown bodies. Hydric iodide does not reduce it. Ammonium sulphide forms $SO_3H.C_6H_3{<}\begin{matrix}CH(OH)\\N\end{matrix}{>}COH$. Hot potash forms sulpho-isatic acid.

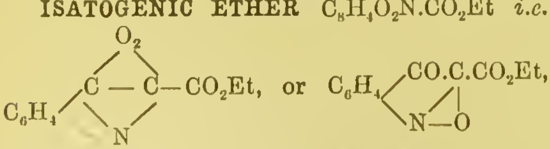
S a l t s.—NaA′ 2aq: deep-red tables; ppd. from its aqueous solution by NaCl.—KA′aq: small golden needles. S. 5 in the cold. Insol. alcohol. Ppd. by KNO_3 from its aqueous solution.—NH_4A' aq: deep-yellow needles, v. sol. water, sl. sol. NH_4Cl.—BaA'_2 4aq: scarlet powder, insol. alcohol, sl. sol. water.—CaA'_2 2aq: small golden needles, m. sol. water.—AgA′ aq: yellow needles, sl. sol. water.

DIISATOGEN $C_{16}H_8N_2O_4$ *i.e.*



$C_6H_4{<}\begin{matrix}CO.CO.CO.CO\\N\text{=====}N\end{matrix}{>}C_6H_4$ (Michael, *J. pr.* [2] 35, 256). Prepared by the action of fuming H_2SO_4 on di-o-nitro-di-phenyl-diacetylene (Baeyer, *B.* 15, 52). Red needles. Sol. nitrobenzene, sl. sol. chloroform, insol. alcohol and ether. With H_2SO_4 and $FeSO_4$ it gives indoïn. It is very readily reduced to indigo by cold NH_4HS, by zinc-dust, and NH_4NaOH or AcOH, by glucose, and alkalis, &c. It combines with ammonium bisulphite.

ISATOGENIC ETHER $C_8H_4O_2N.CO_2Et$ *i.e.*



or $(CO_2Et.CO.CO.C_6H_4)_2N_2$ (Michael, *J. pr.* [2] 35, 255). [115°]. Formed by an isomeric change from o-nitro-phenyl-propiolic ether by the action of cold H_2SO_4 (Baeyer, *B.* 14, 1741; 15, 780). Yellow needles. By most reducing agents it is reduced to indoxylic ether, but ferrous salts give indoxanthic ether (Baeyer, *B.* 15, 780). Isatogenic acid is perhaps formed by shaking o-nitrophenyl-propiolic acid with H_2SO_4, but if so, it is decomposed on diluting with water into CO_2 and isatin.

ISATOIC ACID $C_8H_5NO_3$ *i.e.* $C_6H_4{<}\begin{matrix}CO\\|\\N.CO_2H.\end{matrix}$ *Anthranil carboxylic acid.* [230°]. S. (acetone) 4·4 at 55°.

Formation.—1. By the oxidation of isatin by CrO_3 in HOAc (Kolbe, *J. pr.* [2] 30, 469).—2. By heating anthranil with chloro-formic ether at 130° (Friedländer a. Wleügel, *B.* 16, 2227).— 3. By boiling o-amido-benzoic acid with excess of chloro-formic ether (Niementowski a. Rozauski, *B.* 22, 1672).

Preparation.—(H. Kolbe, *J. pr.* [2] 30, 469). Isatin (100 g.) is powdered and mixed with glacial acetic acid (600 g.). A solution of CrO_3 (200 g.) in glacial acetic acid (600 g.) is slowly added, the temperature being kept below 50°. The flask is left for 12 hours in cold water, and then in water at 50°, and finally at 60°. Isatoic acid then begins to separate as a yellow powder, the separation is completed by pouring into 500 c.c. cold dilute H_2SO_4. Yield 72 per cent.

Properties.—Nearly rectangular prisms, which are yellow (through some impurity) when prepared from isatin. Decomposed at 230°. Sparingly soluble in alcohol, ether, and glacial acetic acid, rather more soluble in chloroform and benzene.

Reactions.—1. Boiled with water it forms o-amido-benzoic (anthranilic) acid: $C_7H_4NO.CO_2H + H_2O = C_6H_4(NH_2)CO_2H + CO_2$.— 2. Conc. HCl, H_2SO_4, and dilute HNO_3 behave in the same way.—3. Gaseous HCl passed into an alcoholic solution forms the hydrochloride of o-amido-benzoic ether.—4. Aqueous *baryta* forms, on warming, o-amido-benzoic acid.—5. *Ammonia* (aqueous or dry) forms o-amido-benzamide. 6. *Aniline* at 60° forms the anilide of o-amido-benzoic acid.—7. HNO_3 (S.G. 1·48) forms nitro-isatoic acid.—8. *Nitrous acid gas* passed into water, containing isatoic acid suspended, forms (α)-nitro-salicylic acid. Anthranilic acid is doubtless first formed, and this is then nitrated and exchanges NH_2 for OH.—9. Heated with *methyl* or *ethyl alcohol* it unites, forming crystalline compounds, carboxylic acids of the methyl or ethyl ethers of *o*-amido-benzoic acid:

$$C_6H_4{<}\begin{matrix}CO\\|\\N.CO_2H\end{matrix} + MeOH = C_6H_4{<}\begin{matrix}CO_2Me\\NH.CO_2H.\end{matrix}$$

The acid $CO_2H.NH.C_6H_4.CO_2Me$ crystallises in needles [176°], while the corresponding $CO_2H.NH.C_6H_4.CO_2Et$ forms needles [126°].— 10. With *benzoyl chloride* at 210° it partly reacts thus: $C_6H_4{<}\begin{matrix}CO\\|\\N.CO_2H\end{matrix} + BzCl$

$= CO_2 + HCl + C_6H_4{<}\begin{matrix}CO\\|\\NBz\end{matrix}$, forming benzoyl-anthranil [123°].—11. *Bromine* forms bromo-isatoic acid, which gives with HCl (β)-bromo-anthranilic acid [208°].—12. It dissolves in cold dilute NaOH with a blue fluorescence, but on standing the fluorescence vanishes and the solution then contains anthranilic acid (Friedländer a. Wleügel, *B.* 16, 2227).—13. *Phenol* at 180° gives phenyl

o-amido-benzoate crystallising in needles [70°] (G. Schmidt a. E. v. Meyer, *J. pr.* [2] 36, 370).—14. Long boiling with glacial *acetic acid* forms an amorphous compound $C_{35}H_{27}N_5O_6$, v. sl. sol. ordinary solvents, which yields *o*-amido-benzoic acid when heated with HCl or dilute H_2SO_4 (G. Schmidt, *J. pr.* [2] 36, 380).—15. Heating with Ac_2O gives acetyl-*o*-amido-benzoic acid [180°] (S.).—16. With *hydroxylamine* it forms *o*-amido-benzoyl-hydroxylamine (E. v. Meyer a. T. Bellmann, *J. pr.* [2] 33, 19) $C_6H_4\left<\begin{array}{l}CO\\|\\N.CO_2H\end{array}\right. + H_2NOH$ $= C_6H_4(NH_2)CO.NH(OH) + CO_2$.—17. With *phenyl-hydrazine* it forms *o*-amido-benzoyl-phenyl-hydrazine $C_6H_4\left<\begin{array}{l}CO\\|\\N.CO_2H\end{array}\right. + PhNH.NH_2$ $= C_6H_4(NH_2)CO.NPh.NH_2 + CO_2$.—18. It does not react with boiling *di-methyl-aniline*.—19. *Pyrocatechin* at 130° reacts thus (M. a. B.): $C_6H_4(OH)_2 + C_6H_4\left<\begin{array}{l}CO\\|\\N.CO_2H\end{array}\right.$ $= CO_2 + C_6H_4(NH_2)CO.O.C_6H_4OH$, forming o-oxyphenyl o-amido-benzoate. 20. Boiled with *formic acid* it forms formyl-o-amido-benzoic acid and a weak base, $C_{31}H_{20}N_4O_6$. This crystallises in rhombohedra (from alcohol). It melts at [280°], with decomposition. Sparingly soluble in water, alcohol, benzene, and chloroform. S. (ether) ·03 at 15°; S. (alcohol) ·11 at 19°. Readily soluble in NaOH,Aq, forming a crystalline salt. Its hydrochloride forms prisms, but is decomposed by water. Heated with conc. HCl at 140° it forms CO_2, formic acid, and the hydrochloride of anthranilic acid (M. a. B.).—21. By treatment with PCl_5 in presence of $POCl_3$ a product is got whence methyl alcohol and ethyl alcohol respectively form crystalline products. The former gives $C_{16}H_{16}N_2O_5$ [210°]; small needles. The latter gives $C_{17}H_{18}N_2O_5$ [170°]; needles. With conc. HCl at 140° the latter gives EtCl and anthranilic acid (M. a. B.).—22. *Bleaching powder* suspended in chloroform changes some of the isatoic acid into an isomer [240°], soluble in alcohol, acetone, and benzene. It dissolves in NH_3,Aq without forming anthranilamide (unlike isatoic acid), but when HCl is added to the solution an acid [260°] is ppd. (M. a. B.).—23. Heated with glacial acetic acid and *bromine* (1 mol.) it forms bromo-isatoic acid, but with more bromine CO_2 is evolved, and di-, tri-, and tetra-bromo-amido-benzoic acids are got.

Chloro-isatoic acid $C_6H_3Cl\left<\begin{array}{l}CO\\|\\N.CO_2H\end{array}\right.$. [c. 268°]. From chloro-isatin (10 g.), CrO_3 (20 g.) and glacial acetic acid (120 g.) as described under bromo-isatin (Dorsch, *J. pr.* [2] 33, 49).

Properties. — Pearly plates (from alcohol-ether). Sl. sol. alcohol, acetone, and glacial acetic acid, insol. benzene, chloroform, ether, and water.

Reactions.—1. Conc. HCl forms chloro-o-amido-benzoic acid [204°].—2. Hot NH_3Aq forms the amide of chloro-amido-benzoic acid.

Di-chloro-isatoic acid $C_6H_2Cl_2\left<\begin{array}{l}CO\\|\\N.CO_2H\end{array}\right.$. [256°].

Formation.—By oxidation of di-chloro-isatin.

Properties.—Yellow prisms (from alcohol-acetone). Melts at 254°–256° with decomposition. V. sol. acetone and glacial acetic acid, sol. alcohol and chloroform, v. sl. sol. ether and benzene. Boiled with water it partly changes to di-chloro-*o*-amido-benzoic acid, as shown by its violet fluorescence (Dorsch, *J. pr.* [2] 33, 51).

Reactions.—1. Conc. HCl slowly converts it, on boiling, into di-chloro-amido-benzoic acid [224°].—2. With NH_3Aq it gives di-chloro-amido-benzamide.

Bromo-isatoic acid $C_6H_3Br\left<\begin{array}{l}CO\\|\\N.CO_2H\end{array}\right.$. [c. 275°].

Formation.—1. By oxidising bromo-isatin. 2. From Br and isatoïc acid suspended in glacial acetic acid at 90° (R. Dorsch, *J. pr.* [2] 33, 32).

Properties.—Pearly plates (from a mixture of alcohol and acetone). Sol. acetone. Sl. sol. alcohol and glacial acetic acid. Insol. water, chloroform, ether, and benzene.

Reactions.—1. With boiling conc. hydrochloric acid it forms (β)-bromo-amido-benzoic acid $C_6H_3Br(NH_2)CO_2H$.—2. With hot NH_3Aq it gives bromo-amido-benzamide.

Di-bromo-isatoic acid $C_6H_2Br_2\left<\begin{array}{l}CO\\|\\N.CO_2H\end{array}\right.$. [255°]. Obtained by oxidising di-bromo-isatin (10 g.) by CrO_3 (10 g.) in presence of glacial acetic acid (60 g.) as described under *bromo*-Isatin.

Properties. — Flesh-coloured prisms (from alcohol-acetone). Sol. glacial acetic acid and acetone, sl. sol. alcohol, chloroform, and benzene, hardly sol. ether, insol. water. Much more stable than bromo-isatoic acid.

Reactions.—1. Boiled for a long time with conc. HCl it gives off CO_2, leaving di-bromo-*o*-amido-benzoic acid.—2. It does not dissolve in NH_3Aq. But if heated with it at 100° for a long time it forms di-bromo-amido-benzamide $C_6H_2Br_2(NH_2)CO.NH_2$ [197°].

Nitro-isatoic acid $C_7H_3(NO_2)NO.CO_2H$. [220°–230°]. Formed by the action of HNO_3 (S.G. 1·48) on isatoic acid. Insol. water and ether, sl. sol. alcohol. Crystallises from equal parts of alcohol and acetone in pearly plates. It resembles isatoic acid, splitting up readily into CO_2 and nitro-*o*-amido-benzoic acid, when boiled with HCl or even with water. Nitro-isatoic acid is converted by aqueous NH_3 into nitro-amido-benzamide. By Sn and HCl it is reduced to di-amido-benzoic acid, CO_2 escaping. Bromine (in glacial acetic acid) converts it into mono-, di-, and tri- nitro-amido-benzoic acids (*q. v.*).

Methyl-isatoic acid $C_6H_3Me\left<\begin{array}{l}CO\\|\\N.CO_2H\end{array}\right.$.

Preparation.—Methyl-isatin (10 g.) is mixed with glacial acetic acid (60 g.) and cooled well while a mixture of CrO_3 (21 g.) in glacial acetic acid (60 g.) is slowly added. After 12 hours at 0° the mixture is heated for 2 hours at 40° and then to 70°. It is poured into water containing H_2SO_4, and the yellow powder crystallised from absolute alcohol (Panaotović, *J. pr.* [2] 31, 122; 33, 58).

Properties.—Pale-yellow crystalline plates

(from boiling alcohol) or trimetric columns (from acetone). At 245° it suddenly increases in bulk, but it melts above 300°, giving off CO_2. V. sl. sol. water, readily sol. boiling alcohol, ether, benzene, and chloroform.

Reactions.—1. Is more stable than isatoic acid, not being decomposed by dilute mineral acids.—2. HNO_3 (S.G. 1·48) dissolves it in the cold. After 12 hours water is slowly added, and the pp. crystallised from benzene. It forms pale-yellow trimetric plates of nitro-methyl-isatoic acid [175°]. This acid is reduced by Sn and HCl to a di-amido-toluic acid.—3. Warmed with HCl (S.G. 1·2), CO_2 is given off, and the hydrochloride of amido-*p*-toluic acid [207°] formed.—4. Warmed with NH_3Aq it gives the amide of amido-toluic acid [178°].—5. With *aniline* in alcohol it forms the corresponding anilide [243°].—6. With *phenyl-hydrazine* it forms the corresponding hydrazide.—7. With MeOH at 180° it forms methylic amido-toluate.

Methyl-isatoic acid $C_9H_7NO_3$ *i.e.*

$$C_6H_3Me\left\langle\begin{array}{l}CO\\ |\\ N.CO_2H\end{array}\right. .$$

[226°]. Formed by boiling an amido-toluic acid $C_6H_3Me(NH_2)CO_2H$ [5? or 3?:1:2] with chloro-formic ether (Niementowsky a. Rozansky, *B.* 22, 1675). Needles or scales; v. sl. sol. benzene and ether, sl. sol. alcohol. Decomposed on fusion. Acids and alkalis decompose it into CO_2 and amido-toluic acid [177°].

Isomeride of isatoic acid *v.* ANTHROXANIC ACID.

ISATYDE $C_{16}H_{12}N_2O_4$. Produced by the reduction of isatin by zinc and dilute H_2SO_4 by alcoholic ammonium sulphide, or by zinc-dust and HOAc (Laurent, *A. Ch.* [3] 3, 382; *A.* 72, 285; Erdmann, *J. pr.* 24, 15; 25, 438; Baeyer, *B.* 12, 1309). Formed also by atmospheric oxidation of an aqueous solution of dioxindole (Baeyer a. Knop, *A.* 140, 10). White powder, with slightly greyish tint, almost insol. water, v. sl. sol. boiling alcohol and ether. Separates from boiling alcohol in minute scales. Decomposed by heat, becoming at first violet-brown. Alcoholic potash forms isatic acid, indin, and other products.

Di-chloro-isatyde $C_{16}H_{10}Cl_2N_2O_4$. Formed by the action of ammonium sulphide on chloro-isatin. White powder; crystallisable; insol. cold, v. sl. sol. hot, water; m. sol. boiling alcohol, sol. hot aqueous potassium sulphide. At 180° it is resolved into chloro-isatin and chloro-indin. Boiling aqueous or alcoholic potash forms potassium chloro-isatate and the salt $C_6H_3Cl(NH_2).CH(OH).CO_2K$.

Tetra-chloro-isatyde $C_{16}H_8Cl_4N_2O_4$. Produced by the action of ammonium sulphide on di-chloro-isatin. White powder, insol. water. Decomposed by heat into di-chloro-isatin and di-chloro-indin. Alcoholic potash forms di-chloro-isatin and di-chloro-o-amido-α-oxy-phenyl-acetic (di-chloro-hydrindic) acid.

Tetra-bromo-isatyde $C_{16}H_8Br_4N_2O_4$. From di-bromo-isatin and ammonium sulphide. Resolved by heat into di-bromo-isatin and di-bromo-indin.

Thio-isatyde $C_{16}H_{12}N_2O_3S$. Formed by slowly adding alcoholic potash to an alcoholic solution of di-thio-isatyde (Laurent, *A. Ch.* [3] 3, 463). White crystalline powder. May be crystallised as minute rectangular scales from hot alcohol. Insol. water, v. sl. sol. boiling alcohol and ether. Cold potash forms indin and other products. Hot potash forms the hydride of indin.

Di-thio-isatyde $C_{16}H_{12}N_2O_2S_2$. When H_2S is passed into a conc. alcoholic solution of isatin the liquid becomes pale yellow and on cooling deposits crystals of sulphur and of isatyde. The filtrate when mixed with water deposits di-thio-isatyde (Laurent). Yellowish-grey amorphous powder. Decomposed by heat. Insol. boiling water, v. sol. warm alcohol and ether. Ammonium bisulphite converts it into 'ammonium sulphisatanite' $NH_4C_8H_6NSO_4$ aq, which crystallises in large pale-yellow tables, v. sol. water, m. sol. alcohol.

Di-bromo-di-thio-isatyde $C_{16}H_{10}Br_2N_2O_2S_2$. Formed, together with di-bromo-tri-thio-isatyde, when H_2S is passed into a boiling alcoholic solution of bromo-isatin (Gericke, *Z.* 1865, 595). Yellowish-white powder; insol. hot water, sol. hot alcohol and ether.

Di-bromo-tri-thio-isatyde $C_{16}H_{10}Br_2N_2OS_3$. Formed as above. Yellowish-white powder.

Isatane $C_{32}H_{26}N_4O_6$. Formed, as a white pp., when di-thio-isatyde is boiled with a solution of ammonium bisulphite (Laurent, *J. pr.* 28, 346). Formed also by the action of sodium-amalgam on an acid solution of isatin (Knop, *J. pr.* 97, 65). Small white cubes (from ether or hot alcohol); insol. water. Decomposed by hot alcoholic potash into dioxindole and indiretin. Its alcoholic solution gives with ammoniacal $AgNO_3$ a white pp. of $Ag_4C_{32}H_{22}N_4O_6$.

ISETHIONIC ACID $C_2H_6SO_4$ *i.e.* $HO.CH_2.CH_2.SO_3H$. *Oxy-ethane sulphonic acid. Sulphonic acid of ethyl alcohol.* Mol. w. 126.

Formation.—1. Discovered by Magnus in 1833 (*P.* 27, 378; *A.* 6, 163) as a product of the action of SO_3 on alcohol or ether. Hence it is found among the residues in the preparation of ether.—2. By boiling ethionic acid with water (Magnus, *A.* 32, 251).—3. By the action of SO_3 on barium ethyl sulphate (Meves, *A.* 143, 196). 4. By the action of nitrous acid on taurine $NH_2.CH_2.CH_2.SO_3H$ (W. Gibbs, *Am. S.* [2] 25, 30). 5. By heating chloro-ethyl-alcohol (chlorhydrin of glycol) with aqueous Na_2SO_3 at 175° (Collmann, *A.* 148, 101).—6. By heating ethylene oxide with aqueous $KHSO_3$ at 100° (Erlenmeyer a. Darmstädter, *Z.* 1868, 342).—7. Probably formed by boiling ethyleno bromide with aqueous Na_2SO_3 (James, *C. J.* 43, 44).—8. By oxidising thio-glycol $HO.CH_2.CH_2.SH$ with nitric acid (Carius, *A.* 124, 260).

Preparation.—SO_3 is added, with shaking, to an equal weight of ether at 0°. As soon as a sample mixed with water gives a *heavy* oil the whole is poured into water and the ethyl sulphate washed with water till neutral, dried over H_2SO_4, treated with its own weight of SO_3, and then poured into water. The two aqueous liquids are boiled for a long time to decompose ethionic acid, and then neutralised by baric carbonate; on evaporating baric isethionate is got (R. Hübner, *A.* 223, 212).

Properties.—Viscid, strongly acid syrup, which gradually dries up to a deliquescent radio-crystalline mass. Is not decomposed at 150°, but blackens at a higher temperature. Its

salts are not decomposed by boiling with water, and may even be heated to 200°, above which temperature, however, they lose water and change to di-isethionates. Potash-fusion gives potassium carbonate, oxalate, sulphate, and sulphite. Berthelot (*Z.* 1869, 682) obtained acetylene, K_2SO_3, and hydrogen. PCl_5 yields $CH_2Cl.CH_2.SO_2Cl$, which is converted by heating with aqueous ammonia into taurine (Kolbe, *A.* 112, 241). Chromic acid oxidises isethionic acid to sulpho-acetic acid $CO_2H.CH_2.SO_3H$.

Salts.—NH_4A': octahedra. [130°] (Strecker); [135°] (Seyberth, *B.* 7, 391). At 235° it changes to ammonium di-isethionate (Carl, *B.* 12, 1604). —KA': rhomboidal prisms, melting between 300° and 350° without loss of weight. May be crystallised from alcohol.—BaA'_2: transparent six-sided plates. [320°]. V. sol. water. S. (60 p.c. alcohol) 6 at 14°.—CuA'_2 2aq: pale-green prisms. —AgA': very hygroscopic pearly needles.

Double salts with Et_2SO_4 (Engelcke, *A.* 218, 270). From NaA', H_2SO_4, and alcohol, and conversion into barium salt $BaA'_2Et_2SO_4$ (?). — $NaA'Et_2SO_4$.

Double salt with Me_2SO_4.—$NaA'Me_2SO_4$. Silky monoclinic tables (from alcohol), very hygroscopic. Decomposed by water at 80°, thus:

$$C_2H_4(OH)SO_3NaMe_2SO_4 + 2H_2O = C_2H_4(OH)SO_3H + 2MeOH + NaHSO_4.$$

Ethyl derivative $EtO.CH_2.CH_2.SO_3H$. *Sulphonic acid of ether.* S.G. $\frac{21}{4}$ 1·359. The sodium salt is obtained by the action of chloroethane sulphochloride on excess of NaOEt (R. Hübner, *A.* 223, 218). Also from $CH_2Cl.CH_2.SO_3Na$ and NaOEt. The free acid is got by boiling with water the product obtained by acting with H_2S on the (molecular?) compound of its lead salt with lead ethyl sulphate. It is a syrup.

Salts.—NaA'. Plates. S. (alcohol) 2·7 at 15°.—NaA' ½aq. Columns.—BaA'_2aq.—$ZnA'_2$6aq. Hygroscopic plates.—$CuA'_2$6aq.

Double compounds with the salts of ethyl sulphuric acid $EtSO_4H$. Got by adding H_2SO_4 and alcohol to $EtO.CH_2.CH_2.SO_3Na$, filtering from Na_2SO_4, and neutralising with a metallic carbonate. The general formula is: $C_2H_5SO_4H, C_2H_5O.C_2H_4.SO_3H$ or $C_6H_{14}S_2O_8H_2$, *e.g.* BaA'' aq. Silky scales.—$(NH_4)_2A'_1A'_2$.—$PbA'_1A'_2$. — $Na_2A'_1A'_2$aq. — $ZnA'_1A'_2$5aq. — $CuA'_1A'_2$4aq. These salts are very soluble in water. The free acid splits up on boiling with water, in the following manner: $C_2H_5SO_4H,EtO.C_2H_4.SO_3H + H_2O = EtO.C_2H_4SO_3H + H_2SO_4 + EtOH$.

Ethyl ether $HO.CH_2.CH_2.SO_3Et$. From AgA' and EtI (Stempnewsky, *J. R.* 1882, 95).

Ethyl derivative of the ethyl ether $EtO.CH_2.CH_2.SO_3Et$. S.G. $\frac{15}{}$ 1·168 (impure). From $CH_2Cl.CH_2.SO_2Cl$ and NaOEt in ether. Not obtained quite pure.

Benzoyl derivative $BzO.CH_2.CH_2.SO_3H$. From potassium isethionate and BzCl (Engelhardt a. Latschinoff, *Z.* 1868, 235).—KA': Leaflets; v. sol. boiling water, sol. hot alcohol.—BaA'_2aq: Large thin tables; m. sol. cold water, sol. boiling alcohol.

Chloride $HO.CH_2.CH_2.SO_2Cl$. Probably formed, together with $CH_2Cl.CH_2.SO_3H$ and $CH_3.CH_2.O.SO_2Cl$, by the action of SO_3 on ethyl chloride, or of $ClSO_3H$ on ethylene (Purgold, *B.* 6, 504). Excess of SO_3 converts it into the chloride of ethionic acid (Claesson, *J. pr.* [2] 19, 253).

Di-isethionic acid $O(CH_2.CH_2.SO_3H)_2$. *Disulphonic acid of ether.* The ammonium salt of this acid is obtained by heating ammonium isethionate to 210° (Carl, *B.* 12, 1604).—$(NH_4)_2A''$. [198°]. Slender leaflets or scales; v. e. sol. water.—BaA''aq: prismatic tables. Formed by heating barium isethionate to 200° (Carl, *B.* 14, 65).

ISINGLASS *v.* Proteïds, *Appendix C.*

ISO-. Compounds whose names begin with iso- are usually described either under the name to which iso- has been prefixed or else under their systematic names as described in the *Introduction to Articles Relating to Organic Chemistry*, vol. i.

ISOMERISM. Even a superficial reader of chemical literature will soon become aware that the term *isomeric* and the kindred expressions *allotropic*, *metameric*, and *polymeric* are by no means always used in consistent senses, and he will have considerable difficulty in clearly realising their exact and relative import; it, therefore, appears desirable to discuss the meanings of these terms, especially from the historical side, and as far as possible to define the sense in which they are severally applicable. The following extracts from the article *Isomerism* in the first edition of this Dictionary, vol. iii. p. 415, 1865, by J. A. Wanklyn, serve to show what views were held at the very outset of the period when the investigation of isomeric substances began largely to engage the attention of chemists:—

'*Isomerism.*—This term is derived from ἴσος equal, and μέρος a part, and its employment by chemists is an expression of the fact that very different chemical compounds have sometimes identically the same ultimate composition. Two or more different bodies which are composed of the same elements, and of the same proportions of these elements (*i.e.* which have the same percentage composition) are said to be *isomeric.* Isomerism is sometimes used in a narrower sense, being made to signify equality of molecular weight, as well as identity in percentage composition. When the compounds have the same percentage composition, but different molecular weights, the term *polymeric* is employed. Thus there are the terms *Isomeric* (in its wide sense), signifying that the different bodies have the same percentage composition; *Polymeric*, signifying that these different bodies have the same percentage composition, but different molecular weights; *Isomeric* (in its restricted sense), sometimes called *Metameric*, signifying that the bodies have the same percentage composition, and likewise the same molecular weight.'

As examples, Wanklyn then cites butyric acid, ethylic acetate, aldehyde, and ethylenic oxide as *isomeric* compounds, using the term in its widest sense: of these butyric acid and ethylic acetate are said to be *polymeric* with aldehyde and ethylenic oxide; butyric acid being *isomeric* (in the restricted sense) or *metameric* with ethylic acetate; aldehyde and ethylenic oxide being also metameric compounds. Subsequently, throughout his article, Wanklyn uses the term isomeric in its wide sense, substituting the term metameric for isomeric used in its restricted sense; thus he speaks of methyl, the simplest alcohol radicle, as metameric with ethyl hydride (his article was written at a time when Schorlemmer's investigation was not fully recognised as affording proof of their identity); he points out that several metameric hexanes are possible; and even quotes 'as a very remarkable

example of metamerism' the different varieties of tartaric acid and racemic acid.

The term *allotropy* is made use of by Wanklyn in an unusually wide sense. Thus he says:—

'Closely related to the term isomerism is the term *allotropy*. Both of them have reference to the same substantial fact, viz. that different substances have sometimes the same ultimate composition; but they differ in their manner of stating it. Isomeric and allotropic are in fact complementary terms, "isomeric" being employed to predicate identity of composition between different bodies, whilst "allotropic" expresses difference between bodies of identical composition. Such being the force of these words, there is a certain propriety in their usage; thus, whilst it is correct to say "butyric acid and acetic ether are *isomeric*," it should be "there are *allotropic* bodies of the formula C_6H_7N." The same reason which enjoins the use of allotropic in this case prescribes it in the instance of single elements; thus, for example, we read of "allotropic kinds of sulphur," but never of isomeric kinds. It is worthy of remark that cases of isomerism occurring in inorganic chemistry are usually described by employing the word allotropy or allotropic, while the reverse obtains in organic chemistry. This may be partly ascribed to there being always a very wide difference—or else no difference at all—in the composition of any definite inorganic substances; and hence the fact of identity or non-identity of composition being so easily ascertainable, it is implied in the form of expression, whilst the fact of difference of properties alone needs to be made the subject of formal predication. Among organic bodies, on the other hand, it continually happens that the differences of composition are quite decided, and yet so very minute as to tax the utmost powers of chemical analysis for their recognition; and hence the superior dignity which the mere affirmation of identity of ultimate composition acquires in the organic department of the science. The principal examples of allotropy or isomerism, *i.e.* of the co-existence of identical ultimate composition with difference of properties, will now be considered.'

He then cites the olefines as examples of polymerism, and afterwards discusses numerous cases of metamerism, several of which were referred to above.

Under the heading *Isomers among Inorganic Substances* the following interesting passages occur at the conclusion of the article:—

'As before remarked, the instances of inorganic isomerism are usually called instances of allotropy—isomeric substances and allotropic substances being nearly equivalent expressions. The elementary substances themselves offer many examples of isomerism. . . . Ozone and oxygen are isomeric bodies. . . . Experiment has shown that the molecular formula for ozone is higher than that for oxygen, but how much higher remains an open question. Sulphur, phosphorus, carbon, and many other elements present *somewhat* similar examples of allotropy or isomerism. Inorganic compounds, such as the various forms of silicic acid, of sesquioxide of iron, of sesquioxide of chromium, of alumina, must be classed among substances affording examples of isomerism. The explanation of the existence of isomerism will have become sufficiently clear from the course which has been followed in describing the different examples of it. "It is of consequence how the atoms of a compound are arranged, as well as what kind of atoms they are," and hence there may be very many totally different substances composed of the same ultimate atoms. This is in fact the whole philosophy of isomerism.'

The definitions given in Kekulé's *Lehrbuch* (1867) are substantially the same as those adopted by Wanklyn; but he specially draws attention to the existence of compounds *isomeric in a restricted sense*, which, according to the state of knowledge of the time, were to be represented by the same rational formulæ, although they either were possessed of different properties—as in the case of the $C_{10}H_{16}$ hydrocarbons and of maleic and fumaric acids, or they were in all essential respects chemically identical but physically different—such as the tartaric acids, mucic and saccharic acids, &c. The existence of compounds such as these latter, in fact, gave rise to the recognition of a distinct kind of isomerism, termed *physical isomerism*.

In the latest edition of Watts' *Fownes* by Tilden (1886), polymerism is included under isomerism, but compounds of the same molecular weight are sub-divided into (1) *metameric* bodies, namely, those which exhibit dissimilar transformations under similar circumstances: propionic acetate, methylic acetate, and ethylic formate are quoted as examples; and (2) *isomeric* bodies, *strictly so-called*, namely, those which exhibit the same or closely similar decompositions and transformations when subjected to the action of the same reagents, such as the $C_{10}H_{16}$ hydrocarbons, the glucoses, the tartaric acids, &c.

It will be noted how incompatible are the definitions given by Wanklyn and in *Fownes* of the term metameric; it has, however, undoubtedly been customary of late years to employ the term metameric in the sense indicated in *Fownes*.

In M'Gowan's translation of Bernthsen's *Organic Chemistry* (1889), the most modern book of its kind, polymerism is not reckoned under isomerism, but the definition given of metamerism is on the whole more in agreement with that quoted from Watts' *Fownes*; after it has been explained that ethers such as methyl-amyl ether, ethyl-butyl ether, and dipropyl ether are isomeric, we read:—

'Such isomerism, which depends upon the grouping together by a polyvalent element of alcohol radicles which are individually unequal, but the sum of whose elements taken together are equal, is called *metamerism*. One of the alcohol radicles may here be replaced by hydrogen. . . . Alcohols and ethers containing an equal number of carbon atoms are therefore metameric.'

We further learn that the isomerism of the higher paraffins, since it is based upon the dissimilarity of the carbon chains, is often termed *chain-isomerism*; that the isomerism between ethylene and ethylidene chlorides, or between primary and secondary propyl alcohols, as it depends upon the difference in position of the substituting halogen or hydroxyl in the same carbon chain, is termed *isomerism of place or position*; and that there is the third kind of isomerism, viz. metamerism. But obviously two different kinds of relationship are thus included under metamerism: that of position-isomerism, which obtains among the ethers themselves, which are necessarily all compounds of one primary type; and that which obtains between the typically different 'equi-molecular' alcohols and ethers, or true metamerism, if the *Watts-Fownes* definition be adopted.

If we consider the origin of the four terms under consideration we find that they were all devised by Berzelius. The term *isomeric* is proposed in his *Jahresbericht*, handed in to the Swedish Academy of Sciences, March 31, 1831 (*cf.* Wöhler's German translation, 1832, ii. pp. 44–8), in the following words:—

'Da es nothwendig ist, für gegebene Ideen bestimmte, und so viel wie möglich consequent gewählte, Ausdrücke zu besitzen, so habe ich vorgeschlagen, Körper von gleicher Zusammensetzung und ungleichen Eigenschaften *isomerische* zu nennen, vom griechischen ἰσομερής (aus gleichen Theilen zusammengesetzt).'

In the next volume of his *Jahresbericht* (Wöhler's translation, 1833, p. 63) he gives a

further all-important definition of the use he would make of the term, thus :—

'Um jedoch nicht Erscheinungen von nicht völlig gleicher Art mit einander zu verwechseln, ist es nothwendig den Begriff vom Worte *Isomerie* genau zu bestimmen. Ich erwähnte dass ich darunter Körper verstehe, die aus einer gleichen absoluten und relativen Atomen-Anzahl derselben Elemente zusammengesetzt sind und gleiches Atomgewicht haben . . . *womit nicht der Fall zu verwechseln ist, wo die relative Anzahl der Atome gleich ist, die absolute aber ungleich.* So ist z. B. die relative Anzahl von Kohlenstoff- und Wasserstoff-Atomen im ölbildenden Gas und im Weinöl absolut gleich; allein in einem Atom vom Gase sind bloss 1 Atom Kohlenstoff und 2 Atome Wasserstoff enthalten, CH_2, während dagegen im Weinöl 4 Atome Kohlenstoff und 8 Atome Wasserstoff enthalten sind, C_4H_8. Um diese Art von Gleichheit in der Zusammensetzung, bei Ungleichheiten in den Eigenschaften, bezeichnen zu können, möchte ich für diese Körper die Benennung *polymerische* (von πολύς, mehrere) vorschlagen.'

It will be clear from this quotation, especially from the words which I have italicised, that Berzelius never intended that polymerism should be regarded as a form of isomerism.

The following passage from the same source clearly exhibits Berzelius's intention as to the use which should be made of the term metameric :—

'Allein es giebt noch andere Verhältnisse, wo Körper, im eigentlichen Sinne des Wortes, isomerisch scheinen, d. h. dieselbe relative und absolute Atomenanzahl derselben Elemente enthalten können, *ohne es jedoch vollständig zu sein.* Ein solcher Fall ist wenn Körper aus zwei zusammengesetzten Atomen der ersten Ordnung bestehen, die sich auf verschiedene Weise gegen einander umlegen, und in Folge dessen ungleiche Körper bilden können; z. B. $\dot{Sn}\dddot{S}(SnOSO_3)$ schwefelsaures Zinnoxydul, und $\ddot{Sn}\ddot{S}(SnO_2SO_2)$ basisches schwefligsaures Zinnoxyd, enthalten eine gleiche absolute und relative Anzahl derselben Elemente, und haben dasselbe Atomgewicht, können jedoch nicht als ein und derselbe Körper betrachtet werden. Bei solchen Körpern ist es der Fall, dass wenn sie eine gewisse Zeit lang bestanden haben, oder wenn die Temperatur geändert wird, eine Umlegung der Bestandtheile in ihnen vor sich geht, ohne dass etwas hinzukommt oder davonweggeht, und dass dadurch eine anders beschaffene Verbindung entsteht, welche Veränderung nicht selten von einer Temperatur-Erhöhung begleitet ist. Um solche Fälle bestimmt von Isomerie zu unterscheiden, können wir dafür die Bezeichnung *metamerische* Körper gebrauchen (von μετά in derselben Bedeutung wie in Metamorphose).'

Berzelius also cites cyanic and cyanuric acids, which were not then regarded as compounds of different molecular weight, as instances of metameric compounds, regarding the conversion of the latter into the former on heating as a case in which 'die Cyanursäure von einem zusammengesetzten Atom der ersten Ordnung, oder einem Oxyd eines ternären Radicals, in ein zusammengesetztes Atom der zweiten Ordnung, nämlich in Cyansäure mit chemisch gebundenem Wasser übergeht.' Cyamelide, into which cyanic acid spontaneously changes, and cyanuric acid, in Berzelius's opinion, were (wenigstens vorläufig) isomeric oxides of the same radicle.

It is clear therefore that the conception involved in the definition of metamerism given in Watts' *Fownes*, and in the first edition of this dictionary, is scarcely in conformity with the use of the term by Berzelius; indeed, in 1840 he speaks of ethylic formate and methylic acetate as isomeric. From the example afforded by the two tin compounds, as well as from the explanation given of the nature of the change from cyanuric to cyanic acid, it is to be supposed that the compounds which he intended should be included in the category of metameric substances were such as we should now term *typically different*, and with this conclusion the modern practice is in distinct accord; yet the modern and the original application of the term are far from being equivalent, the *meta-* in metamorphosis denoting change: the conversion of the one metameride into the other being expressly referred to, it would appear, in fact, that Berzelius distinctly intended to apply the term to those compounds which are capable, in modern phraseology, of undergoing 'isomeric change,' and perhaps to these alone.

It was not until 1840 that Berzelius proposed to substitute the term *allotropic* ('von ἀλλότροπος welches bedeutet, von ungleicher Beschaffenheit;' *B. J.* 1841: inorg. sec. p. 13) for isomeric, in the cases of the existence of modifications of elementary substances. He appears, however, to have contemplated its extension to compounds, judging from the following passage :—

'Es kann dann mehr als eine Ursache von dem was wir Isomerie nennen, geben, nämlich (1) Allotropie, wenn nämlich das vorhin angeführte Beispiel von den beiden Schwefelkiesen darauf beruht, dass der eine davon Sα und der andere Sβ enthält; (2) die ungleiche relative Lage der Atome in der Verbindung . . .; und (3) kann sowohl Allotropie als ungleiche Stellung der Atome in gewissen Fällen zugleich stattfinden.'

The existence of compounds containing allotropes of one of the constituent elements is distinctly suggested here, but there is nothing to indicate in what way allotropes may be regarded as related; that Berzelius had realised that the relation might be that of polymerides would appear to follow from his reference to Frankenheim's experiments on sulphur, in which it is suggested that the different modifications of sulphur form corresponding gases, and that the dark-yellow gas of sulphur, weighing thrice as much as sulphur gas should according to calculation, is not that of the modification occurring in the ordinary sulphur compounds (*v.* ALLOTROPY, vol. i. p. 128: the view here taken is somewhat wider than that adopted by Prof. L. Meyer in that article).

As the term *allotropic* has a general signification, implying only *another condition*, and involves no assumption either regarding the molecular weights of, or as to the nature of the relationship which obtains between, the allotropes, it may with great advantage be employed in place of the term isomeric used in a wide sense; this latter term being preferably restricted to those cases in which there is the very closest similarity in structure. Polymerism, metamerism, and isomerism may in fact all be regarded as varieties of allotropy; there is certainly no reason why carbon compounds should be considered apart from those of other elements, or from elementary substances.

The rational formulæ which are ordinarily made use of are condensed symbolic expressions affording more or less complete information as to the characteristic chemical properties of the compounds which they represent, especially with regard to the manner in which they are formed, and in which they undergo change when submitted to the action of various agents; and equimolecular allotropes which differ either in their mode of formation or in their behaviour under similar circumstances are, as a rule, necessarily represented by different rational formulæ. The formulæ devised for any class of compounds, however, will vary according to the views which

are held as to the valencies of the constituent atoms. At present, formulæ are almost invariably constructed on the hypothesis that the several units of affinity—the valencies—of a polyad atom, such as that of carbon, nitrogen, or sulphur, are of the same value and have identical functions; this conclusion being based on the fact that none of the simple derivatives of methane, ammonia, &c., exist in a greater number of modifications than the hypothesis requires. But it cannot be too positively stated that, notwithstanding the extent to which experimental investigation has been carried, we are yet but on the threshold of the temple in which the mysteries of valency are enshrouded. The valency of the hydrogen atom is determined *ex hypothesi* to be unity, and when the facts generally are passed in mental review, it would seem that this conclusion is no mere hypothesis; it is not improbable also that the valencies of the atoms of at least the majority of metallic elements are invariable; but the valencies of the atoms of the non-metals are *apparently* variable. By valency is here understood atom-fixing power.[1]

Most discussions on valency are dialectical rather than scientific, in consequence of our powerlessness at present to decide what constitutes 'a valency;' the deduction from Faraday's law of electrolysis, to which Helmholtz has directed the attention of chemists (Faraday lect., *C. J. Trans.* 1881. p. 277), that definite, as it were atomic, charges of electricity are associated with the atoms of matter—that a monad bears a single charge, a dyad two, a triad three—is the only approach yet made to a theory of valency, but hitherto chemists have avoided the discussion of the subject from this point of view.

Oxygen and sulphur, nitrogen and phosphorus, carbon and silicon, form gasifiable hydrides, from the composition of which we infer that the atoms of these elements are divalent, trivalent, and tetravalent, respectively; in the case of carbon and silicon there is no reason to suppose that either element ever manifests a higher valency. But both water and ammonia readily combine with other molecules: the formation of such compounds from water is rarely interpreted as evidence of the possession by oxygen of the power of acting as a tetrad; but the water molecule is usually supposed to function in some occult manner as a whole, and to enter into a state of 'molecular combination' different from that of 'atomic combination' in which its constituent atoms exist. The formation of ammonium compounds, however, is more usually regarded as due to the manifestation of a higher degree of valency by the nitrogen. But there is no good reason for explaining the behaviour of oxygen in one way, and that of nitrogen in another.

The question to be decided is, whether a given element may possess two or more degrees of valency; and whether the so-called atomic and molecular forms of combination differ merely in degree and not in kind. Or, to put it in another way:—is the number of atomic charges associated with a given atom invariable or variable; is it possible for an oxygen or sulphur atom, for example, to carry more than two, or for a nitrogen or phosphorus atom to carry more than three, charges? The writer has endeavoured to explain the exhibition of varying degrees of valency on the assumption that, while the number of charges which any given atom can carry is invariable, a single charge may operate in promoting the union of more than two atoms (*cf.* *P. M.* January 1888); that in water, for example, the two charges of the oxygen atom are not fully engaged by those of the hydrogen atoms, and that consequently the oxygen atom is still possessed of a certain amount of *residual affinity*. It may be contended that, according to this hypothesis, a compound formed of say trimethylamine and ethyl iodide, $Me_3N.IEt$, would be an allotrope of a compound of ethyldimethylamine and methyl iodide, $EtMe_2N.MeI$. The most careful experimental study of such compounds (*cf.* V. Meyer a. Lecco, *Ber.* 9, 309; Ladenburg, *Ber.* 9, 561, 1634; Klinger a. Claasson, *A.* 243, 193) has been made, however, with the result that, in the case of ammonium compounds, it is immaterial in what order or manner the radicles are introduced; and the same is true in the case of sulphine compounds: hence it is supposed that nitrogen has five, and sulphur four, affinities of equal value. But this by no means follows, as the occurrence of 'isomeric change' in such cases is in the highest degree probable—the compound abcNId may alone be the stable form into which the allotropes abdNIc, acdNIb, bcdNIa, all spontaneously undergo conversion immediately on formation. There is little doubt that such 'isomeric changes' occur far more frequently than is commonly supposed, and it is most important that the possibility of 'isomeric change' should be very carefully kept in view in determining the constitution of compounds from the study of their behaviour in a limited number of interactions. As valency cannot be determined from any *à priori* considerations, and can only be deduced from the knowledge of the structure of the compounds of the elements whose valency is to be determined, it is obvious that the structure of a substance must be inferred from the widest and most careful study of all its properties: the study of the relationships of allotropic substances is in fact inseparable from that of valency, and the converse is equally true.

In the case of 'unsaturated' carbon compounds, it has been customary of late years to represent the affinities not engaged by other elements as saturating each other: thus, ethylene is formulated as $H_2C{:}CH_2$; acetylene as $HC{⋮}CH$. Thomsen's determinations of the heat of combustion of ethylene and acetylene in comparison with those of saturated hydrocarbons, as well as the general behaviour of such unsaturated compounds, may, however, be held to favour the view that the carbon atoms are possessed of free affinities, as expressed by the formulæ $\begin{matrix} H_2C— \\ | \\ H_2C— \end{matrix}$, $\begin{matrix} HC= \\ | \\ HC= \end{matrix}$. Although the discussion of this question excited considerable attention a few years ago, it has latterly almost entirely fallen into

[1] It appears to me that the term valency must at present be used in a perfectly general sense, and that we cannot restrict our attention to the consideration of gaseous compounds (*v.* EQUIVALENCY): in the case of gases, the problems are for the most part of a very simple kind, and rarely excite differences of opinion; liquids and solids, however, present problems of great complexity.

oblivion; but as very many of the cases of anomalous isomerism, of which an explanation is required, occur among compounds of the ethylenic type, it is one of considerable importance. The possibility of the two forms of combination pictured by the expressions $\begin{array}{c}H_2C\\ \|\\ H_2C\end{array}$ and $\begin{array}{l}H_2C—\\ \;|\\ H_2C—\end{array}$ should also be taken into account, especially in the case of ethylenic derivatives.

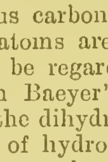
Among the more recondite problems of valency requiring mention is that relating to the number of carbon atoms which form closed chains or rings. It is now regarded as well established that, in addition to the six-atom ring of benzene, five-atom rings also exist; indeed, their formation apparently takes place with peculiar readiness; the existence of both three- and four-atom rings is now also generally held to be established, chiefly in consequence of the researches of W. H. Perkin, jun. (*cf. C. J. Trans.* 1885. 801, *et seq.*). The hydrocarbon obtained by the action of sodium on trimethylene bromide, $BrCH_2.CH_2.CH_2Br$, is almost universally assumed to be the simplest compound of the kind, trimethylene, $\begin{array}{c}H_2C\\ H_2C\end{array}\!\!>CH_2$; as shown by Freund, its discoverer, this hydrocarbon has the remarkable property of being readily absorbed by a solution of hydrogen iodide, forming normal propyl iodide, although it is acted on with extreme slowness by bromine. By the action of ethylenic bromide on the disodium derivative of ethylic malonate, Perkin has obtained an acid which he regards as a trimethylenedicarboxylic acid $\begin{array}{c}H_2C\\ H_2C\end{array}\!\!>C(COOH)_2$; and by employing trimethylenic bromide in place of ethylenic bromide, he has prepared what he regards as tetramethylenedicarboxylic acid $\begin{array}{l}CH_2—CH_2\\ |\qquad\quad |\\ CH_2—C(COOH)_2\end{array}$: both acids closely resemble the hydrocarbon in their behaviour with bromine and halhydrides. The easy resolution of closed carbon chains by halhydrides in this manner, however, is altogether without precedent in the case of five- and six-atom carbon rings, at all events, which, as a rule, cannot be split by means of halhydrides, but are frequently resolvable by bromine; their behaviour is more nearly akin to that of five-atom rings, such as those of furfuran and indole, which also resist the action of bromine, but are resolvable by treatment with agents which are commonly regarded as weaker than bromine (the formation of pyridine derivatives from pyrrole and of quinoline derivatives from indole, which *appears* to involve the resolution at some stage of the operation of the five-atom rings, is contemplated in this statement). The alternative formula for trimethylene, if it be not a closed chain hydrocarbon, is $CH_2.CH_2.CH_2$, which represents it as a compound in which two terminal carbon atoms are each possessed of a *single* free affinity; the possibility of the existence of such compounds has not yet been contemplated by chemists, excepting myself. It is conceivable, I think, that such a compound would be attacked by bromine with difficulty, in consequence of the two unsatisfied carbon atoms failing to assist each other in separating the constituent atoms of the bromine molecule and the impossibility of a 'conducting chain of molecules' being formed between the carbon atoms, as bromine is a dielectric; as solutions of the halhydrides are electrolytes of low resistance, such a conducting chain might, however, be formed in their case, and the requisite electrolysis of the halhydride molecule could thus occur. According to Thomsen, trimethylene has a *higher* heat of combustion than propylene, $CH_3.CH{:}CH_2$; judging from the analogy afforded by benzenoid compounds, it is to be expected, however, that the closure of the chain involved in the formation of the three-atom ring would be attended with a considerable loss of energy, and that propylene would, therefore, have the higher heat of combustion: its behaviour with bromine certainly justifies this view. The confirmation of Thomsen's statement thus becomes of extreme importance. It is a noteworthy fact that ethylenic oxide, according to Thomsen, also has an exceptionally low heat of formation, and that this observer has proposed to represent it as a dimethylene oxide of the formula $CH_2.O.CH_2$. Ethylenic oxide as represented by the conventional formula bears a similar relation to trimethylene that furfuran bears to pentamethylene, thus

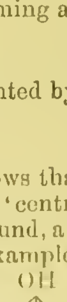
$$\begin{array}{c}CH_2\\ /\;\;\backslash\\ H_2C—CH_2\end{array}\quad \begin{array}{c}O\\ /\;\;\backslash\\ H_2C—CH_2\end{array}\quad \begin{array}{c}CH_2\\ /\quad\backslash\\ H_2C\quad CH_2\\ |\qquad\; |\\ H_2C—CH_2\end{array}\quad \begin{array}{c}O\\ /\quad\backslash\\ HC\quad CH\\ \|\qquad\; \|\\ HC—CH\end{array}.$$

Thomsen's formula for ethylenic oxide is inadmissible, as it indicates a severance of the carbon atoms; if, however, the formula were written $CH_2.CH_2.O$, it would correspond to that given above to trimethylene; Thomsen's observations that both ethylenic oxide and trimethylene have an exceptional heat of combustion may therefore be regarded as mutually confirmatory. It is also to be noticed that the compound formed from ethylenic bromide and a sulphide is not the corresponding sulphide, but the polymeride thereof $\begin{array}{l}CH_2—S—CH_2\\ |\qquad\qquad |\\ CH_2—S—CH_2\end{array}$. If an open chain formula be assigned to trimethylene, Perkin's tri- and tetramethylene derivatives must also be represented by open chain formulæ. Perkin has fully discussed this question, and has pointed out the improbability attaching to such formulæ. The evidence does not appear to be sufficient, however, to permit of a final decision being arrived at with regard to so difficult a question.

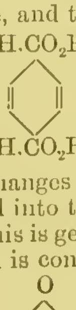
Finally, it is necessary to refer to a problem closely akin to the two previously considered, viz. that relating to the distribution of the *spare* affinities of the carbon atoms in closed chains; of those affinities, that is to say, which are not engaged in the formation of the ring, or in retaining the hydrogen atoms. This problem is chiefly of importance in discussing the structure of benzenoid hydrocarbons and their derivatives. Of the various formulæ proposed for benzene, that of Kekulé always has been, and still remains, the most popular; but it is open to the serious objection that it represents benzene as a compound containing three pairs of carbon atoms in the same condition as the pair in ethylene. Dewar's for-

mula is open to a similar objection. The prism formula of Ladenburg and the diagonal formula of Claus cannot be objected to on this ground, but are open to criticis n in many other respects, and in the light of Von Baeyer's recent researches on the reduction products of terephthalic acid (*cf. A.* 245,103 ; 251,257) these formulæ are generally regarded as finally disposed of (*cf.* Miller, *C. S. Trans.* 1887. 208). A symbol proposed by the writer in February 1887 (*cf. P. M.*), and a year later also by Von Baeyer (*A.* 245, 122), appears to be exempt from the deficiencies which characterise previous formnlæ; bnt it embodies somewhat unconventional conceptions, and therefore has not yet attracted attention. The symbol in question  has been very happily termed the *centric* formula by Von Baeyer; he expressly states that this formula is to be understood to indicate that 'die 6 Kohlenstoffvalenzen des Benzols sich sättigen, ohne dadnrch drei Verkettungen der Kohlenstoffatome zn bewirken' (*A.* 251, 285)—one valency of each atom is directed towards the centre of the ring, and these valencies mutually paralyse each other (*A.* 245, 122). My own words were: 'Of the twenty-fonr affinities of the six carbon atoms twelve are engaged in the formation of the six-carbon ring, while the remaining six react upon each other, acting towards a centre as it were, so that the affinity may be said to be nniformly and symmetrically distributed. . . . I do not consider that, apart from its connexion with the other carbon atoms owing to their association in the ring, any one carbon atom is directly connected with any other atom not contignous to it in the ring . . . each individnal carbon exercises an influence upon each and every other carbon atom . . . there is an excess of affinity beyond what is required to maintain the C_6H_6 ring; but I do not consider that each carbon atom can be considered to have an affinity *free*.'

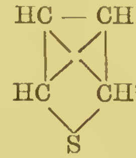
The conclusion here arrived at with regard to benzene, that no direct connexion exists between any but the contiguous carbon atoms in the ring—that para-carbon atoms are not and cannot become nnited—may be regarded as of nniversal application. Von Baeyer's experiments prove, moreover, that the dihydro-terephthalic acid in which an atom of hydrogen is associated with each of the para-carbon atoms to which the carboxyls are attached, unlike terephthalic acid, behaves as an unsaturated compound, forming a tetrabromide, and that it is to be represented by the formula  . From this it follows that the type changes on conversion of the 'centric' compound into the di-addition compound, and probably this is generally the case; for example, when quinol is converted into quinone



Quinol.



Quinone.

It would also follow that in the case of benzenoid compounds four of the six 'spare' affinities cannot act 'centrically.' To what extent this is true in the case of other rings remains to be ascertained; from the remarkable similarity of thiophene and benzene, it would appear probable that the former is to be represented as analogous to benzene in structure, thus  whereas the analogons compounds furfuran and pyrrole more nearly resemble the nnsaturated componnds in their behavionr; but this is perhaps ascribable to the influence exercised by the oxygen or imidogen.

The foregoing brief discussion will suffice to direct attention to the nnmerons problems comprised in the philosophy of isomerism, and to show how far from final are the conclusions as to structure which we are at present able to arrive at.

In a large and rapidly increasing number of instances, it is impossible to assign different rational formulæ to compounds undoubtedly different so long as the system employed takes into account merely the nature of the radicles and the manner in which they are associated as pictured by disposing them in a single plane. If, while assuming the hydrogen atoms in a componnd, snch as methane—in other words the four valencies of the carbon atom—to be equal, it be supposed that the radicles introdnced in place of the hydrogen atoms occupy relatively different positions in the plane, a variety of isomeric derivatives would appear to be possible: *e.g.* two of the form $CRRR_1R_1$, two of the form $CRRR_1R_2$, and three of the form $CRR_1R_2R_3$; R, R_1, R_2, R_3 being different radicles. A special study of methane derivatives from this point of view has been made by Henry, but both his results and our general experience show that isomerides such as are here contemplated do not occnr.

By considering the arrangement of the atoms in space, conclusions have, however, been arrived at which are far moro in harmony with experience. Such a step was first taken in 1874 by Van't Hoff (*La Chimie dans l'Espace*, Rotterdam, 1875), and independently and almost simultaneously by Le Bel (*Bl.* [2] 22, 337; *cf. ibid.* 23, 295). A German adaptation of Van't Hoff's pamphlet entitled, *Die Lagerung der Atome im Raume*, was published in 1877 by Hermann. A full account of the subject is to be found in the previous edition of this dictionary and in Miller's 'Chemistry,' vol. iii.

The fundamental hypothesis of the Van't Hoff system consists, as is well known, in supposing that the carbon atom occupies the centre of a tetrahedron and that its four affinities are directed towards the four solid angles. When *four different* radicles are associated with the carbon atom, but only in such a case, two isomerides are possible, represented by two irregular non-superposable tetrahedra bearing to each other the relation of an object to its reflected image; and, moreover, these isomerides should be of enantiomorphous crystalline form, as

well as optically active and possessed of equal and opposite rotatory powers, as the molecules are unsymmetrical, such tetrahedra exhibiting, in relation to an axis drawn parallel to the corresponding edges, a screw-shaped grouping of the four summits, turning to the right in the one form and to the left in the other. A carbon atom thus situated is termed *asymmetric*, and is represented in a formula by an italicised *C*. The hypothesis serves therefore at once to explain both the existence of isomerides which cannot be represented by formulæ written in a single plane, and to account for the optical activity of certain substances. Thus in the case of tartaric acid, which contains two asymmetric carbon atoms, but is composed of two equal groups, (COOH)(HO)H*C*.*C*H(OH)(COOH), the hypothesis indicates the existence of two optically active isomerides of equal but opposite rotatory powers, and a third inactive isomeride in which the optical effect of the one asymmetric carbon atom is balanced and neutralised by the equal opposite effect of the other; it thus accounts for the existence of dextro-, lævo-, and *meso*-tartaric acids; racemic acid, the fourth modification, apparently, is to be regarded as a 'physical' allotrope formed by the conjunction of the two active isomerides: it would seem that it does not exist in solution. Van't Hoff has shown, in a recent much extended new edition of his pamphlet, that every prevision of the hypothesis with reference to the optical characters of isomerides has been fulfilled in the most complete manner possible by the investigations carried out in the interval since its enunciation by Le Bel and himself (cf. *Dix Années dans l'Histoire d'une Théorie*, Rotterdam, P. M. Bazendijk, 1887); this remarkable agreement of practice with theory has naturally led to the almost universal adoption of the hypothesis.

The hypothesis also provides for a greater number of isomerides in the case of compounds of the ethylenic type than is indicated if the space relationship of the radicles be omitted from consideration; if a compound of the form $R_1R_2C:CR_3R_4$ be represented by two tetrahedra joined so as to have one edge in common, it will be found that only one such figure can be constructed, if either the four radicles are identical, or if only R_1 differs from R_2, or R_3 from R_4; but if R_1 is different from R_2, and R_3 is also different from R_4, although R_1 and R_3, R_2 and R_4, are identical, two such figures may be constructed —this is more readily rendered obvious by the adoption of the simpler plan of writing the symbols of the radicles attached to the two doubly-linked carbon atoms on either side of a line representing the plane of their conjunction. Thus the symbols $\frac{a\ b}{a\ b}$ and $\frac{a\ b}{b\ a}$ represent modifications in which in the one case the two similar radicles are situated symmetrically with reference to a plane at right angles to the axis of the system, and in the other are symmetrically situated with reference to the axis of the system; such modifications may therefore be termed, as Wislicenus has suggested, the *plane* and *axially* symmetric modifications. The isomerism of maleic and fumaric acids is regarded by Van't Hoff as dependent on such a difference in structure.

Such a *stereometric* mode of formulation does not afford an increased number of expressions for acetylenic derivatives; the same is true of benzenoid compounds if Kekulé's symbol be adopted (*cf.* Marsh, *P. M.* Nov. 1888, p. 426). It may be noted, however, that the asymmetric carbon atom hypothesis is applicable to the explanation of the optical activity manifested by a variety of closed chain compounds, such as quercitol and quinic acid, which are derivatives of hexamethylene, and conine and its homologues, which are derivatives of piperidine.

Although the Van't Hoff-Le Bel hypothesis has been very generally accepted as affording a sufficient explanation of a very large number of cases of isomerism difficult to account for in accordance with the existing canons of belief, it is as yet by no means certain that it can be always so regarded; in many cases the difference between isomerides is so great that it is somewhat difficult to believe that it depends on so comparatively simple a difference in structure as the presence of one or more asymmetric carbon atoms would involve. The two isomeric tartaric acids are the veritable image the one of the other; but this is rarely the case: thus hydrobenzoïn differs very considerably from isohydrobenzoïn, as do also mannitol and dulcitol, and to a still greater extent the acids, saccharic and mucic, formed from these latter; in all these cases the isomerism is assumed to depend on mere geometrical differences. In the case of mesotartaric acid, the intra-molecular neutralisation of one asymmetric carbon atom by the other already produces a marked effect, as evidenced by the difference in properties of this acid in comparison with either of the active modifications. It may be, therefore, that in the case of mannitol and dulcitol, and the acids formed by their oxidation, the accumulated effect of the several asymmetric carbon atoms is much greater than in the case of tartaric acid, and hence the greater difference in properties between the isomerides. Very little alteration is involved in the formation of racemic acid, and, as above pointed out, this substance appears to be a mere 'physical' allotrope, hardly a polymeride, of its active constituents; in certain cases the formation of the 'racemic form' is attended with a considerable alteration in properties—in the case of leucine and of camphoric acid, for example, their racemic forms being much less soluble and of higher melting-points than their optically active constituents. In these cases there would seem to be a more intimate union than in the case of racemic acid; the marked difference between saccharic and mucic acid may be due to some such cause as this. But the isomerism of the hydrobenzoïns is more difficult to explain, assuming that they are both compounds of the formula (C_6H_5)(HO)H*C*.*C*H(OH)(C_6H_5). Including a racemic form, four modifications of such a compound appear possible, two of which should be optically active. Neither compound is optically active, and, judging from Zincke's observations, it does not appear probable that, if the one be the meso or inactive modification corresponding to mesotartaric acid, the other is the racemic form. The assumption that the one, perhaps

isohydrobenzoïn, contains the two hydroxyl-groups attached to the one carbon atom, thus $C_6H_5.H_2C.C(OH)_2.C_6H_5$, would satisfactorily account for its behaviour, but has hitherto been rejected as improbable owing to the general belief that compounds of such a character are excessively unstable. But it may be that the presence of the negative phenyl groups confers stability in such a case, much as in the case of chloral hydrate; and it is well to remember that in not a few instances of late years proof has been given of the incorrectness of views based on general considerations, as in the case of phthalic chloride, for example, and the hydroxamic acids.

Still greater difficulties occur in accepting the conclusion that the Van't Hoff hypothesis affords an explanation of the isomerism of unsaturated compounds such as maleic and fumaric acids, which, according to this view, are respectively the plane symmetric and axially symmetric isomerides of the formula

$$\begin{array}{ccc} \text{HC.COOH} & & \text{HOOC.CH} \\ \| & \text{and} & \| \\ \text{HC.COOH} & & \text{HC.COOH} \\ \text{Maleic acid} & & \text{Fumaric acid.} \end{array}$$

It is well known how great are the differences between these two acids, both in physical properties and in general chemical behaviour, and that maleic acid alone yields a corresponding anhydride, fumaric acid being converted into the same anhydride when dehydrated. Ostwald also has shown that the electrical conductivity of their solutions is such as to indicate that maleic acid is a weak acid akin to selenious and phosphorous acids, whereas fumaric acid is a well-marked dibasic acid (*J. pr.* 32, 362). Maleic acid has also a considerably greater heat of combustion than fumaric acid (Thomsen, *J. pr.* 40, 202). Roser has suggested that, whereas fumaric acid is a normal di-carboxylic acid, maleic acid is to be represented by the formula

$$\begin{array}{l} \text{HC.CO} \\ \|\ \ \ >\text{O} \\ \text{HC.C(OH)}_2 \end{array}$$

This formula would afford a satisfactory explanation of the great differences observed between the two acids, and it has been strongly advocated by Anschütz (*A.* 254, 168). No valid argument has yet been advanced which would prevent its adoption.

It may here be pointed out that no attention is paid in applying the Van't Hoff hypothesis to unsaturated compounds to the peculiarities which are manifest in such compounds, and which apparently must be attributed to the presence of unsaturated carbon atoms; a 'double or ethylenic bond' is represented as the precise equivalent of two single bonds, and a 'treble or acetylenic bond' as the equivalent of three single bonds, which is certainly not in accordance with facts, and especially with Thomsen's observations on the heats of combustion of unsaturated compounds.

Wislicenus has not only accepted the Van't Hoff-Le Bel hypothesis in its entirety, but has in the most ingenious manner possible extended its application, and has endeavoured both to elucidate the structure of geometrically isomeric unsaturated compounds, and to explain the 'isomeric changes' which such compounds frequently exhibit (*Abhandlungen der math. phys. Classe der könig. Sächsischen Ges. der Wissenschaften*, Band xiv. Leipzig, 1887).

In the case of maleic and fumaric acid—assuming that these are stereometric isomerides—as pointed out originally by Van't Hoff, the formula $\begin{array}{l}\text{HOOC.CH}\\ \quad\|\\ \text{HC.COOH}\end{array}$ may without hesitation be assigned to the latter, as it is incapable of forming an anhydride, whereas maleic acid, being easily convertible into the anhydride, is represented by the formula $\begin{array}{l}\text{HC.COOH}\\ \|\\ \text{HC.COOH}\end{array}$; in the case of crotonic and isocrotonic acids, however, it is more difficult to find criteria on which to base a choice between the formulæ

$$\begin{array}{ccc} \text{HC.CH}_3 & & \text{CH}_3\text{.CH} \\ \| & \text{and} & \| \\ \text{HC.COOH} & & \text{HC.COOH} \end{array};$$

and similarly in other cases. Wislicenus considers that if a compound of the form $C_2R_1R_2R_3R_4$, consisting of the two systems $R_1R_2C{=}$, and ${=}CR_3R_4$, be derivable from a corresponding acetylenic compound, its constitution can at once be inferred from the fact that when one pair of bonds between the carbon atoms in the acetylenic compound is severed, as the two atoms are still united by double bonds, no rotation of the systems can take place; consequently the added radicles both occupy positions on one side of the common axis of the systems. Thus the tolane dichloride melting at 143°, obtained by chlorinating tolane, is necessarily the *plane symmetric* modification:

$$\begin{array}{ccccc} \text{C}_6\text{H}_5\text{.C} & & & & \text{C}_6\text{H}_5\text{.CCl} \\ ||| & + & \text{Cl}_2 & = & \| \\ \text{C}_6\text{H}_5\text{.C} & & & & \text{C}_6\text{H}_5\text{.CCl} \end{array}.$$

The isomeride of lower melting-point (63°) must therefore be regarded as the axially symmetric compound $\begin{array}{l}\text{C}_6\text{H}_5\text{.CCl}\\ \quad\|\\ \text{ClC.C}_6\text{H}_5\end{array}$. In principle this method appears perfectly sound, but it is based on an assumption with reference to the manner in which the carbon atoms in ethylenic and acetylenic compounds are united, which, as previously pointed out, is perhaps open to question; it also involves the conclusion that the radicles attached to the carbon atoms are incapable of changing their positions, which is also by no means a safe assumption, bearing in mind the extreme readiness with which 'isomeric changes' occur.

A method of more universal application, but involving much more complex considerations, is the following. In saturated compounds in which the carbon atoms are united by single affinities, one carbon system must be capable of rotating about another; moreover, it is to be assumed that the atoms in a molecule—even those which are not directly connected—exercise an influence on each other, and will therefore tend to condition such rotation so that radicles which have the greatest affinity are brought into the closest proximity possible. Thus, on converting ethylene into its chloride, in the first instance the change would take place in accordance with the following scheme:

$$\begin{array}{ccccc} \text{CHH} & & & & \text{CHHCl} \\ \| & + & \text{Cl}_2 & = & | \\ \text{CHH} & & & & \text{CHHCl} \end{array}.$$

But, in consequence of the superior affinity of hydrogen for chlorine, such a system would be unstable, rotation would set in, and the more stable system $\begin{array}{c} CHHCl \\ | \\ CClHH \end{array}$ would result.

To take another case, that of the conversion of tolane tetrachloride into dichloride by reduction; this compound may present three configurations, viz.:

$$\begin{array}{c} CC_6H_5ClCl \\ | \\ CC_6H_5ClCl \end{array} \quad \begin{array}{c} CC_6H_5ClCl \\ | \\ CClClC_6H_5 \end{array} \quad \begin{array}{c} CC_6H_5ClCl \\ | \\ CClC_6H_5Cl \end{array} \cdot$$

It would probably chiefly consist, especially at low temperatures, of the second and third modifications, as the dissimilar radicles are most proximately situated in these; and as these two modifications would both furnish the axially symmetric dichloride on reduction, it is to be supposed that the chief product of reduction will be this dichloride; actually that melting at 63° is chiefly obtained (Blank, *A.* 248, 1), and it is, therefore, to be supposed that this modification is axially symmetric—a conclusion which harmonises with that previously arrived at. To this it may be objected that our knowledge of the relative affinities of the radicles within a compound is purely hypothetical; and that it is by no means certain that dissimilar radicles would in all cases tend to influence and attract each other more than would similar radicles. Thomsen's observations on the heats of combustion of chlorine compounds, in fact, would appear to favour an opposite conclusion. But a more important argument is to be found in the fact that in cases in which the constitution may fairly be regarded as established, the relation is of the obverse order to that required if the contention of Wislicenus be correct: thus, the symmetric or para-diderivative of benzene always has the highest melting-point; the same appears to be true of the symmetric tri- and tetra-derivatives; and, in the case of naphthalene, the axially symmetric isomeride is always that of highest melting-point (*cf. C. S. Proc.* 1888. 93).

Another use which Wislicenus has made of the argument here criticised may now be mentioned. It is a well-known fact that maleic acid is very readily converted into fumaric by the action of acids. Wislicenus supposes that when this conversion is effected, for example, by bromhydric acid, the double bond becomes severed, bromosuccinic acid being formed:

$$\begin{array}{c} HC.COOH \\ \| \\ HC.COOH \end{array} + HBr = \begin{array}{c} HCH.COOH \\ | \\ HCBr.COOH \end{array} \cdot$$

but rotation setting in, the radicles are brought into their preferential positions, viz. $\begin{array}{c} HOOC.CHH \\ | \\ HC.BrCOOH \end{array}$, and when, by the action of the water present, this modification becomes deprived of hydrogen bromide, fumaric acid naturally results. Although in the highest degree ingenious, this conception unfortunately does not appear to be in accordance with the facts, for, as Anschütz points out (*A.* 254, 168), the conversion takes place under conditions under which the succinic derivative is stable, and there is no reason therefore to suppose that such a compound is formed at any stage of the conversion of maleic into fumaric acid; if maleic acid be formulated in the manner advocated by Anschütz, its conversion into fumaric acid by acids is easily understood.

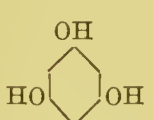
Victor Meyer's researches have led him to carry speculation even further. On submitting benzil to the action of hydroxylamine, Meyer and Goldschmidt obtained an α-dihydroxime which they found was converted into a more stable β-isomeride by heating with alcohol to about 180°; a careful investigation of these compounds was subsequently made by Meyer and Auwers, but they were unable to discover any substantial difference in their chemical behaviour, and they came to the conclusion that both must be regarded as compounds of one and the same formula $C_6H_5.C(N.OH).C(N.OH).C_6H_5$. As the existence of two such compounds was incompatible with the assumption that carbon atoms united by single affinities are free to rotate, Meyer and Riecke (*B.* 21, 946) have put forward an hypothesis as to the nature of the carbon atom itself which serves to account for two kinds of union by single affinities, one in which rotation is impossible, the other in which it can freely take place. Having regard, however, to the readiness with which 'isomeric change' takes place, and to the extremely imperfect state of our knowledge of the exact manner in which polyad elements are held in association, there cannot be any doubt that it is premature to conclude that the benzil dihydroximes are necessarily structurally identical; the study of chemical interchanges is after all but an approximate and fallible mode of determining structure.

Hantzsch and Werner (*Ber.* 23, 11) have quite recently proposed to extend the Van't Hoff conception to the nitrogen atom itself. They suppose that in some nitrogen compounds the three affinities of the nitrogen atom are directed towards three of the solid angles of an irregular tetrahedron, and that the nitrogen atom itself is located at the fourth. In the case of compounds of the form CXY:NZ, which are comparable with carbon compounds of the form CXY:CHZ, it is conceivable that the Z radicle may alter its position in space relatively to the radicles X and Y. and thus give rise to isomerides.

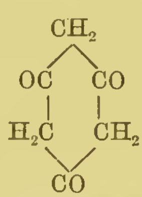
Victor Meyer (*B.* 23, 567) has, however, pointed out that the views of Hantzsch and Werner are in many respects in conflict with the experimental evidence. This memoir is a noteworthy contribution to the discussion of a number of the more obscure cases of isomerism. (The two papers here referred to have been published since this article was in type.)

It is here the place to refer to the numerous discussions which have taken place during late years in cases in which one set of interactions of a compound appear to be in accordance with one formula, while another set favour a different but closely related formula, which have led, in fact, to the recognition of labile or pseudo-forms capable of passing spontaneously into stable forms. For example, it has long been a question whether ethylic acetoacetate is to be represented as $CH_3.CO.CH_2.CO_2Et$ or by the formula $CH_3.C(OH):CH.CO_2Et$. A discussion of such cases has been given by Laar (*B.* 18, 648; 19, 730), who proposes to term such isomerides *tautomeric*. But, as he practically himself admits, the use of such a term savours of tauto-

logy. V. Meyer subsequently brought forward a suggestion of Jacobson's to substitute *desmotropic* for tautomeric. Hantzsch and Herrmann (*B.* 20, 2801), while using the term tautomerism when speaking of compounds capable of passing from the one type into the other, proposed to limit the term desmotropic to each of the states. As the phenomena in question are the outcome of mobility and not of fixity, the new term also appears to be particularly ill chosen, and bearing in mind the intention of Berzelius in introducing the term metameric (see p. 81), it would appear that this old term is a peculiarly appropriate one to use in such cases. Laar suggests that a compound which is capable of an 'alternative' behaviour actually has an alternating structure, the intra-molecular condition being such that the structure is of one kind at one moment and different at another. But, as Hantzsch and Herrmann remark, it is scarcely necessary to make such an assumption. Ethylic succinylosuccinate and its derivatives manifest the peculiarity in question in a high degree, acting sometimes as quinonic compounds and sometimes as quinols, *i.e.* in modes such as correspond to the presence of one or other of the two forms $CO.CH(CO_2Et)$ and $C(OH).C(CO_2Et)$. As a rule only one of the forms is stable, the other being developed in the course of the change; thus phloroglucol appears to be a true trihydroxylbenzene, *i.e.* a phenol; but frequently it affords derivatives of 'triketohexamethylene,' which may with propriety be termed phloroglucone. Thus



Phloroglucol.



Phloroglucone.

It is not improbable that in those cases in which the several forms can be obtained in a definite crystalline form, the necessary stability is conferred by union of the fundamental molecules amongst themselves. The formation of such molecular complexes is rendered probable by a large number of observations; one of the most striking is that recently brought forward by Perkin in the case of orthomethoxybenzaldehyde $CH_3O.C_6H_4.COH$ (*C. J. Trans.* 1889. 549), which is capable of existing in two solid modifications, one unstable melting at 3°, the other stable and melting at 35·5°. A list of similar cases of what is sometimes termed *physical isomerism* is quoted by Perkin.

Having thus briefly touched on the numerous problems which the study of the different kinds of *allotropism* presents, it appears desirable finally to re-direct attention to the terminology of the subject.

The term allotropic, as already pointed out, has a perfectly general meaning and is therefore applicable to the phenomena generally, and may be used in all cases in which the nature of the relationship is obscure.

According to our modern conceptions, truly isomeric substances—substances composed of equal parts—are equi-molecular compounds containing identical radicles arranged in relatively different modes, and on the principle of calling a spade a spade, bearing in mind that it was obviously the intention of Berzelius to limit the scope of the expression, the term isomeric should be used only with reference to such compounds. The space relationship of the radicles being the determining cause of isomerism, although it is not always requisite in order that it may become apparent to express their relationship according to stereometric canons, it is scarcely necessary to make any principal distinction between cases, such, for example, as occur among benzene derivatives and between the tartaric acids; but if it be thought desirable to call attention in some way to the finer isomerism which obtains in cases such as the latter, the term *eikoisomerism*, from εἰκών, a likeness or image, may be suggested as not inappropriate.

Typically different allotropes belonging to different classes of compounds might well be termed *heteromeric*, metameric being reserved for those heteromeric allotropes which change their type with exceptional facility in the course of chemical interchanges; but if the use of the term in this restricted sense be objected to, such allotropes might advantageously be spoken of as *isodynamic*. Allotropes belonging to the same class but consisting of different radicles—the butylic alcohols, for example—might be termed *isonomic*. It appears unnecessary to specially distinguish the physical isomerism manifest in the occurrence of several crystalline forms of different melting-point. The phenomena of pleomorphism generally, as well as those involved in change of state from solid to liquid and gas, and the existence of allotropic forms both of the metallic and non-metallic elements, are now being more and more generally attributed to changes in molecular complexity; and if this be the case, such allotropes mostly partake of the nature of polymeric allotropes. H. E. A.

ISOMORPHISM (ἴσος, equal to; μορφή, form). In the year 1819 Mitscherlich (*A. Ch.* [2] 14. 172) discovered that certain arsenates and phosphates of analogous constitution crystallised in the same form; subsequent investigation (*A. Ch* [2] 19, 350; 24, 264, 355) led to the general conclusion that substances of analogous chemical constitution possess the same or nearly the same crystalline forms, and will under suitable conditions crystallise together in all proportions to form homogeneous mixed crystals; such substances are termed isomorphous. In spite of numerous attempts to widen or otherwise modify it, this definition has lasted to the present time. Owing, however, to recent researches, especially those of Groth, it will be best not to treat isomorphism as an isolated phenomenon, but as a part of that branch of physical chemistry which studies the relations between the chemical composition and crystalline form of bodies, and which from a knowledge of the constitution and chemical properties of a substance seeks to predict its system, form, and crystallographic constants. We are still very far indeed from doing anything approaching to this, for, although attempts have not been wanting—*v.* Schrauf (*Physikalische Mineralogie*, 1868. bd. 2, 166; *Z. K.* 9, 265) and Barlow (*C. N.* 53, 3, 16)—small success has so far attended them,

and at present crystal-form cannot be deduced from a knowledge of chemical constitution and properties alone; if, however, we find that in a given case certain atoms arranged in a certain definite way are accompanied by a certain definite form, we may argue that similar atoms similarly arranged will be accompanied by a similar form. This hypothesis is found to be true, and its verification has resulted in the discovery of relations between the forms of substances more or less chemically allied. These relations may be conveniently discussed under the three following heads:—

I. The same chemical substance possesses two or more forms—*Polymorphism.*

II. Bodies more or less closely related chemically have more or less analogous forms—*Morphotropy*, including *Isomorphism.*

III. Bodies not chemically related possess the same form—*Isogonism.*

Full references, especially for the early history of the subject, will be found in the article *Isomorphie*, by Arzruni, in Fehling's *Handwörterbuch der Chemie*, 1878. vol. 3; for more recent work Fock's *Einleitung in die Chemische Crystallographie*, Leipzig. 1888, may be consulted; while full lists of substances considered isomorphous have been given by Topsoë, *Tidskrift for Physik og Chemi*, 8, 5, 193, 321; 9, 225; summarised by Arzruni above. For the use of isomorphism in determining atomic weights *v.* ATOMIC AND MOLECULAR WEIGHTS, vol. i. p. 336.

POLYMORPHISM. Haüy believed that every substance possessed its own characteristic form, and, in spite of numerous observations tending to establish the chemical identity of calcite and arragonite (*v.* De Lisle, Klapproth, Thenard, and Stromeyer), refused to admit that the same substance could yield two distinct kinds of crystals. In the course of the work on the arsenates and phosphates which led him to announce that two different chemical compounds could possess the same or nearly the same crystalline form, Mitscherlich found that $NaH_2PO_4.H_2O$ gave, according to the conditions, two kinds of crystals, while his discovery in 1823 (*A. Ch.* [2] 24, 264) that sulphur crystallised both in rhombic and oblique forms readily convertible the one into the other by change of temperature alone, established conclusively that the same substance could exist in two different forms; to express these phenomena Mitscherlich proposed the term *dimorphism*, and in 1828 recognised the possibility of *trimorphism.* The existence of several modifications of the same substance may be generally expressed by the terms *polymorphism* or *heteromorphism.* At the present time these terms are usually applied to compounds only, polymorphism, when exhibited by elements, being termed *allotropy* (*q. v.*, vol. i. p. 128). The change of one dimorphous modification into another has been especially studied by Lehmann, and all known cases have been collected and discussed by him in his *Molekularphysik*, 2 vols. Leipzig, 1888 (vol. i. pp. 119–219, vol. ii. pp. 398–415).

MORPHOTROPY. From the time of Mitscherlich onwards the rapid growth of organic chemistry provided a large number of new substances for crystallographic examination, and as the existence of many cases of isomorphism among inorganic substances had been established, numerous attempts were made to introduce the same conception into organic chemistry. In general, however, these efforts were fruitless, and the researches merely resulted in the introduction of new terms and in several attempts at widening Mitscherlich's definition.

Thus Laurent, who investigated the halogen substitution and addition products of naphthalene and salts of the fatty acids, concluded that identity of system is not necessary for isomorphism. Nicklès and De la Provostaye collected cases of analogous angles and introduced new terms, such as hemi-isomorphism, isomeromorphism, and hemimorphism, to express those cases in which crystals of two substances had each a zone with nearly similar angles (*v.* papers by these authors, *C. R.* 11, 15, 20, 23, 26, 27, 29). Pasteur again (*C. R.* 26, 535) found analogies between the tartrates, while other workers in the same direction were Rammelsberg, Marignac, Delafosse, Sella, and Hjortdahl (*J. pr.* 94, 286). Owing to the paucity of results, such researches lost favour till Groth, in 1871 (*P.* 141, 131; *B.* 3, 449), attacked the subject from a new point of view, and set himself to investigate the changes in crystal-form which take place when one or more of the hydrogen atoms of an organic molecule, such as benzene, are substituted by other atoms or groups. The relations observed between the form of the parent substance and the form of the substituted body Groth terms morphotropic relations, while he attributes the actual change of form produced by substitution to the morphotropic force of the elementary atom or group. Benzene, which crystallises in rhombic pyramids, was the first substance examined by Groth; he compared its form with the forms of as many as possible of its hydroxy-, nitro-, amido-, and haloid, substitution products, and his researches have led to the following general statement. The less the chemical character of the combination is changed by substitution the less is also the change of crystal-form, which depends

1. On the specific morphotropic properties of the substituting atom or group;

2. On the chemical nature and crystalline system of the body in which substitution occurs;

3. On the relative positions of the substituting atoms or groups in the molecule.

1. Morphotropic properties of atoms and groups.

(*a.*) The metals. Potassium and ammonium, when substituted for H, only change one axis, thus:—

		a		b		c
Picric acid	rhombic	0·937	:	1	:	0·974
Potassium picrate	„	0·942	:	1	:	1·352

As a rule, all the alkali metals produce the same effect.

(*b.*) Substitution of OH for H in benzene derivatives only alters the crystalline form slightly, and in rhombic substances the ratios of two of the axes remain unaltered, and only the third axis is materially affected.

NO_2 and NH_2 behave much like OH.

		a		b		c
Benzene . . .	rhombic	0·891	:	1	:	0·799
Resorcin . .	„	0·910	:	1	:	0·540
Nitrophenol 1:2 .	„	0·873	:	1	:	0·600?
Dinitrophenol 1:2:4	„	0·933	:	1	:	0·753
Trinitrophenol 1:2:4:6	„	0·937	:	1	:	0·974

(*c*.) Cl, Br, and I act more energetically, but less regularly, than NO_2. The angles of one zone, however, remain like those of the parent substance, while the system is generally altered to one of lower symmetry.

Benzene . .	rhombic	$110 : 1\bar{1}0 =$	96°·30′
Dichlorobenzene	oblique	,, ,,	98°·40′
Tetrachlorobenzene	,,	,, ,,	96°·17′

(*d*.) The influence of the CH_3 group is extremely variable, depending very much on the nature of the substance into which it enters. Among the substituted ammonias it is often without influence; thus, $2NH_4Cl.PtCl_4$, $2NH(CH_3)_3Cl.PtCl_4$, $2N(CH_3)_4Cl.PtCl_4$, all crystallise in the cubic system.

2. Influence of the nature of the parent substance. When the parent substance belongs to the cubic system, substitution has either no influence on the form, or else causes change to a system of lower symmetry. In other systems the axial ratios may alone alter, or the system itself may be changed, according to the morphotropic force of the substituting element or group. If the hydrogen atoms of like functions are replaced singly the system frequently at first changes to one of lower symmetry, but when the substitution is complete returns to the symmetry of the parent substance. The methyl substitution compounds of $2NH_4Cl.PtCl_4$ illustrate this well:—

$2NH_4Cl.PtCl_4$ . .	Cubic
$2NH_3(CH_3)Cl.PtCl_4$.	Rhombohedral
$2NH_2(CH_3)_2Cl.PtCl_4$.	Rhombic
$2NH(CH_3)_3Cl.PtCl_4$.	Cubic
$2N(CH_3)_4Cl.PtCl_4$.	Cubic

As an illustration of the influence of the chemical nature of the parent substance, we may quote the observation of Hintze that, contrary to the general rule, the substitution of the paraffinoid H in $(C_6H_5)_3CH$ by (OH) or Br raises the symmetry, instead of lowering it.

3. Influence of position.—The relative position of the substituting atoms in the molecule has a very great influence on the form of the crystal; but we are very far from being able to connect form and constitution.

As a rule the crystals of isomerides exhibit very few analogies, and in many cases none at all. In the benzene series, however, a few relations have been observed, though even here they are rare, and often more readily detected by a comparison of the isomerides with the parent substance than directly with each other. Thus a comparison of the angles given by Bodewig (*P.* 158, 232) for the three dinitrobenzenes shows that certain analogies do exist, although the compounds do not crystallise in the same system, while *meta*-$C_6H_4(NO_2)_2$ is related to benzene itself, as is shown in the following table:—

		a		*b*		*c*	
C_6H_6	rhombic	0·891	:	1	:	0·799	
$o.C_6H_4(NO_2)_2$	oblique	0·6112	:	1	:	0·5735	$\beta = 67°·53'$
$m.C_6H_4(NO_2)_2$	rhombic	0·9430	:	1	:	0·5384	
$p.C_6H_4(NO_2)_2$	oblique	2·0383	:	1	:	1·0432	$\beta = 87°·42'$

The above examples suffice to show very clearly that the great influence exercised by position renders the discovery of the morphotropic properties of an element or group very difficult. Thus we have stated above that the entry of the nitro- group into benzene leaves the system and axial ratio *a*:*b* unaltered, while the *c* axis is more or less changed. This statement we found held good for o-$C_6H_4(NO_2)OH$, $C_6H_3(NO_2)_2OH(1:2:4)$, $C_6H_2(NO_2)_3OH(1:2:4:6)$, and *m*-$C_6H_4(NO_2)_2$. As soon, however, as we become acquainted with o- and *p*-$C_6H_4(NO_2)_2$ the generality of our statement disappears, and the exact morphotropic value of the NO_2 group remains still undetermined. Although we are not in a position to deduce form from a knowledge of constitution alone, we may often from the chemical analogy of two substances, the form of one of which is known, draw conclusions as to the form of the other; or, *vice versâ*, knowing the form of two substances, and the constitution of one of them, we may draw conclusions as to the constitution of the other. This method has been chiefly employed in inorganic chemistry, but Friedländer (*Z. K.* 3. 168) has made use of it in order to throw light on the constitution of the trinitrobenzene got by nitrating *m*-$C_6H_4(NO_2)_2$. The trinitrobenzene made in this way may be either of three theoretically possible ones. It crystallises, however, in the rhombic system, and has the axial ratios 0·954 : 1 : 0·733, and agrees accordingly with *m*-$C_6H_4(NO_2)_2$. On the other hand it shows little or no analogy to the forms of o- or *p*-$C_6H_4(NO_2)_2$, and it is therefore probable that this substance is symmetrical triuitrobeuzeue 1:3:5. A comparison of its form with that of picric acid $C_6H_2(NO_2)_3OH(1:3:5:6)$, rhombic 0·937 : 1 : 0·974, confirms this view.

Isomorphotropy and Isomorphism. When the products obtained by replacing the hydrogen atoms of the parent substance by two closely-allied atoms or groups are compared together they are often found to crystallise in identical or nearly identical forms; such products are isomorphous, while the substituting atoms or groups are said to possess the same morphotropic force, or to be isomorphotropic. Thus, K and NH_4 are isomorphotropic, and replace the H of acids to give isomorphous salts.

The term morphotropy was first applied to cases in which an atom of H was substituted, but the conception may very conveniently be extended to include all cases of substitution whatever; thus, KBr may be regarded as derived from KCl by substituting Cl by Br, and since KCl and KBr both crystallise in the same system and possess very similar physical characters, they are isomorphous, while Cl and Br are isomorphotropic. The greater the analogies between the substituting atoms the greater is the correspondence between the forms of their compounds, *i.e.* the more closely isomorphous are they; but because two elements are isomorphotropic when in combination with one set of atoms or groups it does not necessarily follow that they are always isomorphotropic, for the morphotropic force of any atom is largely conditioned by the compounds in which it finds itself. Again, Kopp (*P.* 53, 446) has pointed out that although it is often true that two isomorphous substances combine with a third to form two isomorphous compounds (Schröder), we cannot, as has been too frequently done, deduce the isomorphism of elements from the isomorphism of their compounds; there are few elements which cannot by such a mode of reasoning be made isomorphous. Elements are only truly isomorphous when they

actually crystallise in the same forms; if they merely combine with another element or group to form isomorphous compounds they may be spoken of as isomorphotropic in that particular class of compounds. As we have seen, the conception of morphotropy includes that of isomorphism. Now, ever since the latter term was introduced, great difficulties have been felt in defining it, and in finding tests which might authoritatively decide in any given case whether two substances were isomorphous or not. Mitscherlich's definition is vague, for we at once ask, What constitutes chemical analogy? And again, How widely may the angles of two substances differ and the substances still be considered isomorphous? The truth seems to be that no hard and fast line can be drawn between those substances which are so closely related morphotropically as to be considered undoubtedly isomorphous, and those slightly less closely related whose isomorphism is doubtful; while we may pass by imperceptible stages from truly isomorphous bodies to others to which, although they still exhibit relations, this term is as evidently inapplicable. Although it seems impossible in the present state of our knowledge to give a definition which shall distinctly mark off isomorphous bodies from those which are merely closely related morphotropically, this is not in practice attended with any very great inconvenience, for the difficulty is chiefly one of nomenclature; most cases of isomorphism are at once recognised as such, and it is only in comparatively few instances that we must hesitate.

In doubtful cases much assistance may often be obtained by a comparison of the other properties of the two substances. Besides great similarity of form, agreement in several other physical properties has been thought necessary before two substances could be considered isomorphous; and we must now notice in detail the more important of these properties, pointing out the weight which has been attached to each as a test of isomorphism.

Physical properties of isomorphous substances.

(*a.*) *Geometrical properties.* As the name itself implies, near equality of external form is the first and most essential condition for isomorphism. Absolute geometrical isomorphism, however, does not exist except in the case of substances crystallising in the cubic system; in all other systems small differences of angle occur, a fact first noticed by Wollaston. These differences are seldom equally distributed; in rhombic oblique and triclinic crystals the anomalies are often confined to one zone, another zone perpendicular to the first having the same angles in both cases. Here a difficulty meets us, for we ask, How great may these differences become and the substances still remain isomorphous? Unfortunately no definite answer to this question is possible; some authors have admitted much wider differences than others, while others still have gone so far as to admit that the boundaries of the systems may be overstepped. It is perhaps best to restrict the term isomorphous to substances crystallising in the same system with nearly the same angles. It is to be noted that though all substances crystallising in the cubic system have exactly the same angles they are not necessarily isomorphous; to be so they must be either both holohedral or must both possess the same kind of hemihedrism, and must also agree in other properties, such as cleavage and power of forming mixed crystals.

(*b.*) *Cleavage.* Isomorphous bodies possess as a rule the same cleavages: variations in the relative perfection of such cleavages are, however, possible. This property is especially useful in assisting us to detect isomorphism in the cubic system.

(*c.*) *Thermal conductivity.* Jannetaz (*C. R.* 75, 1501) has shown that certain isomorphous substances have axes of maximum and minimum conductivity of like direction and magnitude.

(*d.*) *Coefficient of expansion.* The data are not sufficient for general conclusions to be drawn, and no simple relations have been detected at present.

(*e.*) *Etched figures.* Since these stand in a close relation to crystalline form, Baumhauer has sought to use them as a test of isomorphism. He finds that isomorphous substances give, as a rule, the same sort of etched figures, but that they often differ in orientation.

(*f.*) *Optical properties.* These have been specially compared by Senarmont (*A. Ch.* [3] 33, 391), Topsoë, and Christiansen (*A. Ch.* [5] 1, 5). No general law has been established, but as a rule isomorphous bodies if uniaxial have the same sign of double refraction, and if biaxial have the plane of the optic axes similarly oriented, but biaxial crystals, oblique and triclinic ones especially, exhibit frequent exceptions. Optical properties are, moreover, very sensitive to changes of temperature, which often do not influence isomorphous substances to the same degree (Arzruni, *Z. K.* 1, 165).

(*g.*) *Specific volume.* The relations between chemical composition, S.V., and crystalline form are of special importance, since several authors have considered near equality of S.V. an essential condition for isomorphism. The first of these was Kopp (*A.* 36, 1; *P.* 47, 133; 52, 243, 262; 53, 446), his views may be briefly summarised as follows: (1) The condition for isomorphism is equality or near equality of S.V. The answer to the question, how widely may the S.V.'s differ and the substances remain isomorphous, is given by the empirical formula $D = \frac{v - v_1}{\frac{1}{2}(v + v_1)}$ where v and v_1 are the S.V.'s of the two substances. If $D = 0$ the isomorphism is perfect, but if D is greater than ·33 the substances are not isomorphous; thus the value of D for the two substances $ZnCO_3$ and $CaCO_3$, whose S.V.'s are 28·2 and 36·8 respectively, is ·264; they are, therefore, isomorphous. (2) Kopp has also pointed out that the nearer are the axial ratios of a series of isomorphous bodies the nearer are their S.V.'s. This statement, though criticised by Schröder, appears to hold good, and has received the support of Tschermak (*Sitz. W.* 45 [2] 603) and Schrauf (*P.* 134, 417). The former expresses the law as follows: 'The series of crystal-dimensions and specific volumes is in each group of isomorphous bodies of analogous composition the same.' As an illustration he gives the series of rhombohedral carbonates:

	a : d	
$ZnCO_3$	1 : 0·807	28·2 ?
$MgCO_3$	1 : 0·812	27·9
$(MgFe)CO_3$	1 : 0·814	29·2
$FeCO_3$	1 : 0·819	30·2
$MnCO_3$	1 : 0·822	31·9
$CaCO_3$	1 : 0·854	36·8

Schröder (*P.* 50, 553; 95, 441, 562; 106, 226; 107, 113) at first held views much resembling those of Kopp, but in his later papers he comes to the conclusion that the statements made above are erroneous, and expresses himself thus: 'The specific volumes of isomorphous compounds differ in general quite as much from one another as the specific volumes of corresponding heteromorphous compounds' (Schröder uses the term heteromorphous as opposed to isomorphous, it is now often considered synonymous with polymorphous), and he believes that his results lead him to a new law, viz. 'If two elements or groups, A and B, enter into combination with other elements or groups C, D, E, &c., to form the compounds A C and B C, A D and B D, A E and B E, &c., belonging to the same type and isomorphous by pairs, then the differences of the specific volumes of A C and B C, A D and B D, A E and B E, are always equal.' If, however, the pairs of compounds are not isomorphous, or if the isomorphous pairs belong to different types, the differences are as a rule unequal. Schröder terms bodies of equal S.V. *isosteric*, and the equality of the differences of analogous pairs *parallelosterism*. Adopting this nomenclature, the above law may be shortly expressed thus: 'Isomorphous analogous pairs of like type are also parallelosteric.'

Tschermak (*l.c.*) finds that, although Schröder's criticism of Kopp is unfounded, his own results support Schröder's law, which he enunciates thus: 'Among isomorphous bodies a like difference of composition corresponds to a like difference of specific volume;' thus the difference Br – Cl is about equal to 6·3.

	S.V.		S.V.		S.V.		S.V.
NaBr	33·4	KBr	44·3	AgBr	31·8	AmBr	42·2
NaCl	27·2	KCl	37·9	AgCl	26·0	AmCl	35·2
	6·2		6·4		5·8		7·0

Apparent exceptions to Schröder's law are believed by Tschermak to be due to difference of constitution in the substances compared, and he illustrates this by the following table of difference for the change of composition K to Am:

	S.V.		S.V.
KCl	37·9	KBr	44·3
AmCl	35·2	AmBr	42·2
	2·7		2·1
	S.V.		S.V.
K_2PtCl_6	134·5	K_2SO_4	65·6
Am_2PtCl_6	150·5	Am_2SO_4	74·6
	16·0		9·0

We see from this table that substances of the type M'_2PtCl_6 cannot be directly compared with those of the type M'_2SO_4 or these again with M′C.

Tschermak has, moreover, endeavoured to trace a connection between the varying differences shown by pairs of elements which occur in compounds of similar constitution, and the crystal-system to which these compounds belong.

Cubic	S.V.	*Oblique*	S.V.
Am_2PtCl_6	150·5	$Am_2Cu(SO_4)_2.6aq$	218
K_2PtCl_6	134·5	$K_2Cu(SO_4)_2.6aq$	205
	16·0		13
Am_2IrCl_6	156	$Am_2Mg(SO_4)_2.6aq$	209
K_2IrCl_6	138·3	$K_2Mg(SO_4)_2.6aq$	196
	17·7		13
Tetragonal			
$Am_2CuCl_4.2aq$	137	$Am_2Fe(SO_4)_2.6aq$	212
$K_2CuCl_4.2aq$	133	$K_2Fe(SO_4)_2.6aq$	197
	4		15
Rhombic			
Am_2SO_4	74·6	$Am_2Zn(SO_4)_2.6aq$	211
K_2SO_4	65·6	$K_2Zn(SO_4)_2.6aq$	201
	9·0		10

Thus he finds that for the change of composition Am_2 to K_2 the difference of S.V. is greatest in the cubic system, less in the oblique, still less in the rhombic, and least in the tetragonal system.

In connexion with S.V. we may note that at or about maximum and minimum points of the atomic volume curve (*v.* PERIODIC LAW) occur ductile metals crystallising in the cubic system, *e.g.* Na, Mg, Al, K, Fe, Co, Ni, Cu, Pd, Ag, Pt, Ir, Au, Hg, Pb.

Although isomorphism is usually accompanied by similar values for the S.V.'s, we cannot from the near equality of S.V. alone deduce the isomorphism of two substances, neither can we at the present time attach much weight to Kopp's empirical formula as a test of isomorphism; in a general way, however, his results, in common with those of Tschermak, Schröder, and Schrauf appear to hold good; owing, however, to the great discrepancies which exist between the relative densities of many of the commonest substances as given by different observers, we must be cautious in accepting conclusions often resting on doubtful data.

Special properties of isomorphous substances.

(*a.*) *Formation of layer-crytals.*

(*b.*) *Formation of mixed crystals.*

(*a.*) *Layer-crystals.* These are made by growing a crystal of one substance in a solution of another.

Kopp (*B.* 15, 1653) considers regular growth under these circumstances the best test of isomorphism.

Thus a crystal of common alum when brought into a solution of chrome alum continues to increase regularly; again the sulphates of the type $M''SO_4.7aq$ where M'' = Zn, Mg, Fe, Co, Ni, grow in solutions of one another.

In those cases where the forms of the two substances are the same the new particles have exactly the same orientation as those of the nucleus. Klocke (*Z. K.* 2, 144) has, however, brought to light differences between the phenomena of growth in such cases, and in those where a crystal grows in its own solution. Having produced etched figures on the faces of two potassium alum crystals, he grew one in its

own solution, the other in a solution of ammonia iron alum; in the first case the etched figures were rapidly filled up from the bottom, in the second very much flattened octahedra of ammonia iron alum were developed at certain points on the crystal of common alum, and perfectly parallel to it, they then increased laterally, and covered up the etched figures, which remained unaltered till the new layer reached them.

Although the power of forming overgrowths seems to be a necessary consequence of isomorphism, the property is not confined to isomorphous substances alone, and from the perfect conformity of form and orientation exhibited by isomorphous substances, such as the alums, we may pass by imperceptible stages to cases of regular orientation among substances possessing but little chemical analogy and crystallising in different systems. Thus rutile TiO_2, tetragonal, is often found developed on the basal plane of hæmatite Fe_2O_3, rhombohedral, in such a way that the c axis of the rutile lies in a plane of symmetry of the hæmatite.

A specially interesting and much discussed case of overgrowth is that of calcite $CaCO_3$ rhombohedral $rr' = 74° 55'$ and $NaNO_3$ rhombohedral $rr' = 73° 27'$. When a rhombohedron of $CaCO_3$ is placed in a solution of $NaNO_3$ this substance is deposited on the former in small rhombohedra, whose morphological axis and planes of symmetry are exactly parallel to those of the $CaCO_3$, these rhombohedra grow till they meet, a polysynthetic crystal being the result. Kopp accordingly made a difference between growth in this case and the regular increase of alum crystals; in the light of Klocke's work, and taking into consideration the slight difference of the angles rr′, such a distinction vanishes, and if the formation of overgrowths is a test of isomorphism, these two substances are certainly isomorphous, a view confirmed by the agreement in their other physical characters; the difference in their chemical constitution leads us rather to regard them as an example of isogonism.

Closely connected with the formation of layer-crystals are Thomson's researches on supersaturated solutions (*C. J.* 1879. 196); he has shown that supersaturated solutions of certain salts can readily be crystallised by the addition of crystals of isomorphous salts, while crystals of substances not possessing the same form, or fragments of amorphous bodies, such as glass, have no influence. Thus a supersaturated solution of $MgSO_4.7aq$ is at once crystallised by $ZnSO_4.7aq$, $NiSO_4.7aq$, and also by $CoSO_4.7aq$ and $FeSO_4.7aq$, whose action, however, is less rapid; on the other hand, $Na_2SO_4.10aq$, NaCl, and glass, are quite inactive. Common alum can be crystallised by iron and chrome alums, while other cubic substances, such as NaCl, FeS_2, and Fe_3O_4, are inactive.

This appears to be an excellent test of isomorphism as far as it goes, but it unfortunately is of very limited application.

Although at the present time the formation of layer-crystals cannot be considered a conclusive proof of isomorphism, the success or failure of attempts to obtain them may help us to determine whether two substances crystallising in the cubic system are isomorphous or not.

(A discussion of numerous cases of layer-crystallisation will be found in Lehmann's *Molekularphysik*, Bd. i. pp. 393–407; *v.* also Wackernagel, *Kästners Archiv*, 5, 293, and especially Kopp, *B.* 12, 901.)

(*b.*) *Mixed crystals.* To obtain mixed crystals solutions of two substances are mixed, or in some cases the two substances are simply melted together, and then allowed to crystallise; we thus obtain perfectly homogeneous crystals, which do not, however, contain their components in any fixed ratio.

As a rule only isomorphous substances yield mixed crystals, and their formation is usually considered the best criterion of isomorphism. [Klein (*C. R.* 95, 781), Kopp (*B.* 12, 868; 17, 1105), but *v.* also Brugelmann (*B.* 17, 2359), and especially Lehmann (*l.c.* Bd. i. 420, 456, 461).]

Numerous researches have been undertaken with a view to the elucidation of the constitution and mode of formation of mixed crystals, while other investigators have endeavoured to trace the connexion between their physical properties and those of their components.

Growth of mixed crystals. Mixed crystals are most readily formed when the two substances have nearly equal solubility, and in this case Rammelsberg (*P.* 91, 321) has found that the ratio of the two salts in the mixed crystal is about the same as in the solution, mixed crystals of $ZnSO_4.7aq$ and $MgSO_4.7aq$ afford a case in point; if, however, as more usually happens, the solubilities differ, the first crystals always contain most of the less soluble salt, the last most of the more soluble; such salts are $CuSO_4.5aq$ and $MnSO_4.5aq$. Thomson (*l.c.*) has pointed out that in the case of the crystallisation of supersaturated solutions consisting of a mixture of two substances, the composition of the mixed crystal depends very much on the velocity of crystallisation; if this takes place suddenly the composition of the mixed crystal is much the same as that of the solution, if slowly the less soluble salt is deposited first.

The physical properties of mixed crystals.

(*a*) *Geometrical properties.* Mixed crystals belong to the same system as their components, but exhibit simpler forms; *cf.* calcite and dolomite, and *v.* also Rammelsberg (*l.c.*). In some cases the angles of mixed crystals lie between those of their components, this usually holds good for the naturally occurring mixtures of the rhombohedral carbonates, thus:

Chalybite $FeCO_3$	**rr′** $= 72°{\cdot}59'$
Pistomesite $(FeMg)CO_3$	$= 72°{\cdot}42'$
Magnesite $MgCO_3$	$= 72°{\cdot}32'$

But even in this series exceptions are not wanting, and as a rule no simple relation can be detected between the angles of the mixed crystals and those of its components; thus Groth (*P.* 133, 193) in the case of the permanganates and perchlorates found that the angles of the mixed crystals often lay outside those of their components.

		$a : b : c$
$KClO_4$	rhombic	0·7819:1:0·6396
$K\left\{\begin{matrix}\frac{1}{12}Mn \\ \frac{11}{12}Cl\end{matrix}\right\}O_4$	„	0·7797:1:0·6408
$K\left\{\begin{matrix}\frac{2}{13}Mn \\ \frac{11}{13}Cl\end{matrix}\right\}O_4$	„	0·7839:1:0·6398
$KMnO_4$	„	0·7974:1:0·6492

In the crystal containing 1Mn:11Cl the ratio $b:c$ lies inside the limits, and the other two outside; further increase in the quantity of Mn causes the form of the mixed crystal to approach nearer to that of $KClO_4$. Similar results have been obtained by Arzruni on the alkaline earths (*B.* 5. 1043), Meminar on baryto-cœlestin (*Min. Mit.* 1875. 59), v. Lang on Am_2SO_4 and K_2SO_4 (*Sitz. W.* 1858. 31, 85), Arzruni and Baerwald on compounds of FeS_2 and $FeAs_2$ (*Z. K.* 7, 337), and lastly by Miers in his investigations of proustite and pyrargyrite (*Min. Mag.* 8, 37).

(*b.*) *Optical properties.*

(i.) Index of refraction. In the year 1878 Dufet (*C. R.* 86, 881), from an investigation of $MgSO_4.7aq$, $NiSO_4.7aq$, and $ZnSO_4.7aq$, found that the connection between the chemical composition of isomorphous mixtures and their indices of refraction is one of simple proportionality, so that expressing the results graphically by taking, along two axes at right angles, ordinates proportional to the observed values of μ, and abscissæ proportional to the percentage of one component in the mixture, the resulting curve is a straight line. Fock (*Z. K.* 4, 583) has, however, taken exception to Dufet's work, and although he finds that the changes in the values of the ordinary and extraordinary ray are proportional to the changes in composition for mixed crystals of $SrS_2O_6.4aq$ and $PbS_2O_6.4aq$, yet in mixtures of thallium and potassium alums, and again in mixtures of $MgSO_4.7aq$ and $MgCrO_4.7aq$, he could find no such law; *v.* also Fitz and Sansoni (*Z. K.* 6, 67). Fock's results have in their turn been questioned by Soret (*Z. K.* 11, 197) and Dufet (*C. R.* 99, 990). The former finds that mixtures of thallium and potassium alum and also of ammonium and potassium alum satisfy the law, while the latter has shown that mixtures of $MgCrO_4.7aq$ and $MgSO_4.7aq$ are not sufficiently homogeneous for investigations of this kind.

Dufet's law probably holds good, but further investigation is needed before it can be considered established.

(ii.) Optic axis angle. Wyrouboff (*Bull. Soc. Min. France*, 2, 91, 170) has endeavoured to trace the connection between the angle of the optic axis and the chemical composition in the cases of mixtures of K_2SO_4 and Am_2SO_4, and of K_2CrO_4 and K_2SO_4. His results have been expressed graphically by Mallard (*Bull. Soc. Min. France*, 3, 3), who finds that they give a continuous regular curve, not, however, a straight line. If the optical properties of the components are non-accordant, those of the mixed crystals will be different from either; *v.* especially Senarmont (*l.c.*) on mixed crystals of $KNaH_4C_4O_6.4H_2O$ and $(NH_4)NaH_4C_4O_6.4H_2O$:—

	Optic axis plane	1st mean line	2nd mean line
Potassium salt	010	*a*	*c*
Ammonium .	100	*c*	*b*

Starting from the potassium salt and substituting with NH_4, we observe the following changes; first the obtuse angle diminishes, and more quickly for red than for violet light, then at a certain point the axes for red light coincide, while the axes for violet light still lie in 010, the red axes then begin to diverge in 100, the violet afterwards coincide and follow the red. Wyrouboff (*Z. K.* 13, 648), on ammonium and thallium tartrates, gives the following example :—

	Optic axis plane	2H
Ammonium salt	*b*	42° 38′
Thallium . .	1 to *b*	59° 30′

The mixture had always the cleavage and optic axis plane of the ammonium salt, and a crystal containing 88·7 p.c. of the thallium salt had 2H = 43°30′.

(iii.) Circular polarisation. Bodländer (*Z. K.* 9, 309) investigated mixtures of lead and strontium thiosulphates; he found that the rotation varied directly with the composition.

(iv.) Angle of extinction. Max Schuster has shown that the angle of extinction of certain oblique and triclinic mixed crystals, especially the felspars, varies directly with their chemical composition. His results have been confirmed by Mallard (*Z. K.* 6, 612), who has treated the subject mathematically.

(v.) Specific volume relations. The specific volumes of mixed crystals appear to depend directly on the relative proportions of their compounds. Thus Schröder states (*P.* 95, 441) that

$$V(aCaCO_3 + bFeCO_3) = \frac{aV'(CaCO_3) + bV''(FeCO_3)}{a+b}$$

where V is the specific volume of the mixed-crystal and V′, V″ are those of its components. These results have been confirmed by Tschermak (*l.c.*) thus:

$BaCO_3$ (witherite)	rhombic	V = 45·7
$CaCO_3$ (arragonite)	rhombic	33·9
∴ $(BaCa)CO_3$		= 39·8
while alstonite	rhombic	= 39·5

The specific volumes of artificial mixed crystals have been especially investigated by Retgers (*Z. P. C.* 3, 497). He has studied with great care the mixed crystals formed by (*a*) K_2SO_4 and Am_2SO_4 (*b*) potassium and thallium alums; he finds that the S.G. varies directly with the composition, and expressing his results graphically he obtains as his curve a straight line, a result similar to that obtained by Dufet for the values of μ.

Formation of mixed crystals by isodimorphous substances.—Two substances, X and Y, are said to be isodimorphous if they each exist in two forms A and B, A′ and B′, of which A is isomorphous with A′ and B with B′.

On crystallising a solution containing two isodimorphous substances two series of mixed crystals are obtained, one set having the form A, the other the form B. It often happens that the form A of one salt, X say, is stable under ordinary circumstances, while of the other salt, Y, the form B is stable; in the mixed crystals of the form A the substance X predominates, in mixed crystals of the form B, Y is present in excess. In such cases as these a continuous series of mixed crystals cannot always be obtained. Crystallisation under these conditions has been especially studied by Rammelsberg (*P.* 91, 321). Thus he finds that $MgSO_4.7aq$ is rhombic and $FeSO_4.7aq$ is oblique; from a solution containing both substances two sorts of mixed crystals are obtained, these do not, however, contain their constituents in all possible proportions, but a gap

occurs, the oblique crystals always having more than 1 atom Fe to 2–3 Mg, while the rhombic crystals always contain more than 4 Mg to 1 Fe. Another good example is afforded by $BeSO_4.4aq$ tetragonal and $BeSeO_4.4aq$ rhombic. The mixed crystals are tetragonal when S:Se > 7·33:1, and rhombic when S:Se < 4:1 (Topsoë, *Sitz. W.* [2] 66; *v.* also Schulze, *A.* 125, 49; Wyrouboff, *Bull. Soc. Min. France*, 2, 91).

Cases of crystallisation perfectly analogous to but differing from these have been studied by Rammelsberg (*l. c.*); thus copper sulphate usually crystallises in the triclinic system with 5aq, ferrous sulphate in the oblique system with 7aq. When solutions of copper sulphate and ferrous sulphate are mixed and allowed to crystallise, two sorts of crystals are got, both of which contain Cu and Fe; as long as the proportion Cu:Fe is > 20:1 the crystals possess 5aq and are triclinic, but when there is less Cu the crystals are oblique and contain 7aq.

It is very commonly supposed, when two substances closely allied chemically crystallise in different forms but yield two kinds of mixed crystals, that these substances are isodimorphous, although more than one form of each may not be known; *v.* Fock (*Z. K.* 6, 160), and note the adverse criticism of Wyrouboff (*Bull. Soc. Min.* 5, 32).

The specific volumes of isodimorphous substances have been compared by Rideal (*B.* 19, 589); while Retgers (*l. c.*) has found that in those cases where isodimorphous substances form mixed crystals, each series obeys the law enunciated above, viz. that the relative density varies directly with the composition.

Constitution of mixed crystals.—Since the beginning of the century two opposing views have been held as regards the constitution of these substances.

(*a.*) According to the first or physical theory, as we may call it, the most homogeneous mixed crystal really consists of a very intimate mixture of particles of each of the components. This view, held by Haüy, and maintained by Frankenhein in opposition to Berthollet, has recently received the support of Lehmann and Retgers; the latter says that a mixed crystal is a very intimate but purely mechanical mixture of its components, and finds strong confirmation of his view in the fact that the densities, indices of refraction, &c., of mixed crystals vary directly with their composition.

(*b.*) The supporters of the second or chemical theory maintain that molecules of each substance come together in the solution to form a complex 'liquid-molecule,' while 'liquid-molecules' of the same kind unite on crystallisation and form the mixed crystals. Berthollet held this view, which is perhaps more generally accepted than the other; at the present time its chief exponent is Fock, who believes that the formation of mixed crystals and double salts are phenomena of the same order.

Use of mixed crystals as a test of isomorphism.—As we have seen, much weight has been attached to this property by Mitscherlich, Kopp, and others, but at the present time so many instances are known of the formation of mixed crystals by substances which cannot be considered isomorphous that the test has lost much of its value (*v.* Lehmann, *l. c.*). Retgers (*l. c.*) has proposed that only those substances should be considered isomorphous, the physical properties of whose mixed crystals vary directly with the chemical composition.

ISOGONISM.—Speaking generally we find that if two substances are to be considered isomorphous they must satisfy the two following conditions: (i.) they must agree very closely in form and possess similar physical properties; (ii.) under suitable conditions they must be capable of forming layer- and mixed crystals. In Mitscherlich's definition we find, however, a third condition, viz. analogy of chemical constitution; and the question arises, How far may two substances which satisfy the two conditions above differ in chemical constitution and still be considered isomorphous? This question has received various answers; thus Scheibler (*J. pr.* 83, 273) has announced the isomorphism of most meta-tungstates, although they do not all contain the same number of molecules of water of crystallisation; Marignac (*C. R.* 55, 888) considers the two following series of substances to be isomorphous:—

$K_2TiF_6.H_2O$ — $CuTiF_6.4H_2O$
$K_2NbOF_5.H_2O$ — $CuNbOF_5.4H_2O$
$K_2WO_2F_4.H_2O$ — $CuWO_2F_4.4H_2O$.

And he also makes rhombohedral silicotungstic acid, and the acid silicotungstates of Ba and Ca isomorphous. Some other similar examples are given by Baker (*C. J.* 1879. 760). Klein (*C. R.* 95, 781) believes that the following substances are isomorphous:—

$9WO_3.B_2O_3.2H_2O.22aq$
$9WO_3.B_2O_3.Na_2O.23aq$
$12WO_3.B_2O_3.4H_2O.29aq$ (Marignac).

Klein, following Marignac, amends Mitscherlich's definition thus: 'Isomorphous substances have either an analogous chemical constitution or a very slightly different percentage composition; in the latter case they contain a group of common elements or elements of identical chemical function, this group making up by far the largest portion of the compound.' It seems, however, hardly advisable to widen Mitscherlich's definition; indeed, it is perhaps better if possible to narrow it by defining more closely what is meant by the phrases analogous chemical composition and analogous crystalline form.

Substances, such as the double fluorides described by Marignac, are not so much isomorphous as closely related morphotropically, while from them we may pass through substances exhibiting less and less of chemical analogy to those which agree in form alone, and which may therefore be considered as examples of isogonism (*v.* Retgers, *l.c.*). As an instance of this we may quote the remarkable analogy noticed by Hjortdahl (*C. R.* 88, 584) between the crystals of tin dimethyl and diethyl chlorides and lead chloride, which all crystallise in the rhombic system, and possess the following axial ratios:—

	a b c
Tin dimethyl chloride	0·8341:1:0·9407
Tin diethyl chloride	0·8386:1:0·9432
Lead chloride	0·8408:1:0·9990.

At present it seems that substances which exhibit relations in form and composition may most

conveniently be divided into the following more or less arbitrary groups, between whose limits no absolute line can be drawn:—

(1) Substances very closely related morphotropically, or isomorphous substances.—Bodies belonging to this class possess great chemical analogy, crystallise in the same system with nearly the same forms and angles, exhibit a general agreement in the physical properties of their crystals, and often possess the same specific volume; they are, moreover, under suitable conditions capable of forming mixed and layer-crystals. Such substances are the sulphates of the group $M''SO_4.7H_2O$ (M'' = Fe'', Zn, Mg, Co, Ni) and the alums.

(2) Substances closely related morphotropically.—To this class belong Marignac's double fluorides, and the substances derived from hydrocarbons by substitution; from them we pass on the one hand to isomerides such as the three dinitro-benzenes, which with a minimum difference of chemical constitution possess but little form-analogy, and on the other hand to bodies differing but little in form, but showing less and less chemical analogy, till we reach members of the next class.

(3) Isogonous substances, differing greatly in chemical composition but nearly similar in form.—To this class belong $CaCO_3$ and $NaNO_3$, and the substances described by Hjortdahl above, while all substances crystallising in the cubic system are strictly isogonous (*v.* Sohncke, *Entwickelung einer Theorie der Krystallstruktur*, Leipzig, 1879). A. H.

ISOPRENE *v.* PENTINENES.

ISOPYRINE. An alkaloid obtained by boiling the mashed roots of *Isopyrum thalictroides* with water, filtering, evaporating to a syrup, ppg. with ammonia, and extracting with ether (Hartsen, *C. C.* 1872, 523). White powder with bitter taste, forming an amorphous hydrochloride.

Pseudo-isopyrine. After the roots have been boiled with water they still contain this alkaloid, which may be extracted with alcohol. After removing the alcohol by evaporation ammonia is added to the aqueous residue, and the ensuing pp. treated with ether, whence pseudo-isopyrine separates in needles. It is ppd. from its solution as hydrochloride by adding very dilute HClAq and ammonium chloride (difference from isopyrine).

ISURETIN *v.* FORMAMIDOXIM.

ITABROMOPYROTARTARIC ACID *v.* BROMO-PYROTARTARIC ACID.

ITACHLOROPYROTARTARIC ACID *v.* CHLORO-PYROTARTARIC ACIDS.

ITACONIC ACID $C_5H_6O_4$ *i.e.* $C_3H_4(CO_2H)_2$ or CH_2:C(CO_2H).CH_2CO_2H. (?). Mol. w. 130. [161°]. S.G. 1·6 (Schröder, *B.* 13, 1072). S. 5 at 10°; 8 at 20°. S. (88 p.c. alcohol) 25 at 15° (Baup). R_∞ 44·25 (in a 4·18 p.c. aqueous solution) (Kanonnikoff, *J. pr.* [2] 31, 348). H.C. 476,580 (Louguinine, *C. R.* 106, 1291). *Heat of solution* 5,923 (Gal a. Werner, *Bl.* [2] 47, 160). *Heat of neutralisation* 25,725 (G. a. W.). Shown by Raoult's method to be isomeric and not polymeric with citraconic and mesaconic acids (Paternò, *B.* 21, 2156).

Formation.—1. By the action of heat on citric acid, aconitic acid being first formed (Baup, *A.* 19, 29; Crasso, *A.* 34, 63).—2. By heating itamalic acid $C_5H_8O_5$ (Swarts, *Z.* 1867, 649).—3. By heating citric acid with water at 160° (Markownikoff a. Purgold, *Z.* 1867, 264).—4. By heating aconitic acid with water at 180° (Pebal, *A.* 98, 94).—5. By heating citraconic anhydride with water under pressure (Fittig, *A.* 188, 72).

Preparation.—1. Coarsely-powdered citric acid (125 g.) is distilled from shallow retorts completely filled with it as quickly as the frothing will allow; the oily distillate is separated from the water as completely as possible and left to crystallise (Meilly, *A.* 171, 153; *cf.* Wilm, *A.* 141, 28). A temperature of 160°–175° is favourable to the formation of itaconic acid; at a very high temperature it is mostly converted into citraconic anhydride.—2. Citraconic anhydride (2 vols.) is heated with water (5 vols.) at 150° for 7 hours, and the product poured into flat dishes and left to crystallise (Fittig, *A.* 188, 72).

Properties. — Trimetric octahedra (from water). Strongly acid. Sol. ether. When heated above its melting-point it is resolved into citraconic anhydride and water. Ammonium itaconate gives a brown pp. with $FeCl_3$, soluble in excess of $FeCl_3$, but reppd. on boiling, and redissolved on cooling.

Reactions.—1. Combines with *bromine*, forming ita-di-bromo-pyrotartaric acid (Kekulé, *A. Suppl.* 1, 338; 2, 111; Cahours, *A. Ch.* [3] 67, 129).—2. *Chlorine* forms ita-di-chloro-pyrotartaric acid.—3. Heated with aqueous HBr, HCl, and HI, combination takes place with production of ita-bromo-, ita-chloro-, and ita-iodo-pyrotartaric acids. Excess of HI produces pyrotartaric acid (*Bl.* [2] 4, 374).—4. *Sodium-amalgam* reduces it to pyrotartaric acid (Kekulé).—5. HOCl gives chloro-itamalic acid $C_5H_7ClO_5$.—6. Anhydrous HCy at 145° apparently forms an addition-product, which, when distilled, gives citraconic acid (Barbaglia, *B.* 7, 465).—7. Heated with aqueous K_2SO_3 it forms a gummy salt, possibly sulphopyrotartaric acid $C_5H_8SO_7$ (Wieland, *A.* 157, 34).—8. The *electrolysis* of the potassium salt yields a mixture of gases, apparently containing propylene and acetylene, but not allylene CH_2:C:CH_2 (Béhal, *A. Ch.* [6] 16, 366; *cf.* Aarland, *J. pr.* [2] 6, 256).—9. Cold HNO_3 gives off no CO_2 (Franchimont, *R. T. C.* 3, 422).

Constitution.—The molecular weight is shown by Raoult's method to be the same as that of citraconic and of mesaconic acids. According to Aarland potassium itaconate gives a different allylene on electrolysis from that derived from the potassium salts of citraconic and mesaconic acids; this would lead to the formula CH_2:C(CO_2H).CH_2.CO_2H. Béhal, however, was unable to confirm Aarland's experiments. According to Knops (*A.* 248, 228) the molecular refraction of the itaconic ethers indicates one C:C group. Itaconic acid resembles mesaconic acid, but differs from citraconic acid in requiring heat to enable it to combine with HBr and with bromine. Itaconic acid reacts with aniline, but not with dimethylaniline.

Salts.—KHA″aq: lustrous laminæ; v. sol. water.—×K_2A″: does not crystallise.—(NH_4)HA″: tables. S. 80 at 12°.—(NH_4)HA″aq: needles.—BaH_2A″$_2$aq.—BaA″aq (Petri, *B.* 14, 1634).—CaH_2A″$_2$2aq. S. 7·7 at 12°.—CaA″aq: needles. S. 2·2 at 18°.—SrA″aq.—PbA″aq.—PbA″PbO

(Otto, *A.* 127, 181).—Ag_2A'': almost insol. boiling water.

Methyl ether Me_2A''. (212°). S.G. $\frac{15}{}$ 1·1399 (Anschütz, *B.* 14, 2784); $\frac{18}{4}$ 1·1241 (Knops). R_∞ 60·44. Oil. Polymerises, changing to a solid in which $R_\infty = 57·7$.

Ethyl ether Et_2A''. (229°). S.G. $\frac{15}{}$ 1·051 (Anschütz); $\frac{25}{4}$ 1·0415 (Knops, *A.* 248, 210). $R_\infty = 75·52$. *Polymerised*: $R_\infty = 70·59$. From silver itaconate and EtI (Swarts, *Bull. Acad. royal Belgique* [2] 36, No. 7). Formed also by passing HCl into a solution of itaconic acid in alcohol. Colourless oil. Changes in a few days into a viscid liquid, and ultimately into a brittle, glassy mass, which is completely decomposed on distillation.

Chloride $C_3H_4(COCl)_2$. (87°) at 17 mm. From the anhydride and PCl_5. Colourless pungent liquid. Converted by water into itaconic acid (Petri).

Anhydride $C_3H_4(C_2O_3)$. [68°]. (148°) at 30 mm. Occurs among the products of the distillation of citric acid. Prepared by the action of AcCl on itaconic acid (Anschütz, *B.* 13, 1539) or on silver itaconate suspended in ether (Markownikoff, *B.* 13, 1844). Trimetric prisms; $a:b:c = ·617:1:·455$. Sol. chloroform. Slowly dissolves in water with formation of itaconic acid. When distilled under atmospheric pressure it changes into the isomeric citraconic anhydride.

Amide $C_3H_4(CONH_2)_2$. [192°]. From Me_2A'' and aqueous NH_3 (O. Strecker, *B.* 15, 1639). Small colourless crystals (from water). V. e. sol. hot water, m. sol. alcohol, insol. ether.

Mono-anilide $C_3H_4(CO_2H)(CONHPh)$ or $CO_2H.CH<\begin{matrix}CH_2.NPh\\CH_2.CO\end{matrix}>$ (?). *Itaconanilic acid.* [189°]. Formed by heating itaconic acid (5 g.) with water (50 g.) and aniline (3 g.) to boiling for half an hour, and depositing on cooling as crystals (Michael a. Palmer, *Am.* 9, 200; Gottlieb, *A.* 77, 265). Formed also by allowing a solution of acid aniline itaconate to stand for several days in the cold. Needles (from water). Insol. dilute HClAq, sol. dilute alkalis, and reppd. unchanged by acids.—BaA'_2 (at 170°).—CuA'_2 (at 160°).—AgA'.

Mono-anilide $C_3H_4(CO_2H)(CONHPh)$ (?) [151·5°]. From itaconic anhydride and aniline (Anschütz, *B.* 20, 3215; 21, 958). Not identical with the preceding.

Anilide $C_3H_4(CONHPh)_2$. [185°]. Formed by heating aniline itaconate, or a mixture of itaconic acid, with excess of aniline at 180° (Gottlieb, *A.* 77, 282; O. Strecker, *B.* 15, 1639). Large thin plates; sol. alcohol and ether, sl. sol. water. A mixture of HNO_3 and H_2SO_4 converts it into an amorphous penta-nitro- derivative (Gottlieb, *A.* 85, 40).

Chloro-itaconic acid $C_5H_5ClO_4$. Formed by heating aconic acid $C_5H_4O_4$ with HCl (Swarts, *J.* 1873, 584). Crystalline crusts, sl. sol. cold water. Reconverted by boiling water into aconic acid.

Bromo-itaconic acid $C_5H_5BrO_4$. [164°]. Formed by the dry distillation of ita-di-bromo-pyrotartaric acid $C_5H_6Br_2O_4$ (Swarts, *Bull. Acad. roy. Belgique* [2] 33, No. 1). Also by heating aconic acid with HBr. Its anhydride is similarly formed from ita-di-bromo-pyrotartaric anhydride (Petri). Crystals resembling itaconic acid (from water); v. sl. sol. cold water; resolved by boiling water or by alkaline carbonates into HBr and aconic acid. Reduced by tin or zinc to itaconic acid.

ITAMALIC ACID *v.* Oxy-pyrotartaric acid.

ITAPYRUVIC ACID $C_4H_6O_3$. Obtained, together with water and CO_2, by distilling itatartaric acid at 125°–170° (Wilm, *A.* 141, 37). Viscid mass, v. sol. water and alcohol, volatile with steam.—BaA'_2 aq (at 100°): glassy amorphous mass.—PbA'_2: hygroscopic amorphous mass, sl. sol. water. The silver salt is soluble, but very decomposable.

ITATARTARIC ACID $C_5H_8O_6$. *Di-oxy-pyrotartaric acid.* Formed by gradually adding a solution of HOCl to one of sodium itaconate (2 p.c. solution) at 0° in the dark, and boiling the resulting solution of chloro-oxy-pyrotartaric acid. The acid is ppd. as lead salt, which is subsequently decomposed by H_2S (Wilm, *A.* 141, 28; Morawsky, *J. pr.* [2] 10, 68; 11, 450). Formed also by warming ita-di-bromo-pyrotartaric acid with Ag_2O (Kekulé, *A. Suppl.* 1, 346). Amorphous vitreous deliquescent mass. V. e. sol. water and alcohol; not volatile with steam. Split up by dry distillation into CO_2 and itapyruvic acid. The alkaline salts prevent the ppn. of ferric and cupric salts by alkalis.—$CaA''\frac{1}{2}aq$: crystalline mass, sl. sol. water.—BaA'' (at 100°): amorphous, v. sol. water, and ppd. from aqueous solution by alcohol.—PbA'' aq: monoclinic tablets, v. sl. sol. water.—Ag_2A'': bulky pp., sol. water, but decomposed on boiling its solution.

IVAÏN $C_{24}H_{42}O_3$. Occurs in Iva, the leaves and stem of *Achillea moschata* gathered before flowering (Von Planta, *A.* 155, 150). The volatile oil is first removed by distillation, and the residue is dried and extracted with alcohol, the filtrate is ppd. with lead acetate, freed from lead by H_2S, and evaporated. Dark yellow resinous mass, insol. water, v. sol. alcohol. The alcoholic solution has an extremely bitter taste.

IVY. *Hedera Helix.* When ivy leaves, collected in December, are bruised, exhausted with water, and then treated with alcohol, the alcoholic extract contains a glucoside $C_{32}H_{54}O_{11}$. This may be obtained by evaporating the alcohol, extracting the residue with benzene, and then with acetone, which deposits the glucoside on cooling (Vernet, *C. R.* 92, 360). It forms mammillary groups of silky colourless needles with slightly sweet taste and neutral reaction. It melts at 233°, and at 22° its alcoholic solution has a lævorotatory power of $[\alpha]_D = -47·5°$. It is insol. water, chloroform, and petroleum; sl. sol. acetone, benzene, and ether in the cold, but readily soluble in these liquids when hot. V. sol. boiling alcohol. Sol. cold alkalis. The glucoside has no action on Fehling's solution, but on boiling with dilute H_2SO_4 a sugar is formed which crystallises by slow evaporation of its alcoholic solution in bulky transparent crystals with decided sweet taste, and reduces Fehling's solution, but is not fermented by yeast. The rotatory power of a cold solution of this sugar is $[\alpha]_D = +98·6°$ immediately after its preparation, but some hours afterwards it has been found to fall to $[\alpha]_D = 76·2$. Besides the sugar, there is formed in the hydrolysis of the glucoside a neutral body $C_{26}H_{44}O_6$ [278°–280°], which crys-

tallises in slender prismatic needles, without taste, m. sol. alcohol, insol. alkalis, and dextro-rotatory $[\alpha]_D = 42\cdot6°$.

IXOLITE. A fossil resin found in a bed of bituminous coal at Oberhart. Fluid drops, hardening to a hyacinth-red solid, which forms a yellowish powder. S.G. 1·008. Softens at 76°. Yields pyrocatechin on fusion with potash (Haidinger, *P.* 56, 345; Weidel, *Sitz. W.* [2] 74, 387).

J

JABONINE $C_9H_{14}N_2$ *i.e.* $CH{<}^{CH:CH}_{N-CH}{>}C.CHMe.NMe_2$. *Di-methyl-amido-ethyl-pyridine.* (235°–240°). Formed by distilling pilocarpine or pilocarpidine with baryta (Hardy a. Calmels, *Bl.* [2] 48, 231). The crude product is evaporated several times with HClAq and the base set free with KOH. Colourless oil with fœtid odour. Its hydro-chloride forms confusedly crystalline masses. The double salts $B'HAuCl_4$, $B'AuCl_3$, B'_2PtCl_4, and $B'_2H_2PtCl_6$ are all amorphous.

JABORANDI. The native name for several drugs of a sudorific and salivating character, consisting of the leaves and twigs of various species of *Pilocarpus* and other trees growing in Brazil, Pernambuco, and Paraguay (Holmes, *Ph.* [3] 5, 581, 641; Schelenz, *Ar. Ph.* [3] 7, 414; Baillon, *Ar. Ph.* [3] 7, 327). Jaborandi leaves contain pilocarpine (Byasson, *Ph.* [3] 5, 826; Hardy, *Bl.* [2] 24, 497), which readily changes to jaborine (H. Meyer a. Harnack, *A.* 204, 67). The latter acts like atropine, and is an antidote to pilocarpine. Pilocarpine $C_{11}H_{16}N_2O_2$ gives with MeI a methylo-iodide. Pilocarpidine $C_{10}H_{14}N_2O_2$ is also present in jaborandi (Harnack, *A.* 238, 231). It is crystalline but extremely deliquescent. It is alkaline, and turns yellow in light. V. sol. alcohol, m. sol. water, sl. sol. ether. Its sulphate and hydrochloride are deliquescent; its nitrate forms crystals resembling KNO_3. Its platinum salt $B'_2H_2PtCl_6$ is crystalline. It readily changes when exposed to light into a base jaboridine $C_{10}H_{12}N_2O_3$, which has an amorphous platinum salt. The jaborandine of Chastaing (*C. R.* 94, 968) obtained from pilocarpine and HNO_3 is probably jaboridine (Harnack, *A.* 238, 238). The jaborandine of Parodi (*Revista farmaceutica*, 1875, 3) from *Piper reticulatum* $C_{16}H_{12}N_2O_3$ may be the same.

JABORIC ACID $C_{19}H_{25}N_3O_5$ *i.e.* $C_5H_4N.CMe(OH).CO.O.NMe_3.CMe(C_5H_4N).CO_2H$. Formed, together with NMe_3, jaborine and pilocarpidine, by rapidly heating pilocarpine to 175°, and keeping it at that temperature for half an hour. If the product be extracted with baryta-water and the extract shaken with ether, the ether will contain jaborine, while pilocarpidine and jaboric acid remain in the aqueous solution. In this solution, after removing barium by CO_2, $AgNO_3$ forms a curdy pp. of $C_{19}H_{24}N_3O_5Ag_2NO_3$, whence H_2S removes the silver (Hardy a. Calmels, *C. R.* 102, 1251; *Bl.* [2] 48, 225). Resinous mass, v. sol. water. Not removed from its aqueous solution by ether. With alkalis it forms gummy salts, sol. water and alcohol, and not decomposed by CO_2. Hot conc. KOHAq or boiling HClAq converts it into pilocarpidine and oxy-pyridyl propionic acid $C_5H_4N.CH_2.CH(OH).CO_2H$.

Salts.—AgA': brown powder; ppd. by adding alcohol to a solution of the acid to which a limited quantity of $AgNO_3$ has been added.—$AgA'AgNO_3$: curdy pp.—A'_2PtCl_4: viscous pp.—$A'_4(PtCl_4)_3$: yellow powder.—$A'_2H_2PtCl_6$: sticky pp.—$A'(AuCl_3)_2$.

JABORIDINE $C_{10}H_{12}N_2O_3$. Formed by frequently evaporating pilocarpidine with acid (Harnack, *A.* 238, 234). Syrup; sol. water, m. sol. ether. Acts physiologically like jaborine though weaker. Its hydrochloride is syrupy, and v. sol. water.—$B'_2H_2PtCl_6$ (dried at 100°). [110°–120°]. Amorphous.

JABORINE $C_{22}H_{32}N_4O_4$ *i.e.* $NMe_3{<}^{CMe(C_5H_4N).CO.O}_{O.CO.CMe(C_5H_4N)}{>}NMe_3$ (?). Occurs in jaborandi, and in false jaborandi (the leaves of *Piper reticulatum*). Prepared as described under Jaboric acid. Brittle resin. Insol. water, v. sol. ether, sol. alcohol. Dissolves in a solution of jaboric acid. Dissolves in HClAq, and is reppd. by KOH as a curdy pp. which readily agglomerates under warm water. Boiling conc. KOHAq converts it into pilocarpidine. Boiling HClAq does the same. Poisonous, acting like atropine.

Salts.—The hydrochloride is amorphous, and v. e. sol. water and alcohol.—B'_2PtCl_4: dirty-white gelatinous pp.—$B'PtCl_4$: yellowish-white pp.—$B'H_2PtCl_6$.—$B'(AuCl_3)_2$ (Hardy a. Calmels, *C. R.* 102, 1251).

JALAP. The roots and tubers of certain convolvulaceous plants which yield purgative resins. Officinal jalap consists of the tubers of *Convolvulus Schiedanus*, which contains Convolvulin, a strongly purgative resinous glucoside. Jalap-wood or jalap stalk (Stipites Jalapæ), the root of *C. orizabensis*, contains a different glucoside, Jalapin (Kayser, *A.* 51, 100; *cf.* Mayer, *A.* 95, 161).

JALAPIN $C_{34}H_{56}O_{16}$ or $C_{68}H_{112}O_{32}$. [150°]. Occurs in the root-stalk of *Convolvulus* (or *Ipomœa*) *orizabensis*, and forms the principal portion (soluble in ether) of the jalap resin prepared therefrom (Johnston, *P. T.* 1840, 342; *P. M.* [3] 17, 183; Kayser, *A.* 51, 101; Mayer, *A.* 83, 122; 95, 129; Häule, *Rep.* 48, 365; Planche, *J. Ph.* 13, 165; 24, 169; Weppen, *N. Br. Arch.* 87, 153; Chevallier, *J. Ph.* 9, 306). Occurs also in the resin in scammony root from *Convolvulus Scammonia* (Johnston, *P. T.* 1840, 340; Keller, *A.* 104, 63; 109, 209; Spirgatis, *A.* 116, 289; Planche, *J. Ph.* 13, 165; 18, 183; Marquart, *N. Br. Arch.* 7, 248; 10, 139).

Preparation.—1. Jalap resin is dissolved in a large quantity of alcohol, water is added until the liquid becomes slightly turbid, and the whole boiled with animal charcoal, filtered, ppd. by lead acetate and a little ammonia, filtered, freed

from lead by H_2S, the alcohol distilled off, and the residue kneaded in boiling water, and the jalapin finally extracted with ether (Mayer).—2. Finely-powdered jalap resin is mixed with sand and extracted with ether, which deposits the jalapin on evaporation (Stevenson, *Ph.* [3] 10, 644).

Properties. — Colourless amorphous resin. Softens at 123°, and melts at 150°. Tasteless. V. sl. sol. water; v. e. sol. alcohol, ether, and chloroform; sol. benzene, oil of turpentine, petroleum, and HOAc. Conc. H_2SO_4 dissolves it slowly in the cold, acquiring in a few minutes a maroon colour, but finally becoming black. With K_2CrO_4, $KMnO_4$, $KClO_3$, or KNO_3 there is a brown colour and a smell of rancid butter; while MnO_2 gives a dark-green colour (Stevenson).

Reactions.—1. Boiling dilute HCl splits it up into sugar and jalapinol.—2. Boiling aqueous alkalis convert it into jalapic acid.—3. *Nitric acid* forms ipomic and oxalic acids.

Jalapic acid $C_{34}H_{60}O_{18}$ or $C_{68}H_{118}O_{35}$. [120°]. Formed by dissolving jalapin in aqueous alkalis (W. Mayer, *A.* 92, 125; 95, 129; Spirgatis, *A.* 116, 289). Prepared by boiling jalapin w th baryta-water until the solution is no longer ppd. by acids; the baryta is then removed by H_2SO_4, the excess of sulphate by lead hydrate, and the excess of lead by H_2S. Jalapic acid is then deposited on evaporating. Translucent, amorphous, yellowish, brittle mass. Softens below 100°, and melts about 120°. Has no smell, but an irritating taste and strong acid reaction. V. e. sol. water, v. sol. alcohol, m. sol. ether. In neutral solutions it is ppd. by lead subacetate, but not by any other metallic salt.

Reactions.—1. Fuming HCl splits it up into jalapinol and glucose. According to Spirgatis the products of hydrolysis of jalapic acid (and jalapin) derived from scammony are jalapinolic acid and glucose.—2. Boiling dilute HCl forms (α)-jalapic acid, so-called (Mayer).—3. HNO_3 gives ipomic, oxalic, and isobutyric acids.—4. $KMnO_4$ gives isobutyric, oxyisobutyric, and oxalic acids (Poleck a. Samelson, *C.C.* 1884, 813).

Salts. — Jalapic acid displaces CO_2 from aqueous Na_2CO_3.—$Ba(C_{34}H_{59}O_{18})_2$: obtained on evaporating a solution of jalapic acid mixed with a slight excess of baryta-water after removing excess of baryta by CO_2. Amorphous. — $Ba_3(C_{34}H_{57}O_{18})_2$: obtained by using baryta (2 pts.), water (4 pts.), and jalapic acid, passing CO_2 through the boiling solution, filtering and evaporating. Amorphous mass [100°].

(α) - Jalapic acid, so-called. $C_{28}H_{50}O_{13}$. Formed, in small quantity, in the hydrolysis of jalapic acid by HClAq or dilute H_2SO_4 (Mayer). On cooling it separates with the jalapinol as a soft brown amorphous mass, which is then boiled with baryta-water, and the resulting solution deposits barium jalapinolate on cooling. When the mother-liquor is concentrated silky needles of the Ba salt of '(α)-jalapic' acid are obtained. The salt is decomposed by acetic acid. White flexible needles, melting below water at 80°. Feebly acid in reaction. Sl. sol. cold, m. sol. hot, water; v. e. sol. alcohol and ether. Boiling dilute acids split it up into jalapinol and glucose. HNO_3 gives ipomic acid and oxalic acid. Potash-fusion forms jalapinolic acid and oxalic acid.—$Ba(C_{28}H_{49}O_{13})_2$: White needles; sol. water and alcohol.

JALAPINOL $C_{32}H_{62}O_7$. [62°]. Formed, together with sugar, by the hydrolysis of jalapin and of jalapic acid (W. Mayer, *A.* 95, 145). $C_{68}H_{112}O_{32} + 11H_2O = C_{32}H_{62}O_7 + 6C_6H_{12}O_6$. Prepared by allowing a solution of jalapic acid (2 vols.) mixed with fuming HClAq (1 vol.) to stand for a few days, washing the crystalline product with water, and recrystallising from alcohol, with use of animal charcoal, whence it separates in cauliflower-like groups of crystals. Insol. cold, v. sl. sol. boiling water, v. sol. alcohol and ether. Aqueous alkalis convert it into jalapinolic acid. $KMnO_4$ forms isobutyric acid and (by further oxidation) oxyisobutyric acid (Poleck a. Samelson, *J.* 1884, 1447).

JALAPINOLIC ACID $C_{16}H_{30}O_3$. [64°]. Formed by treating jalapinol with aqueous KOH, ammonia, or baryta. Formed also by fusing jalapin or jalapic acid with KOH (Mayer, *A.* 95, 145; Spirgatis, *A.* 116, 306). According to Spirgatis it is also produced, together with sugar, by the action of mineral acids on jalapin and jalapic acid derived from scammony. Poleck and Samelson (*J.* 1884, 1447) by the action of alcoholic potash on jalapinol obtained, together with isobutyl alcohol, a jalapinolic acid $C_{16}H_{30}O_4$. White tufts of minute thin four-sided prisms. Insol. water, v. sol. alcohol and ether. Lighter than water. Has an acid reaction. Nitric acid oxidises it to ipomic acid and oxalic acid.

Salts.—$(NH_4)HA'_2$: cauliflower heads of minute needles.—NaA' (dried at 100°): slender needles.—BaA'_2 (dried at 120°): minute thin white needles; nearly insol. cold, sl. sol. boiling, water; m. sol. boiling alcohol.—CuA'_2 (dried at 100°): greenish-blue pp. formed on mixing hot aqueous solutions of sodium jalapinolate and $CuSO_4$ (Spirgatis).—$Cu_3A'_2(OH)_2$ (dried at 100°). Ppd. by adding aqueous cupric acetate to a slightly alkaline solution of ammonium jalapinolate. Amorphous dark-bluish-green mass.—PbA'_2. Ppd. by adding lead acetate to an alcoholic solution of jalapinolic acid mixed with a little ammonia. White amorphous mass.—AgA'. From aqueous $AgNO_3$ and alcoholic ammonium jalapinolate. Flocculi.

Ethyl ether EtA'. [32·5°]. From the acid (or from scammony) by saturation of the alcoholic solution with HCl, and ppg. with water. Flat tables.

JAMBOSIN $C_{10}H_{15}NO_3$. [77°]. Occurs in the bark of jambosa root (the root of *Myrtus jambosa*?), from which it may be extracted with ether (Gerrard, *Ph.* [3] 14, 717). White tasteless crystals, sol. cold ether, alcohol, chloroform, and hot petroleum ether. Insol. cold, sol. boiling, water. Conc. H_2SO_4 gives a bright-green colour changing to reddish-brown. Is not a glucoside. Does not form salts with bases. Has no medicinal properties.

JAPACONINE *v.* ACONITE ALKALOIDS.

JAPACONITINE *v.* ACONITE ALKALOIDS.

JAVANINE *v.* CINCHONA BASES.

JECORIN $C_{105}H_{185}N_5SP_3Na_4O_{46}$ (?). A substance obtained from liver (Drechsel, *J. pr.* [2] 33, 425). Occurs also in ox spleen, human brain, and horse's muscle (Baldi, *Ar. Physiol.* 1887, *Suppl.* 100). Amorphous substance. Hygroscopic, insoluble in dry ether, soluble in wet ether, v. sl.

sol. alcohol. Swells up in water forming a sticky mass, which separates into a clear solution and a pp. The latter dissolves in much water. Not ppd. by boiling; ppd. by NaCl. Prevents ppn. of cupric salts by NaOH, forming a blue solution, and on boiling a pp. of Cu_2O. Boiling HCl decomposes it, forming amongst other products stearic acid.

JERVIC ACID. An acid occurring in white hellebore root (*Veratrum album*) (Weppen, *Ar. Ph.* [3] 2, 101, 193), found by E. Schmidt (*Ar. Ph.* [3] 24, 513) to be identical with chelidonic acid.

JERVINE $C_{26}H_{37}NO_3$ (Wright a. Luff); $C_{27}H_{47}N_2O_8$ (Tobien) or $C_{30}H_{46}N_2O_3$ (Will). [237°] (W. a. L.). An alkaloid occurring in the rhizomes of *Veratrum album* (Weppen, *Ar. Ph.* [3] 2, 101, 193; Simon, *P.* 41, 569; Mitchell, *Ph.* [3] 4, 796; Bullock, *Ph.* [3] 6, 1009; Wright a. Luff, *C. J.* 35, 407), and of *V. lobelianum* (Tobien, *Ph.* [3] 8, 808) and *V. viride* (Bullock, *Ph.* [3] 10, 186).

Preparation.– The extract obtained with alcohol containing tartaric acid is used several times to macerate fresh portions of the root, freed from alcohol by distillation, mixed with water, fractionally ppd. by NaOH and taken up by ether. The base first ppd. is pseudojervine, and is the least soluble in ether. Other fractions contain jervine, rubijervine, and veratralbine (Wright a. Luff).

Properties.—Loosely coherent crystals (containing $1\frac{1}{2}$aq or 2aq) (from alcohol). Almost insol. water, sol. alcohol, v. sl. sol. ether (when pure), insol. ligroïn. Conc. H_2SO_4 forms a yellow solution changing through brown to greenish-brown. Boiling alcoholic KOH has no action.

Salts.—The hydrochloride is crystalline, sl. sol. water, v. sl. sol. HClAq (Will, *A.* 35, 116). According to Tobien it gives a rose colour when warmed with nitric acid. The nitrate and sulphate are sl. sol. water.—$B'H_2PtCl_6$ (Will). —$B'HAuCl_4$.—The acetate is sol. water.

Rubijervine $C_{26}H_{43}NO_2$. [236° cor.]. Anhydrous crystals (from alcohol). Dissolves in conc. H_2SO_4, forming a yellow solution changing to brownish-red. The sulphate is crystalline, v. sol. cold dilute H_2SO_4, sl. sol. cold water. The hydrochloride is crystalline and v. sol. water. —$B'HAuCl_4$.

Pseudojervine $C_{29}H_{43}NO_7$. [209°]. Crystals. V. sl. sol. ether. Reacts with conc. H_2SO_4 in the same way as jervine. Not affected by boiling alcoholic KOH.—B'HCl 2aq: crystalline, v. sl. sol. hot water, m. sol. dilute HClAq.—The sulphate is sl. sol. cold, v. sol. hot, water.—$B'HAuCl_4$.

Veratralbine $C_{28}H_{43}NO_5$. Amorphous resinous base. Conc. H_2SO_4 forms a yellow solution turning crimson and exhibiting green fluorescence. Alcoholic potash does not saponify it. Its salts are amorphous.

JUGLONE $C_{10}H_6O_3$ *i.e.*

$$\begin{array}{l} HC{:}C(OH).C.CO{:}CH \\ \quad | \qquad\qquad\quad \| \qquad\quad | \\ HC{:}CH — C.CO{:}CH \end{array}.$$

Oxy-(α)-naphthoquinone. Nucin. Regianin. [154°]. Formed by the oxidation of (α)-hydrojuglone which occurs in the green shell of the walnut (Vogel a. Reischauer, *C. C.* 1858, 543; *B.* 10, 1544; Phipson, *C. R.* 69, 1372; *C. N.* 52, 39; Mylius, *B.* 17, 2411). Formed also by allowing (1,4')-di-oxy-naphthalene to stand for 24 hours mixed with $K_2Cr_2O_7$ and dilute H_2SO_4 (Bernthsen a. Semper, *B.* 20, 934).

Preparation.—Dry ripe walnut shells are repeatedly extracted with cold ether. The ethereal solution is shaken with a dilute solution of CrO_3 (10 pts. $K_2Cr_2O_7$ + 13 pts. H_2SO_4 in 500 pts. of water). The ether is distilled off, and the residue, after removing tarry impurities by boiling with a little ether, is crystallised from a mixture of chloroform and ligroïn. The yield is 150 grms. from 100 kilos (Bernthsen a. Semper, *B.* 18, 204).

Properties.—Thin glistening red prisms or needles. Sublimable in small quantities. Somewhat volatile with steam. Easily soluble in chloroform and acetic acid, sparingly in ether, ligroïn, and cold alcohol, almost insol. water. It stains the skin brown. Dissolves in dilute NaOH with a fugitive purple colour, in H_2SO_4 with a blood-red colour. It is decomposed by hot water or hot acids. By boiling with HNO_3 it is oxidised to a di-nitro-oxy-phthalic acid. On heating with water or HCl it decomposes into insoluble amorphous bodies. Its alkaline solution is oxidised by the air to oxy-juglone $C_{10}H_6O_4$. With aqueous dimethylamine it gives dimethyl-amidojuglone $C_{10}H_5O_3(NMe_2)$, and with alcoholic aniline it gives phenyl-amido-juglone $C_{10}H_5O_3(NHPh)$. On fusion with KOH it yields *m*-oxy-benzoic acid (Mylius, *B.* 18, 463). Finely powdered juglone gradually added to an alkaline solution of hydrogen peroxide is oxidised to *c*-oxy-phthalic acid (B. a. S.). Juglone and its oxim do not dye materials mordanted with metallic oxides (Kostanecki, *B.* 22, 1347). Juglone yields naphthalene when distilled with zinc-dust. Reducing agents yield (α)-hydrojuglone.

Salt.—$(C_{10}H_5O_3)_2Cu$: nearly insoluble microscopic violet prisms.

Acetyl derivative $C_{10}H_5O_2(OAc)$: [155°]; flat yellow tables or thin prisms; sublimes in long thin plates; volatile with steam; sparingly soluble in water and cold alcohol, easily in hot alcohol, ether, benzene, chloroform, and CS_2; yields an intense green colouration with alcoholic KOH.

Mono-oxim $C_{10}H_5(OH)\left\{\begin{array}{l}O\\NOH\end{array}\right.$. [187°]. Glistening red needles or thin prisms; easily soluble in alcohol and acetic acid, very slightly in water; dissolves with a blood-red colour in H_2SO_4 and in dilute NaOH (Bernthsen a. Semper, *B.* 18, 203).

Di-oxim $C_{10}H_5(OH)(NOH)_2$. From juglone (1 mol.) and hydroxylamine hydrochloride (2 mols.) at 140° (Bernthsen a. Semper, *B.* 19, 168). Brownish-yellow needles (from HOAc). Puffs off at 225°. Sl. sol. alcohol and acetic acid. Alkalis dissolve it, forming an orange solution.

Phenyl-amido-juglone $C_{10}H_5O_3(NHPh)$. [230°]. Formed by heating an alcoholic solution of juglone and aniline (Mylius, *B.* 18, 472). Red tables. Sublimable. V. sl. sol. alcohol. Dissolves in alkalis with a purple-red colour.

Di-methyl-amido-juglone $C_{10}H_5O_3(NMe_2)$. [150°]. Formed by dissolving juglone in dimethylamine solution (Mylius, *B.* 18, 464). Brownish-violet tables. Soluble in benzene, chloroform, and CS_2, sparingly in alcohol, ether, and acetic acid, insoluble in water. By $SnCl_2$ it

is reduced to dimethylamido-hydrojuglone. On heating with strong HCl it splits off dimethylamine, giving oxy-juglone.

Oxyjuglone $C_{10}H_6O_4$ *i.e.*

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CH:C(OH).C.CO:C(OH)
|          ||      |
CH:CH  —   C.CO:CH
```

Di-oxy-naphthoquinone. [c. 220°]. Formed by heating di-methyl-amido-juglone with HCl. Formed also by oxidation of an alkaline solution of juglone by exposure to the air. Prepared by oxidation of juglone with an alkaline solution of potassium ferricyanide; yield 50 p.c. of theory (Mylius, *B.* 18, 466). Small yellow trimetric tables. Sparingly soluble in alcohol, ether, benzene, and CS_2.

Salts.—$A''Na_2$: easily soluble red needles.—$A''K_2$: sparingly soluble red needles.—$A''Ag_2$.—$A''Cu$: amorphous red pp.

Benzoyl derivative $C_{10}H_4O_2(OBz)_2$: [170°]; small yellowish-white crystals; easily soluble in benzene, sparingly in alcohol and acetic acid, insoluble in water.

JUGLOXIM *v.* *Oxim* of JUGLONE.

JUGLONIC ACID *v.* DI-NITRO-OXY-PHTHALIC ACID.

JUNIPER OIL. The berries of the juniper, which are used for flavouring gin, yield on distillation an essential oil $C_{10}H_{16}$ (155°–163°). S.G. $\frac{25}{}$ ·839 (Blanchet, *A.* 7, 165; Soubeiran a. Capitaine, *A.* 34, 325). The oil is lævorotatory; it gives no solid bromide, but after heating the oil to 260° it is partly changed to a product boiling about 180°, and this gives cinenetetrabromide. According to Wallach (*A.* 227, 288) it contains pinene (*v.* TERPENES). The product of distillation of the wood of the juniper contains a sesquiterpene $C_{15}H_{24}$, which forms a hydrochloride $C_{15}H_{24}H_2Cl_2$ melting at 118° (Wallach, *A.* 238, 82).

JUTE *v.* CELLULOSE.

K

KACOTHELINE $C_{21}H_{22}O_9N_4$ (not $C_{20}H_{22}O_9N_4$) *i.e.* $C_{21}H_{22}(NO_2)_2O_5N_2$. Prepared by dissolving brucine in an excess of cold nitric acid (1, 2 S.G.) and warming to 50°–60° till the solution has become yellowish-red; the kacotheline separates out in small crystals (*cf.* vol. i. p. 654). On oxidation with CrO_3 and H_2SO_4 it yields the same product $C_{16}H_{18}N_2O_4$ as brucine. By treatment of kacotheline, suspended in boiling HCl, with bromine-water it is converted into an acid $C_{19}H_{24}N_2O_7$. This acid by further oxidation with CrO_3 and H_2SO_4 yields the above oxidation-product $C_{16}H_{18}N_2O_4$. On reduction with tin and HCl it yields a base $C_{21}H_{23}(NH_2)N_2O_5$ (Hanssen, *B.* 20, 452).

Base $C_{21}H_{25}N_3O_5$ *i.e.* $C_{21}H_{23}(NH_2)N_2O_5$. [232°]. Formed by reduction of *kacotheline* with tin and HCl. Needles. Atmospheric oxidation or Fe_2Cl_6 produces a blue-black colouration. Insoluble in water and alcohol, dissolves in aqueous NaOH with a reddish-yellow colour. Its methylo-iodide forms glistening plates easily soluble in water.—$B''H_2Cl_2$: large glistening crystals (Hanssen, *B.* 20, 453).

KAIRINE *v.* (*B.* 4)-OXY-(*Py.* 4)-METHYL-QUINOLINE TETRA-HYDRIDE.

Kairine A *v.* (*B.* 4)-OXY-(*Py.* 4)-ETHYL-QUINOLINE TETRA-HYDRIDE.

KAIROCOLL $C_{11}H_{13}NO_2$ *i.e.*

```
            CH2.CH2
C6H3(OH)<      |
            N — CH2.
            |
            CH2.CO2H
```

[66°]. Long fine needles. Sol. alcohol and ether, sl. sol. water. Prepared by heating (*B.* 4)-oxy-quinoline tetra-hydride with chloro-acetic acid (O. Fischer, *B.* 16, 718).

KAIROLINE is described as METHYL-QUINOLINE TETRA-HYDRIDE.

Amido-kairoline *v.* AMIDO-(*Py.* 4)-METHYL-QUINOLINE TETRAHYDRIDE.

Nitro-kairoline *v.* NITRO-(*Py.* 4)-METHYL-QUINOLINE TETRA-HYDRIDE.

KAIROLINE-*m*-CARBOXYLIC ACID *v.* (*Py.* 4)-METHYL-QUINOLINE TETRA-HYDRIDE-(*B.* 3)-CARBOXYLIC ACID.

KAKOSTRYCHNINE *v.* CACOSTRYCHNINE.

KAMALA. A yellow dye, used in India, contained in the seed capsules of *Mallotus philippensis*, and occurring in commerce as a yellowish-brown powder composed of minute resinous globules. It contains MALLOTOXIN (*q.v.*) (A. G. a. W. H. Perkin, jun., *B.* 19, 3109).

KAORI GUM. The product of a coniferous tree (*Dammara australis*) growing in New Zealand. When distilled with steam it yields a terpene $C_{10}H_{16}$, (157°–158°), S.G. $\frac{18}{}$ ·863 (Rennie, *C. J.* 39, 240; *cf.* Thomson, *A. Ch.* [3] 9, 499; Muir, *C. J.* 27, 733). It is feebly lævorotatory, and yields a small quantity of cymene when treated with PCl_5.

KAWAIN. A crystalline resin, occurring along with METHYSTICIN (*q.v.*) in Kawa-kawa, the root of *Macropiper methysticum* (Gobley, *J. Ph.* [3] 37, 19; O'Rorke, *C. R.* 50, 598; Cuzent, *C. R.* 50, 436; 52, 206; Nölting a. Kopp, *Monit. Scient.* [3] 4, 9, 20). It is not a glucoside. On oxidation it yields benzoic acid.

KELLIN. A glucoside in *Ammi Visnaga* (Mustapha, *C. R.* 89, 442). Small silky needles, v. sl. sol. cold water, sol. alcohol, v. sol. ether. Has a bitter taste. Gives a white pp. with Nessler's reagent. Emetic and narcotic.

KEPHIR *v.* MILK.

KERATIN *v.* PROTEÏDS, *Appendix C.*

KETATES (*ethers of ketones*). Bodies constructed on the type $\begin{matrix}X\\Y\end{matrix}\!\!>C<\!\!\begin{matrix}O.R'\\O.R''\end{matrix}$ (Morley a. Green, *B.* 17, 3015). Bodies of the form $\begin{matrix}X\\Y\end{matrix}\!\!>C<\!\!\begin{matrix}SR'\\SR''\end{matrix}$ or $\begin{matrix}X\\Y\end{matrix}\!\!>C<\!\!\begin{matrix}OR'\\SR''\end{matrix}$ may be called thioketates.

KETINE. A name given by V. Meyer and Treadwell (*B.* 14, 1150; 15, 1059, 1055) to the product of the reduction of nitroso-acetone with tin and HCl. Its di-carboxylic ether is formed

in like manner by reducing nitroso-aceto-acetic ether. Ketine $C_6H_8O_2$ appears to be di-methyl-

$$\text{pyrazine}\ \begin{matrix}\text{CH. N.CMe}\\ \Vert\qquad\ \ \vert\ \Vert\\ \text{CMe.N.CH}\end{matrix}\ \text{or}\ \begin{matrix}\text{CH .N:CMe}\\ \Vert\qquad\quad \vert\\ \text{CMe.N:CH}\end{matrix}\text{, and will be}$$

described as such (*cf.* Oeconomides, *B.* 19, 2524; Japp, *C. J.* 51, 98). Meyer (*B.* 21, 19) proposes to use the name aldine instead of pyrazine

$$\text{for the group}\ \begin{matrix}\text{CH.N.CH}\\ \Vert\qquad \vert\ \Vert\\ \text{CH.N.CH}\end{matrix}\ \text{or}\ \begin{matrix}\text{CH:N.CH}\\ \vert\qquad\ \ \Vert\\ \text{CH:N.CH}\end{matrix}\text{. Other}$$

alkyl-pyrazines are formed in like manner by the reduction of the nitroso- derivatives $HO.N:CH.CO.C_nH_{2n+1}$, of ketones of the form $CH_3.CO.C_nH_{2n+1}$. As ketine di-carboxylic acid does not form an anhydride it has probably the

$$\text{formula}\ \begin{matrix}\text{CO}_2\text{H.C — N:CMe}\\ \Vert\qquad \vert\\ \text{CMeN:C.CO}_2\text{H}\end{matrix}\ \text{rather than}$$

$$\begin{matrix}\text{CMe.N:C.CO}_2\text{H}\\ \Vert\qquad \vert\\ \text{CMe.N:C.CO}_2\text{H}\end{matrix}\text{, whence the symmetrical formula}$$

for ketine given above (Oeconomides).

KETIPIC ACID. A name given to DI-METHYL-DIKETONE DI-CARBOXYLIC ACID, as it might perhaps be called di-keto-adipic acid.

KETO-. This prefix is employed by some chemists to denote the displacement of H_2 in the group $C.CH_2.C$ by O. Thus quinone might be called di-keto-benzene, while aceto-acetic acid would be β-keto-butyric acid. The prefix 'keto-' does not indicate the introduction of a new organic group, whereas the corresponding prefix 'aldehydo-' indicates the introduction of the group CHO, and 'carboxy-' is used to denote the introduction of CO_2H. In order to avoid the confusion likely to arise from this circumstance the term 'keto-' is avoided in the headings of articles in this Dictionary: substances which might have such names given them are described as ketones, quinones, or oxy-compounds. The prefix KETO- has also been used as indicating substitution of hydrogen by the ketonic group $CO.CH_3$, thus Erdmann (*B.* 21, 635) terms $CH_3.CO.C_{10}H_6.OH$ *keto-naphthol*. In keto- compounds the group CO.CH may often be regarded with equal propriety as C(OH):C, and such compounds are named in accordance with the latter formula. Thus phloroglucin may be described as tri-keto-benzene hexahydride or as tri-oxy-benzene.

DI-KETO- HEPTANE *v.* METHYL BUTYL DI-KETONE.

DI-KETO-HEXANE *v.* METHYL PROPYL DI-KETONE.

α-β-**DIKETO-HEXYLENE** *v.* METHYL-ALLYL-DIKETONE.

KETO-HEXA-HYDRO-BENZOIC ACID CY-ANHYDRIN *v. Nitrile* of OXY-ISOPHTHALIC ACID HEXAHYDRIDE.

DI-KETO-HYDRINDENE *v.* INDONAPHTHO-QUINONE.

DI-KETO-INDONAPHTHENE *v.* INDONAPHTHOQUINONE.

KETO-LACTONIC ACID $C_8H_{10}O_4$. [181°]. When α-acetyl-β-ethyl-succinic ether is heated it partly breaks up into alcohol and ethyl keto-lactonate, which, on saponification, gives potassic ketolactonate (S. Young, *C. J.* 43, 175; *A.* 216, 45). It is also formed, together with $CO_2H.CHEt.CH_2Ac$, by boiling the ether ($CO_2Et.CHEt.CHAc.CO_2Et$) with dilute HCl, and may be extracted from the product by ether. The free acid crystallises from water, and is sl. sol. cold water, m. sol. hot water.

Salts.—$BaA'_2 2H_2O$.—AgA'.

Reaction.—1. Heated with *baryta* the following reaction occurs: $2C_8H_{10}O_4 + 3BaO + H_2O = 2BaCO_3 + Ba(C_7H_{11}O_3)_2$. The new acid, $C_7H_{12}O_3$, appears to be liquid; it forms a very soluble and unstable silver salt.—2. Cold *baryta* produces an unstable dibasic acid, $C_8H_{12}O_5$, by assimilation of H_2O.

Constitution.—Ketolactonic ether is formed from $CO_2Et.CHAc.CHEt.CO_2Et$ by splitting off HOEt. Inasmuch as $CO_2Et.CMeAc.CHEt.CO_2Et$ does not form in the same way the ether of a crystalline acid it is probable that the H which is here displaced by methyl goes to form alcohol in the formation of the ketolactonic ether. And since ketolactonic ether appears to be a lactone it should be

$$\begin{matrix}\text{CO}_2\text{Et.C.CHEt.CO};\\ \Vert\qquad\qquad \vert\\ \text{CH}_3\text{.C.O ——}\end{matrix}$$

$$\text{the acid being}\quad \begin{matrix}\text{CO}_2\text{H.C.CHEt.CO}\\ \Vert\qquad\qquad \vert\\ \text{CH}_3\text{.C.O ——}\end{matrix}$$

KETOLE Another name for INDOLE (Jackson, *B.* 14, 879).

KETONES. The ketones, in their simplest form, contain a carbonyl group CO attached to two monad hydrocarbon radicles. If the two radicles are identical, as in acetone (dimethyl-ketone) $CH_3.CO.CH_3$, the compound is a *simple* ketone; if different, as in methyl-ethyl-ketone $CH_3.CO.CH_2.CH_3$, it is a *mixed* ketone.

Just as the fatty acids of the series $C_nH_{2n}O_2$ may be derived from the hypothetical carbonic acid $CO(OH)_2$ by replacing one hydroxyl group by a monad hydrocarbon radicle, so the ketones may in turn be derived from the fatty acids by replacing the remaining hydroxyl group by a second radicle:

HO.CO.OH	$CH_3.CO.OH$	$CH_3.CO.CH_3$
Carbonic acid	Acetic acid	Acetone.

There is therefore a simple ketone derivable from each fatty acid by the introduction of a hydrocarbon radicle, identical with that which is attached to the carboxyl group of the acid, in place of its hydroxyl group.

If one of the radicles in a ketone is hydrogen the resulting compound is an aldehyde:

$CH_3.CO.H$	$CH_3CO.CH_3$
Aldehyde	Acetone

and owing to this similarity in constitution, the aldehydes and ketones have many reactions in common. In the case of formic acid the radicle attached to carboxyl is hydrogen, and the ketone therefore coincides with the aldehyde:

H.CO.OH	H.CO.H
Formic acid	Formaldehyde.

From this point of view the ketones may be regarded as homologues of formaldehyde.

Compounds containing two carbonyl groups are termed *diketones*; those containing three, *triketones*.

Fatty ketones.

Formation.—1. By the destructive distilla-

tion of the calcium salts, or, better still, of the barium salts, of acids of the series $C_nH_{2n}O_2$:

$$(CH_3.CO.O)_2Ca = CH_3.CO.CH_3 + CaCO_3.$$

If a mixture of the salts of two acids is employed, a mixed ketone, containing the hydrocarbon radicles of both acids, is formed:

$$(CH_3.CO.O)_2Ca + (C_4H_9.CO.O)_2Ca = 2CH_3.CO.C_4H_9 + 2CaCO_3$$

(Williamson, *C. J.* 1852, 238).

If one of the salts is a formate, an aldehyde is formed, a hydrogen atom from the formate attaching itself to the carbonyl-group:

$$(CH_3.CO.O)_2Ca + (H.CO.O)_2Ca = 2CH_3.CO.H + 2CaCO_3$$

(Piria, *Cimento*, 3, 126; *A.* 100, 104; Limpricht, *A.* 97, 368).

In the preparation of ketones by the destructive distillation of salts it is advantageous, if the molecular weight of the ketone is high, to conduct the distillation under reduced pressure (Krafft, *B.* 15, 1693).

2. By the destructive distillation of the calcium compounds of primary alcohols (Destrem, *A. Ch.* [5] 27, 7). In this reaction the alcoholates are converted, with evolution of olefins and hydrogen, into salts of fatty acids:

$$(C_2H_5O)_2Ca = 2C_2H_4 + CaO + H_2O;$$

$$(C_2H_5O)_2Ca + 2H_2O = (C_2H_3O_2)_2Ca + 4H_2;$$

and the calcium acetate is then decomposed by the heat, yielding acetone. A portion of the acetate, however, reacts with the calcium oxide, evolving methane.

3. By heating a mixture of the sodium compound of an alcohol and the sodium salt of a fatty acid in a current of carbon monoxide, mixtures of higher ketones are formed, along with sodium salts of higher organic acids (Geuther, *A.* 202, 288). The constitution of these ketones is not known with certainty, and the process in which they are formed is not understood.

4. By the action of acyl chlorides on zinc-alkyls (Freund, *A.* 118, 1; *cf.* Pawlow, *A.* 188, 101). The acyl chloride is added to the zinc-alkyl, at first gradually, afterwards more rapidly, cooling with ice during the operation. The mixture is then decomposed with excess of water:

$$CH_3.COCl + Zn(C_2H_5)_2 = CH_3.CCl(OZnC_2H_5).C_2H_5;$$

$$2CH_3.CCl(OZnC_2H_5).C_2H_5 + 2H_2O = 2CH_3.CO.C_2H_5 + 2C_2H_6 + ZnCl_2 + Zn(OH)_2.$$

If the mixture is allowed to stand too long before adding water, the additive compound formed in the first stage of the process reacts with a second mol. of alkyl chloride, exchanging its halogen for alkyl and generating a compound which, on treatment with water, yields a tertiary alcohol.

5. By the oxidation of secondary alcohols:

$$CH_3.CH(OH).CH_3 + O = CH_3.CO.CH_3 + H_2O.$$

6. By the oxidation of secondary acids of the lactic series with potassium bichromate and dilute sulphuric acid. Thus hydroxy-isobutyric acid yields acetone:

$$(CH_3)_2C(OH).CO_2H + O = (CH_3)_2CO + CO_2 + H_2O.$$

7. Certain ketonic acids part with carbon dioxide, forming ketones. This decomposition takes place very readily in the case of the β-ketonic acids. Thus when ethylic acetoacetate is warmed with a caustic alkali it is hydrolysed, and the liberated acid splits off carbon dioxide, thus:

$$CH_3.CO.CH_2.CO_2H = CH_3.CO.CH_3 + CO_2.$$

8. Alcohols containing a hydroxyl-group attached to a doubly-linked carbon-atom do not appear to be capable of existing in the free state, and change, at the moment of their formation, into either aldehydes or ketones, the former transformation occurring when the hydroxyl group is situated at the end of, the latter when it is within, the chain:

$$CH_2{:}CH(OH) = CH_3.CHO$$

$$CH_2{:}C(OH).CH_3 = CH_3.CO.CH_3$$

(Erlenmeyer, *B.* 13, 309; 14, 320).

9. When secondary or secondary-tertiary glycols are treated with dehydrating agents, such as phosphorus pentoxide or zinc chloride, they part with water, forming ketones. Probably an unsaturated alcohol is first produced, and this changes, at the moment of its formation, into a ketone (*v.* preceding paragraph):

$$CH_3.CH(OH).CH(OH).CH_3 - H_2O = CH_3.CH{:}C(OH).CH_3 = CH_3.CH_2.CO.CH_3.$$

Primary glycols, when thus treated, yield aldehydes. Tertiary glycols (pinacones) are dehydrated even by boiling with dilute sulphuric acid, forming ketones, the reaction being accompanied in this case by the migration of an alkyl group:

$$\underset{\text{Pinacone}}{(CH_3)_2C(OH).C(OH)(CH_3)_2} - H_2O = \underset{\text{Pinacolin}}{(CH_3)_3C.CO.CH_3}.$$

10. When the homologues of acetylene are passed into a solution of mercuric chloride heated to 90°-95° they take up the elements of water, yielding ketones (Kutscherow, *B.* 17, 13):

$$CH_3.C{:}CH_3 + H_2O = CH_3.CO.CH_3.$$

Acetylene itself yields aldehyde.

11. Ketones, especially acetone, are formed in the destructive distillation of wood, sugar, citric acid, and various other organic compounds.

Properties and Reactions.—The lower members of the ketone series are liquids, with a peculiar ethereal odour, boiling without decomposition. The higher homologues, beginning with $C_{13}H_{26}O$, are crystalline solids.

The ketones are isomeric with the aldehydes containing the same number of atoms of carbon. They closely resemble the aldehydes in many of their reactions, but are distinguished from them by not reducing ammoniacal silver solutions. Like the aldehydes, many of the ketones combine with the *hydrogen sulphites of the alkalis* to form crystalline double compounds. The rule given by Grimm (*A.* 157, 262) that only those ketones combine with hydrogen sodium sulphite which contain the group $CH_3.CO$, holds very generally: an exception is propiono (diethyl ketone) $CO(C_2H_5)_2$, which forms a double compound, although with difficulty. These compounds are used in separating and purifying the ketones: on treating the double compound with sodium carbonate the ketone is liberated. The ketones, like the aldehydes, unite with *hydrocyanic acid* to form nitriles of hydroxy-acids: $(CH_3)_2CO + HCN = (CH_3)_2C(OH).CN$ (Urech, *A.* 164, 258; Tiemann a. Friedländer, *B.* 14, 1971); and these nitriles react with ammonia, yielding nitriles of amido-acids: $(CH_3)_2C(OH).CN + NH_3 = (CH_3)_2C(NH_2).CN + H_2O$ (T. a. F.). — In

presence of caustic potash, acetone unites with *chloroform* to form acetone-chloroform $(CH_3)_2C(OH).CCl_3$, which when heated with water to 180° yields hydroxy-isobutyric acid and hydrochloric acid (Willgerodt, *B.* 14, 2451; 16, 1585).—*Sodium amalgam*, acting on aqueous solutions of the ketones, reduces them to secondary alcohols; thus acetone is converted into isopropyl alcohol: $(CH_3)_2CO + H_2 = (CH_3)_2CH.OH$ (Friedel, *C. R.* 55, 53). At the same time, a second reaction occurs in which 2 mols. of the ketone are united during the process of reduction, forming a tertiary glycol, or pinacone: $2(CH_3)_2CO + H_2 = (CH_3)_2C(OH).C(OH)(CH_3)_2$.—The ketones are less susceptible of oxidation than the aldehydes, and, unlike the latter, can never yield by oxidation an acid containing the same number of carbon atoms. They are best oxidised by boiling them with a mixture of potassium bichromate and dilute sulphuric acid. Popoff (*A.* 161, 300) has formulated the following rules regarding the products formed in the oxidation of the ketones—rules to which, however, there are occasional exceptions: The ketone is broken up at a point between the carbonyl group and one of the alkyl groups, the combined carbonyl being oxidised to carboxyl, and the separated alkyl being oxidised, if primary, to a fatty acid with the same number of atoms of carbon as the alkyl itself, and if secondary, to a ketone, which may in turn be further oxidised. If a ketone contains two dissimilar alkyls, the carbonyl group will remain attached to that carbon atom which has most hydrogen combined with it, unless in the case of a tertiary alkyl or a radicle of the benzene series, when the carbonyl group will remain in combination with the non-hydrogenated carbon atoms. If the two dissimilar alkyls are both primary, or both secondary, or both tertiary, the carbonyl will remain attached to the alkyl of lower molecular weight. The following equations illustrate these rules:

$$CH_3.CO.CH_3 + 3O = CH_3.CO_2H + H.CO_2H.$$

$$CH_3.CO.\vdots CH_2.CH_3 + 3O = CH_3.CO_2H + CH_3.CO_2H.$$

$$CH_3.CH_2.CH_2.CO.\vdots CH(CH_3)_2 + 2O$$
$$= CH_3.CH_2.CH_2.CO_2H + CO(CH_3)_2.$$

$$CH_3.\vdots CO.C(CH_3)_3 + 3O = H.CO_2H + (CH_3)_3C.CO_2H.$$

$$CH_3.\vdots CO.C_6H_5 + 3O = H.CO_2H + C_6H_5.CO_2H.$$

In several cases, however, a subordinate reaction, in which the ketone is oxidised in a way the reverse of that predicted by the rule, occurs simultaneously.—*Chlorine* and *bromine* give substitution compounds.—*Phosphorus pentachloride* replaces the oxygen of ketones by two chlorine atoms.—*Ammonia* reacts less readily with ketones than with aldehydes. With acetone it forms diacetonamine $C_6H_{13}NO$, and triacetonamine $C_9H_{17}NO$.—With *hydroxylamine* in aqueous solution the ketones yield the ketoximes:

$$CH_3.CO.CH_3 + NH_2.OH$$
$$= CH_3.C(N.OH).CH_3 + H_2O.$$
Acetoxime

The ketoximes are generally solid crystalline compounds, volatile without decomposition. Concentrated hydrochloric acid decomposes them into hydroxylamine and ketone.—In like manner *phenylhydrazine* reacts with the ketones, eliminating water and forming ketohydrazones:

$$CH_3.CO.CH_3 + C_6H_5.NH.NH_2$$
$$= CH_3.C(N.NHC_6H_5).CH_3 + H_2O.$$
Acetonephenylhydrazone

The ketohydrazones of the fatty series are for the most part oily liquids, which may be distilled under reduced pressure. Acids decompose them into phenylhydrazine and ketones (E. Fischer, *B.* 16, 661).—*Nitrous acid* converts the ketones into isonitroso-ketones. The reaction occurs more readily, however, with ethereal salts of nitrous acid; thus when a mixture of amyl nitrite and acetone is warmed with hydrochloric acid isonitroso-acetone is formed:

$$CH_3.CO.CH_3 + C_5H_{11}.O.NO$$
$$= CH_3.CO.CH{:}N.OH + C_5H_{11}.OH.$$

Sodium ethoxide may be substituted for hydrochloric acid in the foregoing reaction, but in this case the sodium compound of the isonitroso-ketone is formed and must afterwards be decomposed by acetic acid (Claisen, *B.* 20, 252, and 656; Claisen a. Manasse, *B.* 20, 2194). The isonitroso-ketones are also readily obtained by the action of nitrous acid on aceto-acetic acid and its homologues:

$$CH_3.CO.CH_2.CO_2H + HNO_2$$
Aceto-acetic acid
$$= CH_3.CO.CH{:}N.OH + CO_2 + H_2O$$
Isonitroso-acetone

(V. Meyer a. Züblin, *B.* 11, 695; Ceresole, *B.* 15, 1328).—Concentrated *nitric acid* converts the ketones into dinitro-paraffins: thus propione $CH_3.CH_2.CO.CH_2.CH_3$ yields dinitroethane $CH_3.CH(NO_2)_2$ (Chancel, *Bl.* 31, 504).—The ketones react with the *mercaptans*, eliminating water and yielding 'mercaptoles' (thioketates); ethyl thiodimethylketate is formed when gaseous hydrochloric acid is passed into a mixture of acetone and mercaptan:

$$(CH_3)_2CO + 2C_2H_5.SH = (CH_3)_2C(S.C_2H_5)_2 + H_2O$$

(Baumann, *B.* 18, 887). The mercaptoles are liquids, insoluble in water, not volatile without decomposition, stable towards alkalis and dilute acids.—Under the influence of *dehydrating agents*, such as sulphuric acid, zinc chloride, hydrochloric acid, &c., the ketones readily undergo condensation, two or more molecules combining, with elimination of water, to form more complex compounds. Thus 2 mols. of acetone unite to form mesityl oxide $(CH_3)_2C{:}CH.CO.CH_3$, and 3 mols. to form either phorone $(CH_3)_2C{:}CH.CO.CH{:}C(CH_3)_2$ or mesitylene (1, 3, 5-trimethylbenzene) $C_6H_3(CH_3)_3$, according as 2 or 3 mols. of water are eliminated in the process.

Benzene ketones. Ketones of this class may either contain two benzene radicles directly attached to carbonyl, as in benzophenone (diphenyl ketone) $C_6H_5.CO.C_6H_5$, or the carbonyl group may unite a benzene radicle and a fatty radicle, as in acetophenone (phenyl-methyl-ketone) $C_6H_5.CO.CH_3$; or one or both of the benzene radicles may be attached to carbonyl by means of a fatty group, as in phenyl-benzyl-ketone $C_6H_5.CO.CH_2.C_6H_5$, or di-benzyl-ketone $C_6H_5.CH_2.CO.CH_2.C_6H_5$.

Preparation.—Many of the methods already described for the preparation of the fatty ketones are also applicable in the case of the benzene

ketones. Thus benzophenone may be obtained by the distillation of a benzoate:

$$(C_6H_5.CO.O)_2 = (C_6H_5)_2CO + CaCO_3,$$

and acetophenone by distilling a mixture of a benzoate and an acetate:

$$(C_6H_5.CO.O)_2Ca + (CH_3.CO.O)_2Ca = 2C_6H_5.CO.CH_3 + 2CaCO_3.$$

Again, acetophenone may be obtained by the action of benzoyl chloride on zinc methyl; but if it is desired to introduce a benzene radicle in place of the halogen of the acyl chloride the mercury compound of that radicle must be employed: $C_6H_5.COCl + Hg(C_6H_5)_2 = (C_6H_5)_2CO + Hg(C_6H_5)Cl$. The benzene ketones are also formed, like the fatty ketones, by the oxidation of the corresponding secondary alcohols:

$$\underset{\text{Diphenylcarbinol}}{(C_6H_5)_2CH.OH} + O = (C_6H_5)_2CO + H_2O;$$

and of secondary glycolic acids containing benzene radicles:

$$\underset{\text{Benzilic acid}}{(C_6H_5)_2C(OH).CO_2H} + O = (C_6H_5)_2CO + CO_2 + H_2O;$$

further, by splitting off carbon dioxide from ketonic acids of the benzene series:

$$\underset{\text{Benzoylacetic acid}}{C_6H_5.CO.CH_2.CO_2H} = C_6H_5.CO.CH_3 + CO_2.$$

By shaking phenylacetylene with sulphuric acid of 75 p.c. it takes up the elements of water, yielding acetophenone:

$$C_6H_5.C{:}CH + H_2O = C_6H_5.CO.CH_3$$

(Friedel a. Balsohn, *Bl.* [2] 35, 55).

The following modes of formation are peculiar to benzene ketones:—

1. By the action of an acyl chloride on a benzene hydrocarbon in presence of aluminium chloride: $CH_3.COCl + C_6H_6 = CH_3.CO.C_6H_5 + HCl$ (Friedel a. Crafts, *A. Ch.* [6] 1, 507). In this reaction the acid radicle always attaches itself to a benzene nucleus, and never to a fatty group. In like manner ketones containing two benzene radicles directly united to carbonyl may be prepared by acting on a benzene hydrocarbon with carbonyl chloride in presence of aluminium chloride: $COCl_2 + 2C_6H_6 = CO(C_6H_5)_2 + 2HCl$.

2. The last-mentioned class of ketones may also be obtained by heating a mixture of a benzene carboxylic acid and a benzene hydrocarbon with phosphorus pentoxide:

$$C_6H_5.CO.OH + C_6H_6 = C_6H_5.CO.C_6H_5 + H_2O.$$

3. By the oxidation of hydrocarbons in which two benzene radicles are united by a methylene-group:

$$C_6H_5.CH_2.C_6H_5 + O_2 = C_6H_5.CO.C_6H_5 + H_2O.$$

Ketone-alcohols are obtained by polymerising benzene aldehydes with potassium cyanide:

$$\underset{\text{Benzaldehyde}}{2C_6H_5.CHO} = \underset{\text{Benzoïn}}{C_6H_5.CO.CH(OH).C_6H_5}.$$

Ketone-phenols are formed when acyl chlorides of the benzene series act on phenols in presence of zinc:

$$C_6H_5.COCl + C_6H_5.OH = \underset{p\text{-Hydroxybenzophenone}}{C_6H_5.CO.C_6H_4.OH} + HCl.$$

The acid radicle enters the nucleus of the phenol in the para- position to the hydroxyl group.

Properties and Reactions.—The benzene ketones are liquids and solids, boiling without decomposition and having a pleasant aromatic odour.

In most of their reactions they closely resemble the fatty ketones. Popoff's rules (*v. supra*) apply to the oxidation of the benzene ketones: the carbonyl group always remains attached to a benzene nucleus to which it is directly united. Like the fatty ketones, the benzene ketones react with hydroxylamine and with phenyl-hydrazine eliminating water and yielding hydroximes and hydrazones. On reduction with sodium-amalgam they form secondary alcohols; but heating with hydriodic acid, or distillation with zinc-dust, reduces them to the corresponding hydrocarbons:

$$(C_6H_5)_2CO + 2H_2 = \underset{\text{Diphenylmethane}}{(C_6H_5)_2CH_2} + H_2O.$$

By fusion with caustic alkalis they yield a salt of a benzene acid together with a hydrocarbon:

$$C_6H_5.CO.C_6H_5 + KOH = C_6H_5.CO_2K + C_6H_6.$$

They are less subject than the fatty ketones to undergo condensation with elimination of water, and those which contain two benzene radicles directly attached to the carbonyl group do not exhibit this tendency at all.

Only those benzene ketones combine with hydrogen sodium sulphite in which the carbonyl is attached to two fatty groups, one of which is methyl: thus, benzyl-methyl-ketone $C_6H_5.CH_2.CO.CH_3$ and methyl-phenylethyl-ketone $C_6H_5.CH_2.CH_2.CO.CH_3$ form double compounds; acetophenone $C_6H_5.CO.CH_3$ does not.

Diketones. The diketones contain two carbonyl groups attached to hydrocarbon radicles. If the two carbonyl groups are directly united, the compound is an α-diketone; if they are united by a carbon atom, it is a β-diketone; if by a chain of two carbon atoms, a γ-ketone, and so on.

Some of the diketones, such as benzil $C_6H_5.CO.CO.C_6H_5$, have been known for a considerable time; but the majority are of recent discovery. Their chief interest lies in the ease with which the two carbonyl groups may be made to condense with one or more molecules of some other substance to form closed-chain compounds. In this way glyoxalines, quinolines, pyrazoles, furfurans, pyrrholes, thiophens, and similar compounds have been prepared.

α-Diketones. These may be regarded as homologues of the dialdehyde *glyoxal*, CHO.CHO. They may be obtained by the action of chlorine, or, better, of nitric acid, on α-ketone-alcohols:

$$\underset{\text{Benzoïn}}{C_6H_5.CO.CH(OH).C_6H_5} + O = \underset{\text{Benzil}}{C_6H_5.CO.CO.C_6H_5} + H_2O$$

(Laurent, *A. Ch.* [2] 59, 402; Zinin, *A.* 34, 188). By hydrolysing the isonitrosoketones by boiling them with dilute sulphuric acid:

$$\underset{\text{Isonitroso-ethylmethyl ketone}}{CH_3.CO.C(N.OH).CH_3} + H_2O = \underset{\text{Diacetyl}}{CH_3.CO.CO.CH_3} + NH_2.OH$$

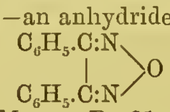
(Von Pechmann, *B.* 21, 1411).

The benzenoid α-diketones react with *caustic potash* to form secondary glycolic acids, the two

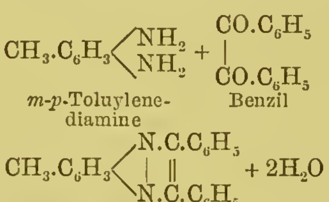
hydrocarbon radicles attaching themselves to the same carbon atom:

$$C_6H_5.CO.CO.C_6H_5 + KOH = (C_6H_5)_2C(OH).CO_2K$$
Benzil — Potassium benzilate (diphenylglycolate)

(Liebig, *A.* 25, 25; Zinin, *A.* 31, 329). In like manner glyoxal yields glycolic acid. The fatty α-diketones, however, condense to form quinones (*q. v.*).—α-Diketones react with 2 mols. of *hydroxylamine* to form dihydroximes. Benzil dihydroxime is remarkable as occurring in three isomeric modifications, all of the formula $C_6H_5.C(N.OH).C(N.OH).C_6H_5$, an isomerism which is explained by Victor Meyer by means of tridimensional formulæ (Auwers a. V. Meyer, *B.* 22, 705; *cf.* also Hantzsch a. Werner, *B.* 23, 11). These three hydroximes, when heated, part with water, yielding in each case the same closed-chain compound—an anhydride:



(Auwers a. V. Meyer, *B.* 21, 810).—With *o-diamines* the α-diketones yield quinoxalines (azines):



m-p-Toluylene-diamine — Benzil

Diphenyltoluquinoxaline

(Hinsberg, *B.* 17, 322; *cf.* Witt, *B.* 19, 915). For an account of the behaviour of α-diketones with *aldehydes* and *ammonia* v. vol. i. p. 465.

β-Diketones. The lowest member of this series which is a true diketone and not a di-aldehyde is acetyl-acetone $CH_3.CO.CH_2.CO.CH_3$. By the action of aluminium chloride on acetyl chloride a crystalline substance of the formula $C_{12}H_{14}O_6Al_2Cl_8$ is formed, which, on treatment with water, evolves carbon dioxide and yields acetyl-acetone (Combes, *C. R.* 103, 814). A general method for the preparation of β-diketones consists in acting on a mixture of a fatty or a benzene-fatty ketone and the ethyl salt of a carboxylic acid with sodium ethoxide. The latter substance produces condensation between the ethereal salt and the ketone with elimination of alcohol:

$$C_6H_5.CO.OC_2H_5 + CH_3.CO.CH_3$$
Ethyl benzoate — Acetone
$$= C_6H_5.CO.CH_2.CO.CH_3 + C_2H_5.OH.$$
Benzoyl-acetone

In reality it is the sodium compound of benzoyl-acetone $C_6H_5.CO.CHNa.CO.C_6H_5$ which is formed, and it is necessary to decompose this compound with carbon dioxide in order to obtain the free diketone (Claisen, *B.* 20, 655). Di-acyl derivatives of acetic acid are decomposed on boiling with water, eliminating water and generating β-diketones:

$$(C_6H_5.CO)_2CH.CO_2H = (C_6H_5.CO)_2CH_2 + CO_2$$
Dibenzoylacetic acid — Dibenzoylmethane

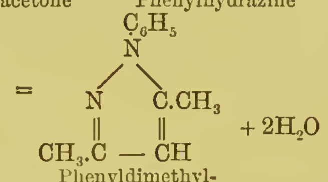
(Baeyer a. W. H. Perkin, jun., *B.* 16, 2128; E. Fischer a. Kuzel, *B.* 16, 2239).

The methylene group in the β-diketones is attached to two electro-negative carbonyl groups. For this reason one atom of hydrogen in this group, like the hydrogen in the methylene group of aceto-acetic ether or malonic ether, is replaceable by an alkali metal when presented to it in the form of an ethoxide. By treating the alkali compound thus obtained with the halogen compound of an alkyl or acid radicle, the radicle can be introduced in place of the alkali metal:

$$(C_6H_5.CO)_2CHNa + C_6H_5.COCl$$
Sodium dibenzoyl-methane — Benzoyl chloride
$$= (C_6H_5.CO)_3CH + NaCl$$ (Baeyer a. Perkin, *l.c.*).
Tribenzoylmethane

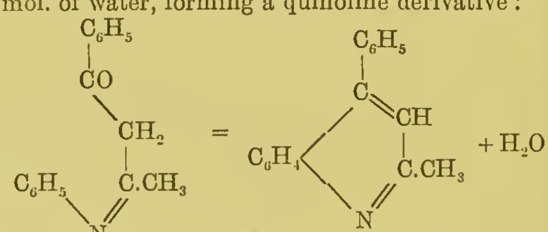
The β-diketones react with 1 mol. of *phenylhydrazine* eliminating 2 mols. of water, and forming pyrazoles:

$$CH_3.CO.CH_2.CO.CH_3 + C_6H_5.NH.NH_2$$
Acetyl-acetone — Phenylhydrazine



Phenyldimethyl-pyrazole

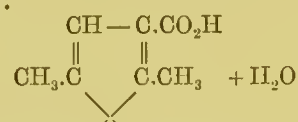
(Knorr, *B.* 20, 1104).—*Aniline* reacts with β-diketones in two stages: thus when benzoyl-acetone is heated with aniline at 150° the two substances first unite, parting with 1 mol. of water: $C_6H_5.CO.CH_2.CO.CH_3 + C_6H_5.NH_2 = C_6H_5.CO.CH_2.C(N.C_6H_5).CH_3 + H_2O$; and when the compound thus obtained is heated with concentrated sulphuric acid, it parts with a second mol. of water, forming a quinoline derivative:



α-Methyl-γ-phenylquinoline

(C. Beyer, *B.* 20, 1770). This is a general method for the preparation of quinolines containing alkyls in the α-γ-positions.

γ-Diketones.—In these compounds the two carbonyl-groups are united by an ethylene radicle. The lowest member of the series, acetonyl-acetone, was obtained by Paal (*B.* 18, 58) by heating pyrotritaric acid with water at 150°–160°:

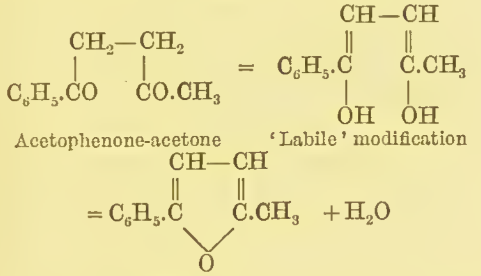


$= CH_3.CO.CH_2.CH_2.CO.CH_3 + CO_2$. Acetophenone-acetone is obtained by heating acetophenone-aceto-acetic acid (prepared by acting with bromacetophenone on sodaceto-acetic ether, and hydrolysing the ether thus formed):

$$CH_3.CO.\underset{\displaystyle CO_2H}{\underset{|}{C}H}.CH_2.CO.C_6H_5$$
$$= CH_3.CO.CH_2.CH_2.CO.C_6H_5 + CO_2$$ (Paal, *B.* 16, 2865).

By treatment with *dehydrating agents*, such as fuming hydrochloric acid or acetic anhy-

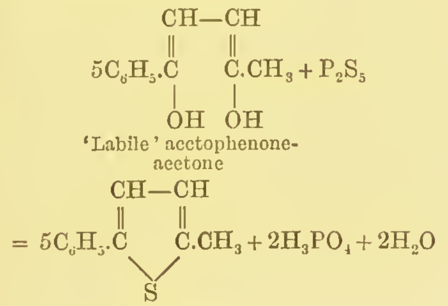
dride, the γ-diketones are converted into furfurans. It is supposed that in this reaction the diketone first forms a 'labile' modification containing two hydroxyl groups, and that this then parts with water to form the furfuran:



Acetophenone-acetone 'Labile' modification

Phenylmethyl-furfuran

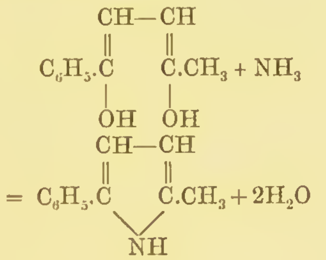
(Paal, *B.* 17, 2756). An unsaturated ketone isomeric with phenylmethylfurfuran is formed at the same time.—*Phosphorus pentasulphide* converts γ-diketones into thiophens, whilst with *ammonia* they yield pyrroles, the reaction in both cases being supposed to be preceded by the above-mentioned transformation of the diketone into its 'labile' modification:



'Labile' acetophenone-acetone

Phenylmethylthiophen

and



Phenylmethylpyrrole

(Paal, *B.* 18, 367).

An *unsaturated* γ-diketone, *anhydraceto-phenonebenzil* (*αβ-dibenzoylstyrolene*) is formed by the action of caustic potash on a mixture of benzil and acetophenone:

$$\begin{array}{l} C_6H_5.CO \\ \quad | \quad + CH_3.CO.C_6H_5 \\ C_6H_5.CO \end{array}$$

$$= \begin{array}{l} C_6H_5.C{:}CH.CO.C_6H_5 \\ \quad | \\ C_6H_5.CO \end{array} + H_2O$$ (Japp a. Miller, *C. J.* 47, 35).

Quinones. If the two carbonyl groups of a diketone occur in a closed chain of six carbon atoms, the resulting compound belongs to the class of the quinones. This group of diketones will be treated of separately (*v.* Quinones).

Triketones. A triketone in which the three carbonyl groups are directly united has been obtained in the following manner (von Pechmann, *B.* 22, 852): Dibenzoylbromomethane $C_6H_5.CO.CHBr.CO.C_6H_5$ (prepared by the action of bromine on dibenzoylmethane, *v. supra*) is converted by treatment with potassium acetate into the acetate of dibenzoylcarbinol $C_6H_5.CO.CH(OC_2H_3O).CO.C_6H_5$, which, when brominated, yields $C_6H_5.CO.CBr(OC_2H_3O).CO.C_6H_5$. When this compound is heated above its melting-point (101·5°) it breaks up into acetyl bromide and *diphenyltriketone*:

$$C_6H_5.CO.CBr(OC_2H_3O).CO.C_6H_5$$
$$= C_2H_3OBr + C_6H_5.CO.CO.CO.C_6H_5.$$

Diphenyltriketone, like some other compounds in which a carbonyl-group is situated between two electro-negative groups, unites with 1 mol. of water to form a hydrate; this has probably the constitution $C_6H_5.CO.C(OH)_2.CO.C_6H_5$.

The formation of another triketone, *tribenzoylmethane*, in which the three carbonyl-groups are attached to the same carbon atom, has already been referred to. F. R. J.

DIKETO-PENTANE *v.* Methyl ethyl diketone.

αβ-DIKETO-PROPYL-BENZENE *v.* Phenyl-methyl-diketone.

KINIC ACID. Synonym of Quinic acid.

KINO. The dried juice, obtained from incisions in the trunk of *Pterocarpus marsupium* (Malabar). The name has also been given to the dried juice from other trees, *e.g. Eucalyptus resinifera* (Australia), *Pterocarpus erinaceus*, and *Coccoloba uvifera* (America). Kino greatly resembles catechu, and is used in dyeing and in medicine. It occurs in small brittle opaque reddish-black fragments, partly soluble in water, almost entirely soluble in alcohol, insoluble in ether. It has no odour, but a very astringent taste. Used in medicine as an astringent. It gives off pyrocatechin when distilled (Eissfeld, *A.* 92, 101). Potash-fusion forms phloroglucin and protocatechuic acid (Hlasiwetz, *A.* 134, 122; Stenhouse, *A.* 177, 187). Kino contains kinoïn and kino-red and other bodies. Kinoïn has been described as a 'tannin' (Bergholz, *cf.* Etti, *B.* 17, 2241).

Kinoïn $C_{14}H_{12}O_6$. Occurs together with kino-red, &c., in gum kino, from which it is extracted by first boiling with dilute HCl, and then extracting the solution with ether; yield $1\frac{1}{2}$ p.c. (Etti, *B.* 11, 1879). Colourless prisms. Sl. sol. cold, readily sol. hot, water. On heating to 120° it gives kino-red ($C_{28}H_{22}O_{11}$). On heating with HCl to 130° it is decomposed into methyl chloride, pyrocatechin, and gallic acid.

Kino-red $C_{28}H_{22}O_{11}$. [160°–170°]. A red resin occurring in kino and left undissolved when it is boiled with dilute HCl. It is also formed by heating kinoïn. It is sl. sol. water, v. sol. alcohol. $FeCl_3$ gives a dirty green colouration. It dissolves in alkalis. It ppts. a solution of gelatin. On fusion it yields a red amorphous anhydride $C_{28}H_{20}O_{10}$, which also ppts. a solution of gelatin. The anhydride is also formed by heating kino-red with dilute HClAq. Kino-red yields phenol and pyrocatechin when distilled.

KOSIN $C_{31}H_{38}O_{10}$. [142°]. Obtained from cusso or kousso, the dried flowers of the Abyssinian koso tree (*Hagenia Abyssinica*), used by the inhabitants as a remedy against tape worm (Flückiger a. Buri, *Ar. Ph.* [3] 5, 193; *Ph.* [3] 5, 562). The anthelmintic properties of koso seem to be due to kosin. Sulphur-yellow trimetric crystals. Nearly insol. water, v. sol

alcohol, ether, benzene, CS_2, chloroform, and HOAc. Dissolves in aqueous alkalis and Na_2CO_3, and is reppd. by acids. $FeCl_3$ colours its alcoholic solution permanently red. Conc. H_2SO_4 does not decompose it at 15°, but on warming it forms isobutyric acid and a red amorphous body $C_{22}H_{21}O_{10}$ (?). Potash-fusion gives formic, butyric, and oxalic acids. Sodium-amalgam yields a volatile oil $C_{23}H_{46}O_2$ and an amorphous yellow substance $(C_5H_5O_2)_x$.

Acetyl derivative $C_{31}H_{32}Ac_6O_{10}$. From kosin and Ac_2O.

KOUMISS *v.* MILK.

KYANETHINE *v.* CYANETHINE.

KYANPHENINE *v.* CYAPHENINE.

KYANPROPINE *v.* CYANPROPINE.

KYNURENIC ACID *v.* OXY-QUINOLINE CARBOXYLIC ACID.

KYNURIC ACID *v.* CYNURIC ACID.

KYNURIN *v.* OXY-QUINOLINE.

L

LABURNINE. An alkaloid said to occur along with cytisine in laburnum seeds (Husemann a. Marmé, *Z.* [2] 1, 161; 5, 677). Light crystalline groups of monoclinic prisms; v. sol. water, sl. sol. alcohol, nearly insol. ether.

LAC. A substance surrounding the eggs of *Coccus laccæ* on the twigs of various trees in Bengal and Sumatra. These twigs are called stick-lac. The lac is removed by melting and squeezing through canvas, when the hardened drops are known as seed-lac. After bleaching by chlorine or charcoal and making into sticks it is known as shell-lac or shellac. Lac is used for making sealing-wax, varnishes, and a red dye called lac dye. Lac contains 68 to 88 p.c. resin (about half of which is soluble in ether), a small quantity of wax and of a red dye, and a larger quantity of a substance insoluble in alcohol. The wax [60°] contains ceryl and myricyl alcohols and their stearic, palmitic, and oleic ethers (Benedikt a. Ulzer, *M.* 9, 579). Shellac may be freed from wax by dissolving in boiling dilute Na_2CO_3, filtering, and ppg. with HCl. If the boiling be continued too long, liquid shellac is produced. Shellac freed from wax gives azelaïc acid when oxidised by $KMnO_4$ (Benedikt a. Ehrlich, *M.* 9, 163).

Liquid shellac $C_{46}H_{72}O_{12}$. Formed by boiling shellac (1,000 g.) with NaOH (300 g.) and water (20,000 g.) for 2 hours. When cold, sulphuric acid is added and the liquid shaken with ether (B. a. E.). Thick liquid; insol. water, v. sol. alcohol and ether. Forms salts with Pb, Ag, Zn, Ba, and Ca.—$C_{46}H_{70}Mg_2O_{13}$: amorphous, v. sol. water; ppd. on heating, but redissolves on cooling.

Laccaïc acid $C_{16}H_{12}O_8$ (?). Obtained from lac dye by treating with HClAq, filtering, boiling the residue with water, ppg. the solution with lead acetate, and decomposing the pp. with H_2S (R. E. Schmidt, *B.* 20, 1285). Brownish-red powder composed of minute tables (from alcohol-ether), m. sol. alcohol, sl. sol. water, nearly insol. ether, insol. benzene. Decomposes, without previous fusion, at about 180°. Alkalis form a crimson solution which has an absorption spectrum like that of carminic acid. Baryta gives a violet pp.: $FeSO_4$ a black pp.: $FeCl_3$ a black colouration only. It reduces ammoniacal $AgNO_3$ but not Fehling's solution. Conc. HNO_3 yields picric and oxalic acids. Conc. HClAq at 180° forms a substance $C_{28}H_{16}O_{11}$. Laccaïc acid dyes like carminic acid, but its solution in H_2SO_4 shows a different absorption spectrum.—$K_3C_{16}H_9O_8$ (dried at 100°): flocculent pp. formed by adding alcoholic potash to an alcoholic solution of the salt. $BaC_{16}H_{10}O_8$: brownish-red pp. formed by adding NH_3 and $BaCl_2$.

LACMOID.

Preparation.—1. A mixture of resorcinol (20 pts.), sodium nitrite (1 pt.), and water (1 pt.) is slowly heated to 110°, at which temperature a vigorous reaction sets in, the melt is then kept at 115°–120° till it has become quite blue and the evolution of NH_3 has ceased (Traub a. Hock, *B.* 17, 2615).—2. By the action of H_2O_2 on ammoniacal resorcin solution (Wurster, *B.* 20, 2938).—3. By fusing resorcin (15 g.) with KNO_2 (18 g.) (Benedikt a. Julius, *M.* 5, 534).

Properties.—Glistening brown powder. It is easily soluble in methyl, ethyl, and amyl alcohols, acetone, acetic acid, and phenol, less easily in ether and water, insoluble in benzene and petroleum-spirit. It dissolves in strong HCl or H_2SO_4 with a blue colour. It decomposes below 200°.

Lacmoid differs from litmin, the colouring matter of litmus, in being soluble in strong alcohol. Litmin is insoluble in strong alcohol, though soluble in dilute (50 p.c.) spirit. The solution of litmin in 50 p.c. alcohol is bleached after a time, while that of lacmoid retains its colour for months. The absorption spectra of the two substances do not differ markedly (Hartley, *R. Dublin Soc.* 5, 159).

LACTAM. The anhydride of an amido- acid $R''(NH_2)(CO_2H)$ containing the group $R''<\begin{smallmatrix}CO\\NH\end{smallmatrix}>$ (Baeyer, *B.* 15, 2102).

LACTAMIC ACID is α-AMIDO-PROPIONIC ACID.

Di-lactamic acid is α-IMIDO-DI-PROPIONIC ACID.

LACTAMIDE *v. Amide of* LACTIC ACID.

LACTARIC ACID $C_{15}H_{30}O_2$. Prepared by pressing the juice out of the mushroom (*Lactarius piperatus*) and extracting the residue with ether or boiling alcohol (Chuit, *Bl.* [3] 2, 153). White leaflets (from alcohol); v. sol. hot alcohol, ether, $CHCl_3$, CS_2, and benzene, v. sl. sol. cold alcohol and petroleum spirit, insol. water.

Salts.—NaA′: greasy scales, decomposing at 250°.—KA′: silvery scales, decomposing at 245° without melting.—KHA′$_2$: silky scales. [115°].—NH_4A': [92°]; white leaflets, decomposed by boiling water.—CaA′$_2$: scales. When distilled it forms the ketone $(C_{14}H_{29})_2CO$ [82°].—BaA′$_2$: white amorphous pp. Insol. water, alcohol, and ether.—$Pb_4HA'_9$. [114°]. Thin transparent leaflets.

Methyl ether MeA'. [38°]. White scales. Sol. ligroïn and ether.

Ethyl ether EtA'. [36°]. White scales. V. sol. warm alcohol, ether, chloroform, and CS_2.

Amide $C_{15}H_{19}O.NH_2$. [108°]. Trimetric needles.

LACTIC ACID $C_3H_6O_3$ *i.e.* $CH_3.CH(OH).CO_2H$. *a-Oxy-propionic acid. Ethylidene-lactic acid. Fermentation lactic acid.* Mol. w. 90. S.G. $\frac{20}{4}$ 1·2403 (Brühl); $\frac{15}{4}$ 1·2485 (Mendeléeff, *C. R.* 50, 52). $\mu_\beta = 1{\cdot}4469$. $R_\infty = 31{\cdot}18$.

Isomerides.—Lactic acid is isomeric with hydracrylic acid, and appears to be chemically identical with sarcolactic acid (*v. infra*).

In 1863 Wislicenus got from ethylene chlorhydrin and KCN, by saponifying the product, a lactic acid which formed a crystalline zinc salt ZnA'_2 2aq. He called it ethylene lactic acid, thought it was identical with Liebig's sarcolactic acid (*A.* 128, 4). Dossios (*A.* 146, 168) said that sarcolactic acid gave, on oxidation, malonic acid. Wislicenus held (*A.* 167, 346) that his ethylene lactic acid was not hydracrylic acid, for by the action of HI he was unable to obtain β-iodo-propionic acid. He said also that his ethylene lactic acid differed from sarcolactic, although it accompanied sarcolactic acid in extract of meat. Erlenmeyer (*A.* 191, 261) showed that Wislicenus's ethylene lactic acid from glycol chlorhydrin is hydracrylic acid, and could be converted by HI into β-iodo-propionic acid. The acid accompanying sarcolactic acid is, according to Siegfried (*B.* 22, 2711) the acetyl derivative of lactic acid.

Occurrence.—1. Discovered by Scheele in sour milk and first recognised as a peculiar acid by Berzelius.—2. In opium (Smith, *Ph.* [2] 7, 50; Buchanan, *B.* 3, 182).

Formation.—1. by the lactic fermentation of milk-sugar, cane-sugar, or glucose (*v.* FERMENTATION, vol. ii. p. 543).—2. By the oxidation of propylene glycol by the oxygen of the air in presence of platinum-black (Wurtz, *A.* 105, 206; 107, 192).—3. By boiling α-chloro-propionic acid with water and Ag_2O (Wurtz, *A. Ch.* [3] 59, 165; Buff, *A.* 140, 156). In like manner from α-bromo-propionic acid (Friedel a. Machuca, *A.* 120, 286).—4. By the action of nitrous acid upon alanine (Strecker, *A.* 75, 27, 42).—5. By the reduction of pyruvic acid by sodium-amalgam (Wislicenus, *A.* 126, 227) or with zinc in presence of dilute acetic acid (Debus, *C. J.* 16, 260).—6. From aldehyde by combination with HCy and saponification of the resulting nitrile (Wislicenus, *A.* 128, 6; Simpson a. Gautier, *A.* 146, 254).—7. By heating di-chloro-acetone with a large quantity of water at 200° (Linnemann a. Zotta, *A.* 159, 247).—8. By boiling glucose with aqueous NaOH (Hoppe-Seyler, *B.* 4, 346).—9. When glucose (20 g.) is allowed to stand with potash (40 g.) and water (200 c.c.) at 40° in a flask loosely plugged with cotton wool, it is converted within 24 hours into lactic acid (8 g.) and another acid, soluble in alcohol (Nencki a. Sieber, *J. pr.* 132, 499). Lactic acid may possibly be thus formed in animals from sugar. The decomposition occurs even in very dilute solutions, thus even 9 g. of glucose and 9 g. of potash dissolved in 3 litres of water and kept at 35°–40° are converted in 10 days into potassium lactate. Na_2CO_3 does not decompose sugar at 40°, nor does NH_3, but NaOH, NMe_4OH and neurine do convert it into lactic acid. Creatinine and guanidine produce no lactic acid. Milk sugar and maltose behave like glucose. Lactic acid is formed when glucose (dextrose) (1 pt.), water (10 pts.) and KOH (2 pts.) are left, even in an atmosphere of hydrogen, for 48 hours at 35°. No sugar is left (Nencki a. Sieber, *J. pr.* [2] 26, 1; Kiliani, *B.* 15, 701).—10. By heating cane-sugar with baryta at 150° (Schützenberger, *Bl.* [2] 25, 289).—11. Among the products of the distillation of glycerin with KOH (Herter, *B.* 11, 1167), and formed, together with formic and oxalic acids, by boiling glycerin with potash solution (Debus, *A.* 109, 229).

Preparation.—1. The filtered solution of sour whey evaporated nearly to dryness, in strong alcohol, is mixed with alcoholic tartaric acid, as long as any precipitate of tartrate of potassium, sodium, and calcium is formed; the liquid decanted after 24 hours, and evaporated; the residue dissolved in water; the solution digested with carbonate of lead, till lead dissolves in it; the filtrate evaporated, neutralised with carbonate of barium, again filtered, and diluted with water; the whole of the barium precipitated with sulphate of zinc; and the filtrate evaporated till lactate of zinc crystallises out (Berzelius, *Lehrb.* Ausg. 5, v. 241).—2. Three kilos of cane-sugar and 15 g. of tartaric acid (which serves to invert the cane-sugar) are dissolved in 13 kilos of boiling water; $1\frac{1}{2}$ kilos of levigated chalk added after two days, together with 60 g. of stinking cheese, suspended in 4 kilos of sour milk (decaying cheese favours the production of lactic acid and retards its conversion into butyric acid); the mixture set aside at a temperature between 30° and 35°, and well stirred every day till, in the course of six or eight days, it is converted into a stiff paste of lactate of calcium; this paste is boiled for an hour with 15 g. of quick-lime and 10 kilos of water; the solution strained through a cloth filter and evaporated to a syrup; the crystalline mass, which forms in four days, pressed, first by itself, then three or four times, after having been each time stirred up, with $\frac{1}{10}$ of its weight of cold water; and the lactate of calcium thus purified is dissolved in twice its weight of boiling water. To the solution of every 32 pts. of the calcium salt there is then added a mixture of 7 pts. oil of vitriol and 7 pts. water; the lactic acid, while still hot, is strained through linen to separate it from sulphate of lime; the filtrate obtained from 7 pts. of oil of vitriol is boiled with $1\frac{3}{8}$ pts. carbonate of zinc for a quarter of an hour (by longer boiling a very sparingly soluble basic salt is formed); the liquid is filtered boiling hot; the colourless crystalline grains of lactate of zinc, which separate on cooling, are freed from sulphuric acid by washing with cold water; and additional quantities of crystalline grains are obtained by evaporating the mother-liquor almost to the end. Lastly, 1 pt. of the zinc salt is dissolved in $7\frac{1}{2}$ pts. of boiling water; sulphuretted hydrogen passed through the solution as long as sulphide of zinc is precipitated; and the filtrate boiled and evaporated on the water-bath to a syrup, whereupon 8 pts. of the zinc salt yield 5 pts. of syrupy lactic

acid (Bensch, *A.* 61, 174). By this process, 100 pts. of cane-sugar yield 117 pts. of lactate of calcium, which, if the sugar was white, is colourless, and does not require to be purified by pressure (*cf.* Engelhardt a. Maddrell, *A.* 63, 83; 70, 241; Boutron a. Fremy, *J. Ph.* 27, 341). 3. Lautemann (*A.* 113, 242) recommends the following modification of Bensch's process of preparation:—Retaining the proportions of sugar, tartaric acid, milk, and cheese indicated by the latter, he takes one-third more water, uses 1,200 g. oxide of zinc (commercial zinc-white) instead of levigated chalk, and keeps the temperature as constantly as possible between 40° and 45° during the fermentation. After eight or ten days, the inside of the vessel is lined with white crystals of lactate of zinc, which can be obtained pure by one or two crystallisations from boiling water. The lactic acid prepared from the zinc salt generally contains mannite, which does not completely crystallise out from the concentrated acid. To separate this, the aqueous acid is shaken up with ether, and then the ethereal layer is pipetted off and evaporated: it then leaves pure lactic acid.—4. The following mixture is recommended by C. O. Harz (*Vierteljahrsschrift pr. Pharm.* 20, 501); 3 pts. milk-sugar, 36 pts. ordinary water, 0·5 to 0·75 pt. flour containing a large proportion of gluten, a little beer-yeast, 6 pts. of soda-crystals, or 3 pts. of sodium bicarbonate. When the fermentation has once been set up by milk-sugar, it may be continued by addition of cane-sugar.—5. By the action of NaOH or KOH on dextrose or levulose, the operation being performed as follows:—A solution of 500 grms. of cane-sugar in 250 c.c. of water and 10 c.c. dilute sulphuric acid (3 pts. H_2SO_4 to 4 pts. H_2O) is heated to 50° in a closed vessel for 3 hrs. After cooling, 400 c.c. of aqueous NaOH (50 p.c.) is slowly added. The mixture is then warmed to 60°–70° till it no longer reduces Fehling's solution, the calculated quantity of H_2SO_4 (same strength as before) is then added, and the Na_2SO_4 made to crystallise out by cooling and agitation. The mass is extracted with 93 p.c. spirit and filtered, the filtrate is divided into two portions, one half being neutralised with $ZnCO_3$ filtered hot and the other half added. On cooling, the zinc lactate crystallises out in a nearly pure state; the yield is 200 grms. (Kiliani, *B.* 15, 699; *cf.* Hoppe-Seyler, *B.* 4, 346).

Properties.—Colourless syrup with very sour taste. Hygroscopic. Miscible with water and alcohol, sl. sol. ether. Does not solidify at −24°.

Reactions.—1. When gradually heated it gives off water at 130° leaving solid lactide. At 250° to 300° the products are CO, CO_2, aldehyde, and lactide.—2. Dilute H_2SO_4 at 130° gives aldehyde and formic acid (Erlenmeyer, *Z.* 1868, 343): $CH_3.CH(OH).CO_2H = CH_3.CHO + HCO_2H$. 3. When gently heated with conc. H_2SO_4 it gives off CO freely (Pelouze, *A. Ch.* [3] 13, 257).—4. Boiling *nitric acid* forms oxalic acid.—5. Distillation with NaCl, dilute H_2SO_4, and MnO_2 yields aldehyde and chloral (Städeler, *A.* 69, 332).—6. Distillation with MnO_2 and dilute H_2SO_4 yields aldehyde and CO_2.—7. Fuming H_2SO_4 gives methane disulphonic acid (Strecker, *A.* 118, 291).—8. *Chromic acid mixture* gives acetic acid and CO_2 (Chapman a. Smith, *Z.* 1867, 477).—9. $KMnO_4$ gives pyruvic acid.—10. PCl_5 acting on dry calcium lactate gives chloro-propionyl chloride $CH_3.CHCl.COCl$ whence water forms α-chloro-propionic acid. 11. HIAq reduces it to propionic acid (Lautemann, *A.* 113, 217).—12. A concentrated solution of potassium lactate submitted to electrolysis yields aldehyde and CO_2 (Kolbe, *A.* 113, 244; Brester, *Z.* 1866, 680).—13. Distillation with quicklime yields alcohol: $C_3H_6O_3 = CO_2 + C_2H_6O$ (Hanriot, *C. R.* 101, 1156; *Bl.* [2] 45, 80).—14. Heated at 170° in a stream of gaseous HBr, or at 100° in sealed tubes with conc. HBrAq, it yields α-bromo-propionic acid (Kekulé, *A.* 130, 11).—15. *Bromine* at 100° decomposes lactic acid (Beilstein, *A.* 120, 227). Br acting on an ethereal solution of lactic acid forms tri-bromo-pyruvic ether (Wichelhaus, *A.* 143, 10; Klimenko, *J. R.* 8, 125).—16. The dry distillation of calcium lactate produces CO_2, ethylene, propylene (Gossin, *Bl.* [2] 43, 49), acrylic acid, phenol (?) (Claus, *A.* 136, 287), and other products.—17. Distillation of calcium lactate with soda-lime yields acetic, propionic, butyric, hexoic, and other fatty acids. Heating calcium lactate with KOH at 280° yields formic, acetic, propionic, butyric, and oxalic acids (Hoppe-Seyler, *H.* 3, 352).—18. Among the products of the putrefactive fermentation of calcium lactate are hydrogen, CO_2, acetic, propionic, butyric, and *n*-valeric acids and ethyl alcohol (Pasteur, *Bl.* 1862, 52; Strecker, *A.* 92, 80; Fitz, *B.* 11, 1898; 12, 479; 13, 1309).—19. Heating with *m*-amido-benzoic acid forms $CH_3.CH(OH).CO.NH.C_6H_4.CO_2H$ crystallising from water in small prisms [162°] (Pellizzari, *A.* 232, 154), which at 240 forms an anhydride $\begin{array}{l} CH_3.CH \\ \;| \\ CO \end{array}\!\!>N.C_6H_4.CO_2H$. [243°]. The corresponding acetyl derivative $CH_3.CH(OAc).CO.NH.C_6H_4.CO_2H$ melts at 148°.

Estimation.—The substance, acidified with H_2SO_4, is extracted with ether, the ethereal solution evaporated, the residue treated with water and the aqueous solution ppd. with lead acetate and filtered. The filtrate is then ppd. with alcoholic NH_3, and the pp. of $Pb_3O_32(C_3H_6O_3)$ washed with alcohol, dried, weighed, ignited, and weighed again (Palm, *Fr.* 26, 33).

Salts.—The crystalline lactates do not effloresce in the air, but give off water *in vacuo.* They are not decomposed at 150°. They are insoluble in ether and, for the most part, sparingly soluble in cold water.—Ammonium salt forms deliquescent prisms, and gives off NH_3 when exposed to air.—NaA′ (at 140°): amorphous, deliquescent mass, v. sol. water and alcohol, ppd. by ether from its alcoholic solution.—$Na_2C_3H_4O_3$ *i.e.* $CH_3.CH(ONa).CO_2Na$: obtained by the action of sodium on the preceding at 130°. Hard, deliquescent, brittle mass. Decomposed by cold water, with evolution of heat, into NaOH and $NaC_3H_5O_3$. Absorbs CO_2 from the air, forming Na_2CO_3 and sodic lactate. Basic sodium lactate appears to dissolve without decomposition in perfectly dry alcohol. With MeI it gives NaI and $CH_3.CH(OMe).CO_2Na$ (Wislicenus, *A.* 125, 49).—Potassium salt crystallises with difficulty.—$BaA'_2 4aq$ (at 100°):

large cauliflower-like bundles of rectangular needles (Hans Meyer, *B.* 19, 2454). Deliquescent, v. sol. dilute alcohol, insol. absolute alcohol and ether.—$BaH_2A'_4$: crystals, v. sol. water. Not altered by exposure to air.—CaA'_2 5aq: small white mammillated crystals (from water or alcohol). S. 10·5 in the cold. Extremely soluble in boiling water. Sol. hot, nearly insol. cold, alcohol. At 100° it becomes CaA'_2, and at 280° it is converted into $CaC_6H_8O_5$ (Wurtz a. Friedel, *A. Ch.* [3] 63, 134).—$CaH_2A'_4$ 3aq: crystals resembling wavellite; sol. absolute alcohol (Engelhardt a. Maddrell, *A.* 63, 119).—$CaK_2A'_4$: octahedra. Deposits CaA'_2 when dissolved in warm water (Strecker, *A.* 91, 352).—$CaNa_2A'_2$ 2aq: granules (S.).—$CaClA'$ 3aq: prisms, v. e. sol. water (E. a. M.).—$Ca_3(CHO_2)(C_3H_5O_2)Cl_2$ 10aq: from calcium chloride, formate, and lactate (Böttinger, *A.* 188, 329). Long needles.—SrA'_2 3aq: very soluble.—MgA'_2 3aq: prisms, insol. alcohol, less soluble than the corresponding sarcolactate. S. 3·6 in the cold; 16·7 at 100°.—$Al_2A'_6$: triclinic octahedra (Hans Meyer, *B.* 19, 2454).—$AlNa_3A'_6$ 5aq: rectangular prisms and tables.—FeA'_2 3aq: small greenish crystals. S. 2·1 at 10°; 8·5 at 100°. Insol. alcohol.—Ferric lactate is a brown amorphous deliquescent mass, v. sol. water.—MnA'_2 3aq: amethyst-coloured monoclinic crystals, m. sol. cold, v. sol. hot, water.—CoA'_2 3aq: peach-blossom coloured needles, nearly insol. cold, m. sol. boiling water, insol. alcohol.—NiA'_2 3aq: apple-green needles.—ZnA'_2 3aq: shining crusts, or large crystals irregularly grouped. S. 1·07 at 8° (Buff, *A.* 140, 160); 1·8 at 10° (Wislicenus, *A.* 126, 228); 1·9 at 15° (Strecker, *A.* 105, 316); 16·7 at 100°. Almost insol. alcohol, which partly converts it into amorphous ZnA'_2aq, which again takes up 2aq when exposed to the air (Klimenko, *J. R.* 12, 98).—$ZnA'_2N_2H_6$.—$ZnA'_2N_3H_9$ (Lutschak, *B.* 5, 30).—$ZnNa_2A'_4$ 2aq.—CdA'_2: small needles. Anhydrous when deposited from a boiling solution. Insol. alcohol. S. 10 in the cold; 12·5 at 100°.—$BiC_6H_9O_6$ (Brüning, *A.* 104, 194).—CuA'_2 2aq: dark-blue monoclinic tables (Schabus, *J.* 1854, 405). S. 16·7 in the cold; 45 at 100°. S. (alcohol) ·9 in the cold; 4 at 78°. Decomposed at 200° giving aldehyde, lactide, and CO_2 (Engelhardt, *A.* 70, 249).—$CuC_3H_4O_3$: v. sl. sol. water.—$Hg_2A'_2$aq: rose-coloured or crimson crystals, sl. sol. water, obtained by mixing the boiling solutions of mercurous nitrate and sodium lactate (E. a. M).—Prisms of the mercurous salt $Hg_2A'_2$ are also formed by boiling aqueous lactic acid with HgO (Brüning).—$SnC_3H_4O_2$: crystalline powder, insol. water. — PbA'_2: gummy; v. sol. water. — $PbC_3H_4O_3$ (Moldenhauer, *A.* 131, 333). — $Pb_3A'_2O_2$aq: heavy granular pp., formed when lactic acid is mixed with lead acetate and alcoholic NH_3.—$UrOA'$: yellow crystalline crusts. — AgA'aq: silky needles. S. 5 in the cold. V. sol. hot, nearly insol. cold, alcohol.

Nitroxyl derivative $CH_3.CH(ONO_2).CO_2H$. S.G. $\frac{13}{}$ 1·35. Formed by dissolving lactic acid in a mixture of conc. HNO_3 and H_2SO_4, and ppg. with water (Henry, *B.* 3, 532). Thick oil. Sl. sol. water, v. e. sol. ether. Decomposes in the cold into HCy and oxalic acid (Henry, *B.* 12, 1837).

Acetyl derivative $C_5H_8O_4$ *i.e.* $CH_3.CH(OAc).CO_2H$. [167°] (Siegfried). Formed by heating ethyl lactate with AcCl and saponifying the product by heating it with water at 150° for 3 hours (Perkin, *Z.* 1861, 166; Wislicenus, *A.* 125, 60). Formed also by boiling a solution of zinc acetate and sarcolactate or lactate (Siegfried, *B.* 22, 2715). Occurs in extract of meat. Thin needles, v. e. sol. water. Inactive. Volatile with steam. Decomposed by long boiling with water into acetic and lactic acids. Bases quickly effect this decomposition. When first prepared it is soluble in alcohol, but on keeping it becomes insoluble in alcohol, does not then melt below 300°, and is saponified with great difficulty by alkalis. HI produces no β-iodo-propionic acid. — BaA'_2 4aq: brittle gumlike mass, v. sol. water, sol. alcohol.—Copper salt: amorphous deliquescent bluish-green mass.—ZnA'_2: gummy mass. Its solutions become quickly acid, from conversion into acetic acid and zinc lactate.

Benzoyl derivative $C_{10}H_{10}O_4$ *i.e.* $CH_3.CH(OBz).CO_2H$. [112°]. S. ·25 in the cold. Obtained by heating lactic acid with benzoic acid at 180° (Strecker, *A.* 80, 42; 91, 360). Formed also by the action of BzCl on calcium lactate (Wislicenus, *A.* 133, 277). Tables or needles; m. sol. boiling water, v. sol. alcohol and ether. Converted by boiling water into benzoic and lactic acids. When recrystallised from water benzoyl-lactic acid is always accompanied by an oily hydrate $C_{10}H_{10}O_4$ aq, which in dry air is slowly converted into the crystalline acids.—BaA'_2 6aq: thin six-sided plates.—AgA'.

Amide $C_3H_7NO_2$ *i.e.* $CH_3.CH(OH).CONH_2$. [74°]. Obtained by the action of gaseous or alcoholic NH_3 on lactide (Wurtz a. Friedel, *A. Ch.* [3] 63, 108). Formed also by saturating ethyl lactate with ammonia and allowing the liquid to stand (Brüning, *A.* 104, 197); and by heating ammonium lactate in a slow current of dry NH_3 at 130° (Engel, *C. R.* 98, 574). Small prisms, v. sol. water and alcohol. Does not combine with acids or bases, but is decomposed by them on boiling into NH_3 and lactic acid.

Benzoyl derivative of the amide $CH_3.CH(OBz).CONH_2$. [124°]. From benzoyl-lactic ether and alcoholic NH_3 (Wislicenus, *A.* 133, 257). White needles, may be sublimed; sl. sol. water, v. sol. alcohol. Resolved by boiling KOH into lactic and benzoic acids and NH_3. Prolonged treatment with alcoholic NH_3 forms benzamide and lactamide.

Isomeride of the amide $C_3H_7NO_2$. Formed by heating ammonium lactate in a current of dry NH_3 at 100° (Engel, *C. R.* 98, 574). Pale amber-coloured syrup. Decomposes at 200°. In contact with water it immediately forms ammonium lactate.

Ethylamide $CH_3.CH(OH).CO.NHEt$. [48°]. (260°). From lactide and NH_2Et. Crystalline (Wurtz a. Friedel, *A. Ch.* [3] 63, 110). Decomposed by alkalis into ethylamine and lactic acid.

Anilide $C_9H_{11}NO_2$ *i.e.* $CH_3.CH(OH).CO.NHPh$. [58°]. Formed by heating lactic ether with aniline at 150° (Leipen, *M.* 9, 48). Colourless prisms; sl. sol. water, insol. ligroïn, v. sol. ether, chloroform, and alcohol.

o-Toluide $C_{10}H_{13}NO_2$. [72°]. From o-toluidine and lactic ether. Crystalline powder (from benzene). Insol. ligroïn (Leipen, *M.* 9, 50, 51).

p-Toluide $C_{10}H_{13}NO_2$ *i.e.* $CH_3.CH(OH).CO.NHC_6H_4Me$. [102°]. From *p*-toluidine and ethyl-lactate. White needles. V. sl. sol. water.

Cyanamide CN.NH(CO.CH(OH).CH_3). *Lacto-cyanamide.* Formed by dissolving lactide (20 g.) in a strong alcoholic solution of potassic cyanide (16 g.), passing in CO_2 to remove free alkali and evaporating to crystallisation (Mertens, *J. pr.* 125, 33). It forms a silver derivative.

Methyl ether $C_4H_8O_3$ *i.e.* $CH_3.CH(OH).CO_2Me$. (145° i.V.). S.G. $\frac{0}{0}$ 1·1180 (Schreiner, *A.* 197, 1; *B.* 12, 179). Colourless neutral liquid. Combines with $CaCl_2$. Is immediately decomposed by water.

Ethyl ether $C_5H_{10}O_3$ *i.e.* $CH_3.CH(OH).CO_2Et$. *Ethyl lactate.* (154·5° i.V.). S.G. $\frac{0}{0}$ 1·0546. Formed by distilling calcium lactate with $KEtSO_4$ (Strecker, *A.* 81, 247; 91, 355). Formed also by heating lactic acid (dried at 145°) with alcohol (F. a. W.) and by passing alcohol vapour into lactic acid at 175° (Wislicenus, *A.* 125, 58). Colourless liquid, immediately decomposed by water (Schreiner). Forms with $CaCl_2$ the compound $CaCl_2$4EtA′ crystallising in granules. Chloral gives a liquid compound, whence phosphorus pentachloride forms liquid $CCl_3.CHCl.O.CHMe.CO_2Et$. S.G. $\frac{11}{}$ 1·42 (Henry, *Bull. Acad. Roy. Belg.* [2] 37, No. 5). Lactic ether is a weak hypnotic (Pellacani a. Bertoni, *C. C.* 1887, 1149).

Acetyl derivative of the ethyl ether $CH_3.CH(OAc).CO_2Et$. (177°) at 733 mm. V.D. 5·70 (calc. 5·54). S.G. $\frac{17}{17}$ 1·046. From ethyl lactate and AcCl (Wislicenus, *A.* 125, 58). Neutral oil, gradually decomposed by water into alcohol and $CH_3.CH(OAc).CO_2H$. Miscible with alcohol and ether.

Benzoyl derivative of the ethyl ether $CH_3.CH(OBz).CO_2Et$. (288° cor.). From ethyl lactate and BzCl at 100°, or from silver benzoyl-lactate and EtI (Wislicenus, *A.* 133, 272). Oil, miscible with alcohol and ether. Resolved by water at 150° into lactic acid and benzoic ether. Alcoholic NH_3 gives $CH_3.CH(OBz).CONH_2$.

Nitroxyl derivative of the ethyl ether $CH_3.CH(ONO_2).CO_2Et$. (178°). S.G. $\frac{13}{}$ 1·153. From ethyl lactate, HNO_3, and H_2SO_4 (Henry, *B.* 3, 532).

Butyryl derivative of the ethyl ether $CH_3.CH(O.C_4H_7O).CO_2Et$. (208°). S.G. ^{0} 1·024. From α-chloro-propionic ether and potassium butyrate (Wurtz, *A.* 112, 235).

Isopropyl ether $CH_3.CH(OH).CO_2Pr$. (167°) (Silva, *Bl.* [2] 17, 97).

Ethylidene ether $CH_3.CH\genfrac{<}{}{0pt}{}{O.CHMe}{CO.O}\!\!>$. (151°). Formed by heating lactic acid with acetic aldehyde at 150° (Leipen, *M.* 9, 46). Liquid, sl. sol. water. Quickly decomposed by hot water into its components.

Tri-chloro-ethylidene ether

$CH_3.CH\genfrac{<}{}{0pt}{}{O}{CO.O}\!\!>CH.CCl_3$. [45°]. (223°). Prepared by heating syrupy lactic acid with excess of chloral for a short time at 150°, and distilling the product with steam (Wallach, *A.* 193, 1). Colourless crystals, readily sol. alcohol, ether, and CS_2, insol. water.

Methyl derivative $C_4H_8O_3$ *i.e.* $CH_3.CH(OMe).CO_2H$. The Na salt is formed, together with the methyl ether, by treating $CH_3.CH(ONa)CO_2Na$ with MeI. The free acid is a syrup, volatile with steam. It forms an amorphous silver salt $C_4H_7AgO_3$, v. sol. water.

Methyl ether of the methyl derivative $C_5H_{10}O_3$ *i.e.* $CH_3.CH(OMe).CO_2Me$. (135°–138°) (Markownikoff a. Krestownikoff, *A.* 208, 343). From basic sodium lactate $CH_3.CH(ONa).CO_2Na$ and MeI (Wislicenus, *A.* 125, 53).

Ethyl ether of the methyl derivative $C_6H_{12}O_3$ *i.e.* $CH_3.CH(OMe).CO_2Et$. (135·5° i.V.). S.G. $\frac{0}{0}$ ·9906. From α-bromo-propionic ether and NaOMe (Schreiner, *A.* 197, 1). Colourless liquid, nearly insol. water.

Ethyl derivative $C_5H_{10}O_3$ *i.e.* $CH_3.CH(OEt).CO_2H$. *Ethyl-lactic acid.* (195°–198°). Obtained by decomposing its ether $CH_3.CH(OEt).CO_2Et$ with caustic potash or lime. Formed also, together with CH_2I_2 and acrylic acid, by the action of NaOEt on iodoform (Butlerow, *A.* 114, 206; 118, 325; *Bl.* 1861, 9). Liquid, partly decomposed by distillation. Miscible with water, alcohol, and ether, but separated from its aqueous solution by $CaCl_2$ or Na_2SO_4. Decomposes carbonates. Alkalis do not convert it into lactic acid and alcohol. When heated with conc. HIAq there is formed lactic acid and EtI.

Salts.—CaA'_2 2aq: flat prisms, v. sol. water. —AgA′: bunches of slender silky needles (from hot water).

Ethyl ether of the ethyl derivative $C_7H_{14}O_3$ *i.e.* $CH_3.CH(OEt).CO_2Et$. (155° i.V.) (Schreiner, *B.* 12, 179). S.G. $\frac{0}{0}$ ·9498. V.D. 5·05 (calc. 5·06). Formed by the action of NaOEt on α-chloro-propionic ether (Wurtz, *A. Ch.* [3] 59, 169). Formed also by treating lactic ether with sodium and EtI (Wurtz a. Friedel, *A. Ch.* [3] 63, 103). Also from silver ethyl-lactate and EtI. Colourless liquid, nearly insol. water, sol. alchohol and ether. Alkalis convert it into alcohol and ethyl-lactic acid.

Amide of the ethyl derivative $CH_3.CH(OEt).CONH_2$. *Lactamethane.* [63°]. (219°). Formed by allowing $CH_3.CH(OEt).CO_2Et$ to stand a few days with aqueous NH_3 (Wurtz, *A. Ch.* [3] 59, 174). Broad plates, sol. water, alcohol, and ether. Decomposed by distillation with potash into NH_3 and lactic acid.

Phenyl derivative $CH_3.CH(OPh).CO_2H$. *Phenoxy-propionic acid.* [113°]. Formed from α-chloro-propionic acid (25 g.), strong caustic soda (to neutralisation), and sodic phenylate (24 g.). The liquid is evaporated till it becomes thick, dissolved in water, and treated with HCl (L. Saarbach, *J. pr.* 129, 152). Glassy needles (from water). Sl. sol. cold water, volatile with steam, v. sol. hot water, alcohol, and ether. Aqueous solutions give a yellow pp. with $FeCl_3$. Its salts are soluble in water.—NaA′. Exhibits rotatory action while dissolving in water. Deliquescent.—KA′ 1½aq at 130°.—CaA'_2 2aq.—AgA′: sharp needles, blackened by light.

Ethyl ether of the phenyl derivative EtA′. (244°). S.G. $\frac{18}{}$ 1·360. Formed when an alcoholic solution of the acid is allowed to stand.

More rapidly by passing HCl into such a solution.

Amide of the phenyl derivative $CH_3.CH(OPh).CONH_2$. [130°]. Formed from the ether by aqueous ammonia. Crystallises from hot water in long needles. V. sol. alcohol and ether. Dissolves in hot HCl, on cooling crystals of the hydrochloride of the amide separate.

Bromo-phenyl derivative $CH_3.CH(OC_6H_4Br).CO_2H$. *Bromo-phenoxy-propionic acid.* [106°]. Formed by the action of bromine water on a solution of phenylated lactic acid. Crystallised from alcohol. V. sol. alcohol and ether, sl. sol. water. Boiling aqueous NaOH cannot turn out the bromine, hence Br is in the benzene nucleus (Saarbach, *J. pr.* [2] 21, 157).—NaA′. Deliquescent needles.

Thymyl derivative $C_6H_3PrMe.O.CHMe.CO_2H$. Formed by heating thymol with α-chloro-propionic acid in presence of a 50 p.c. solution of KOH, acidifying with HCl, and adding ammonium carbonate (Scichilone, *G.* 12, 48). The acid from synthetical thymol crystallises in prisms [74°], v. sol. alcohol, ether, and chloroform. The acid from natural thymol crystallises in needles [48°], and forms very soluble and amorphous Ba and Ag salts.

p-Benzyl-phenyl derivative $C_6H_5.CH_2.C_6H_4.O.CHMe.CO_2H$. [102°]. From *p*-benzyl-phenol, KOH, and α-chloro-propionic acid (Mazzara, *G.* 12, 264).

Benzyl-p-tolyl derivative $C_6H_5.CH_2.C_6H_3Me.O.CHMe.CO_2H$. [115°]. Formed in like manner (Mazzara). Small crystals, sl. sol. water, v. sol. alcohol and ether. Its solutions give a yellow turbidity with ferric salts and crystalline pps. with lead acetate and $AgNO_3$.

Allophanyl derivative $NH_2.CO.NH.CO.O.CHMe.CO_2H$. [190°]. Formed by passing gaseous cyanic acid into an ethereal solution of lactic ether and saponifying the resulting allophanyl-lactic ether with conc. HClAq at 100° (Traube, *B.* 22, 1572). Minute colourless needles, m. sol. cold, v. e. sol. boiling, alcohol or water. When heated above 190° it splits up into lactic and cyanic acids.—AgA′: white powder, decomposed by boiling water.—PbA'_2: crystalline pp.

Ethyl ether of the allophanyl derivative EtA′. [170°]. Colourless needles, v. sol. hot alcohol and hot water, v. sl. sol. ether. Decomposed by alkalis into CO_2, ammonia, alcohol, and lactic acid. Ammonia yields biuret.

Isoamyl ether $C_5H_{11}A'$. [131°].

Monobasic anhydride $C_6H_{10}O_5$ *i.e.* $CH_3.CH(OH).CO.O.CHMe.CO_2H$. *Dilactic acid.* Formed when aqueous lactic acid is left for several months over sulphuric acid *in vacuo* (Wislicenus, *A.* 164, 181). Requires 1 mol. of KOH for each mol. of $C_6H_{10}O_5$ to neutralise it, but the neutral solution gradually becomes acid from liberation of free lactic acid, potassium lactate being also formed. By heating lactic acid at 140° this anhydride is formed together with lactide. It may also be formed from α-bromo-propionic acid and potassium lactate (Brüggen, *Z.* 1869, 338). It forms amorphous Mg and Ca salts. The ethyl ether $CH_3.CH(OH).CO.O.CHMe.CO_2Et$ (c. 235°). S.G. $\frac{0}{}$ 1·134 is formed by the action of chloro-propionic ether on potassium lactate (Wurtz a. Friedel, *A. Ch.* [3] 63, 112). It is decomposed when heated with water into lactic acid and alcohol.

Di-ethyl ether of the di-basic anhydride $C_{10}H_{18}O_5$ *i.e.* $(CH_3.CH(CO_2Et))_2O$ or $CH_3.CH(OEt).CO.O.CHMe.CO_2Et$. (190° *in vacuo*). Formed by treating α-chloro-propionic ether with $CH_3.CH(ONa).CO_2Et$ at 115° (Brüggen, *A.* 148, 224). Scarcely attacked by conc. KOHAq. Alcoholic KOH gives lactic acid and ethyl-lactic acid. NH_3 in ether forms an oily amide $C_8H_{15}NO_4$, decomposed by KOH giving lactic and ethyl-lactic acids.

Neutral anhydride $C_6H_8O_4$ *i.e.*

$$CH_3.CH\genfrac{<}{>}{0pt}{}{CO.O}{O.CO}CH.CH_3.$$ *Lactide.* [124·5°]. (255°). V.D. 4·81 (calc. 4·96) (Henry, *B.* 7, 753). Formed by the dry distillation of lactic acid (Gay-Lussac a. Pelouze, *A.* 7, 43; Pelouze, *A.* 53, 116; Engelhardt, *A.* 70, 243; Wurtz a. Friedel, *A. Ch.* [3] 63, 101). Prepared by passing dry air through lactic acid at 150° (Wislicenus, *A.* 167, 318). Monoclinic tables (from alcohol). May be sublimed. V. sl. sol. hot water, but gradually converted thereby into lactic acid. Bases quickly convert it into lactic acid. Ammonia gives lactamide. Ethylamine gives the ethylamide of lactic acid. $CH_3.CH(OEt).CO_2Et$ forms a compound $C_{13}H_{22}O_7$ (270°) decomposed by potash into alcohol and lactic acid.

Nitrile C_3H_5NO *i.e.* $CH_3.CH(OH).CN$. *Aldehyde cyanhydrin.* (183°). Formed in the cold by allowing a mixture of aldehyde (1 mol.) and anhydrous HCy to stand for 9 days (Maxwell Simpson a. Gautier, *Bl.* [2] 8, 277). Liquid, not solidified at −21°. Partially decomposed into its components by distillation. Miscible with water, alcohol, and ether. Aqueous KOH forms KCy and aldehyde (or aldehyde-resin). Conc. HClAq acts violently upon it; at 0° the products are lactic acid and NH_4Cl.

Sarcolactic acid $C_3H_6O_3$ *i.e.* $CH_3.CH(OH).CO_2H$. *Paralactic acid* (Heintz, *P.* 75, 391). $[\alpha]_D = 3·5°$. Occurs in muscular tissue, thymus and thyroid gland, urine after much exercise, spleen, lymphatic glands, and in pig's bile (Liebig, *A.* 62, 278, 326; Wislicenus, *A.* 167, 302; Strecker, *A.* 123, 354; Colasanti a. Moscatelli, *H.* 12, 416; *G.* 17, 548; 18, 548; Marceuse, *B.C.* 1887, 92; Nebelthau, *Zeit. Biol.* 25, 123; Hirschler, *H.* 11, 41; Gleiss, *Pf.* 41, 69). Sarcolactic acid is absent from living blood, but occurs in blood after death (Salomon, *Virchow's Archiv*, 113, 356; *cf.* Berlinerblau, *C. C.* 1888, 757; Vissokovitch, *C. C.* 1888, 117). Sarcolactic acid may occur sometimes along with ordinary lactic acid as a product of fermentation (Maly, *B.* 7, 1567). Its presence is then due to *micrococcus acidi paralactici*, which can convert glucose into sarcolactic acid (Nencki a. Sieber, *M.* 10, 532). Sarcolactic acid is formed in the fermentation of inosite by cheese (Helger, *A.* 160, 336). It is also formed by the action of nitrous acid on the amido-propionamide present in urine. A dextro-

rotatory lactic acid is formed by the action of *Penicillium glaucum* on ordinary ammonium lactate (Lewkovitch, *B.* 16, 2720).

Preparation.—1. Chopped flesh is exhausted with cold water; the extract mixed with baryta-water; the albumen coagulated by boiling and removed by filtration; and the clear liquid concentrated by evaporation. Sulphuric acid is added to the syrupy residue, and it is shaken with ether, which leaves sarcolactic acid when evaporated.—2. Extract of meat (1 pt.) is dissolved in warm water (4 pts.) and ppd. with 90 p.c. alcohol. The filtrate is evaporated to a syrup, mixed with 4 pts. of alcohol, filtered, evaporated, acidified by H_2SO_4 and extracted with ether (Klimenko, *J. R.* 12, 17; *Bl.* [2] 34, 321).

Properties.—Dextrorotatory syrup, forming lævorotatory salts. Resembles ordinary lactic acid in its reactions. In a dry atmosphere it changes in the cold to a lævorotatory anhydride $[\alpha]_D = c. -86°$. At 140° it forms ordinary lactide, whence water produces ordinary inactive lactic acid (Strecker, *A.* 105, 313).

Reactions.—1. Hot dilute *sulphuric acid* splits it up into formic acid and aldehyde.—2. *Chromic acid mixture* gives CO_2 and acetic acid.

Salts.—CaA'_2 4aq (Engelhardt, *A.* 65, 359). S. 8 in the cold. V. sol. boiling water and alcohol.—CaA'_2 5aq changes into CaA'_2 5aq on recrystallisation.—MgA'_2 4aq. More soluble in water and alcohol than ordinary magnesium lactate.—NiA'_2 3aq.—ZnA'_2 2aq. Forms more distinct crystals than ordinary zinc lactate. S. (of ZnA'_2 2aq) 5·7 at 14·5°; the solubility of ordinary zinc lactate being 1·7 (Wislicenus). S. (98 p.c. alcohol) ·104.—ZnA'_2 3aq. Ppd. by adding alcohol to an aqueous solution of the zinc salt.—AgA' $\frac{1}{2}$aq: flat needles.

Ethyl ether EtA'. $[\alpha]_D = -14·2°$. From the silver salt and EtI (Klimenko).

Chloro-lactic acid *v.* Chloro-oxy-propionic acid.

Chloride of lactic acid *v. Chloride* of α-Chloro-propionic acid.

LACTIDE *v. Neutral anhydride* of Lactic acid.

LACTIM. A compound of the form

$$R''\left<\begin{matrix}C.OH\\ \| \\ N\end{matrix}\right. \quad \text{(Baeyer, } B. \text{ 15, 2093).}$$

LACTIMIDE C_3H_5NO *i.e.*

$$CH_3.CH\left<\begin{matrix}CO\\NH\end{matrix}\right>. \quad [275°].$$

Produced together with ethylamine and CO_2 by heating alanine in dry HCl at 190° as long as water comes off (Preu, *A.* 134, 372). The brown amorphous product is treated with lead hydroxide and H_2S and recrystallised from alcohol. Colourless needles; may be sublimed. V. sol. water and alcohol. Has a bitter taste. Its solution does not dissolve Ag_2O or give a pp. with $ZnCl_2$ or $AgNO_3$.

LACTO-ALBUMEN *v.* Milk.

LACTO-ALBUMOSE *v.* Milk.

LACTO-BIONIC ACID. $C_{12}H_{22}O_{12}$. Formed by treating a solution of milk sugar (1 pt.) in water (7 pts.) with bromine (1 pt.) at ordinary temperatures for some days; the bromine is next removed by a stream of air and H_2S; the HBr is removed with white lead followed by Ag_2O and the metals with H_2S; on treating the syrup so obtained with glacial acetic acid the lacto-bionic acid is left. The product is purified by conversion into lead salt, with specially prepared basic lead acetate, and decomposition of the same with H_2S (Emil Fischer a. Jacob Meyer, *B.* 22, 362). Colourless syrup of strong acid reaction, v. sol. water, v. sl. sol. alcohol, insol. ether. Shows no tendency to crystallise. Does not reduce alkaline copper solutions even on boiling. On warming a short time with dilute mineral acids it splits up into galactose and gluconic acid.

$$C_{12}H_{22}O_{12} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_7.$$

LACTOCYANAMIDE *v.* Lactic acid, p. 112.

LACTONES. Anhydrides of oxy-acids formed by elimination of water between the hydroxyl and carboxyl groups, both being in the same carbon chain. The name is derived from *lactide* which, until its vapour density had been determined, was written $CH_3.CH\left<\begin{matrix}O\\CO\end{matrix}\right>$. Lactones are usually derived from γ- or from δ- oxy-acids. The formula $R''R'C\left<\begin{matrix}CH_2.CH_2\\O.CO\end{matrix}\right>$ represents a γ-lactone, while $R''R'C\left<\begin{matrix}CH_2.CH_2\\O.CO\end{matrix}\right>CH_2$ is a δ-lactone (Fittig, *A.* 200, 21; 208, 67; 216, 52).

Formation.—1. γ-Oxy-acids split up in the cold, and immediately on heating their aqueous solution into water and a γ-lactone.—2. Formed by boiling their carboxylic acids with dilute H_2SO_4 (Erdmann, *A.* 228, 176).—3. From ethers of γ-oxy-acids on distillation, alcohol being split off, *e.g.* oxy-iso-caproic ether (Bredt), oxy-valeric ether (Kissling).—4. From unsaturated acids (*v. A.* 227, 8, 26), *e.g.*:

$$CH_2:CH.CH(CO_2H)_2 = CO_2 + \begin{matrix}CH_2.CH_2.CH_2\\ | \qquad\qquad | \\ O \text{———} CO\end{matrix}$$

Properties.—Volatile liquids, neutral to litmus. Volatile with steam.

Reactions.—1. γ-Lactones do not take up water to form an oxy-acid by mere boiling. On the other hand most δ-lactones in presence of water, cold or hot, are partially converted into acid, and tend to assume equilibrium with 65 p.c. of lactone to 35 p.c. of acid (Fittig a. Wolff, *A.* 216, 137; Hantzsch, *A.* 222, 28).—2. All lactones are converted into salts of the corresponding oxy-acids by boiling with aqueous solutions of alkalis, alkaline earths, and sometimes even with $CaCO_3$ (Fittig, *A.* 208, 116). 3. All lactones form compounds with NH_3, which easily split up into their components (Wolff, *A.* 229, 278). These compounds are probably acid amides.—4. No lactone at present known reacts with hydroxylamine, but a few aromatic lactones readily react with phenyl-hydrazine (*e.g.* phthalide). Hence the fact of an oxygen compound reacting with phenyl-hydrazine cannot be taken (as previously assumed) as a proof of its aldehydic or ketonic nature. This can only be proved by its behaviour towards hydroxylamine (V. Meyer a. Münchmeyer, *B.* 19, 1706). The compound formed with phthalide appears to be $HO.CH_2.C_6H_4.CO.N_2H_2Ph$ being formed by direct addition (Wislicenus, *B.* 20, 401).—5. Lactones (1 mol.) appear to react with oxalic ether (1 mol.) in presence of NaOEt

(1 mol.). Phthalide gives $C_{12}H_{10}O_5$ [122°] and valerolactone also gives a crystalline compound (Wislicenus, *B.* 20, 2061).

Lactones are for the most part described in this Dictionary under the oxy-acids of which they are the anhydrides.

LACTONIC ACID *v.* Galactonic acid.

Lactonic acids. Acids which are at the same time lactones. When warmed with alkalis they give rise by assimilation of water to acids of higher basicity.

LACTONITRILE *v. Nitrile* of Lactic acid.

LACTO-PROTEÏN *v.* Milk.

LACTOSE or *Milk sugar v.* Sugar and Milk.

LACTOSIN $C_{36}H_{62}O_{31}$. Occurs in the roots of all the caryophyllaceæ, being most conveniently obtained from *Silene vulgaris* (A. Meyer, *B.* 17, 685). White amorphous powder (anhydr.), $[\alpha]_D = +168$; or small glistening crystals $(+H_2O)$, $[\alpha]_D = +211·7$. It forms gummy solutions with water, but is sparingly soluble in alcohol. The aqueous solution of the crystallised lactosin gives no pps. with neutral or basic lead acetate, although a pp. is produced by lead acetate and NH_3. Fehling's solution is not reduced on short boiling. By boiling with dilute H_2SO_4 it is inverted into lactose and a new sugar.

LACTUCARIUM. A brownish viscid substance obtained by evaporating juice which exudes from incisions in the leaves and stem of certain species of lettuce, especially *Lactuca virosa.* It has an odour resembling opium and acts as a narcotic. According to Ludwig (*Ar. Ph.* [2] 7, 129) it contains (50 p.c. of) 'lactucone' $C_{40}H_{64}O_3$, a crystalline substance [150°–160°] soluble in boiling alcohol, 'lactucic acid,' lactucin, a wax, and oxalic acid. According to Hesse (*A.* 234, 243) lactucarium contains the acetyl derivatives of (α)- and (β)-lactucerol.

LACTUCERIN $C_{40}H_{64}O_3$ (L.), or $C_{28}H_{44}O_2$ (K.), or $C_{38}H_{62}O_3$ (H.). *Lactucone.* [210°]. Obtained by washing lactucarium with benzene and extracting the residue with boiling alcohol; the crystals obtained may be purified by shaking their ethereal solution with aqueous KOH, and ppg. by the addition of alcohol and water (Lenoir, *A.* 60, 83; Kassner, *A.* 238, 220). Lactucerin so prepared forms minute white needles [200°], but after sublimation in CO_2 it melts at 210°. On fusion with KOH it gives lactucol $C_{13}H_{20}O$, hydrogen, and acetic acid. It is dextrorotatory. According to Hesse, lactucerin consists of the mono-acetyl derivatives of (α)- and (β)-lactucerol. From the milk juice of *lactuca canadensis*, by crystallising from hot alcohol. Flowers (*Ph.* [3] 10, 44) obtained a 'lactucerin' [89°] crystallising in colourless needles.

Lactucone $C_{14}H_{24}O$(?). [296°]. Microscopic needles. Insoluble in water, difficultly soluble in alcohol. Occurs in French lactucarium from *Lactuca altissima*, from which it is extracted with 90 p.c. alcohol. Acetic anhydride does not act upon it even at 200°. By distillation with P_2S_5 it gave a hydrocarbon of the constitution $C_{14}H_{22}$, boiling between 247°–252° (Franchimont, *B.* 12, 10).

Lactucol $C_{13}H_{20}O$. [162°]. Obtained by fusing lactucerin with KOH (Kassner, *A.* 238, 224). Needles. Dextrorotatory; $[\alpha]_D = 46°$.

Acetyl derivative $C_{13}H_{19}AcO$. [200°]. Like lactucol and lactucerin its solutions in ether, chloroform, and CS_2 are dextrorotatory; $[\alpha]_D = 68°$.

(α)-**LACTUCEROL** $C_{36}H_{60}O_2$. [166°–181°]. Obtained by exhausting lactucarium with ligroïn and extracting the residue with alcohol. The crystals so obtained are saponified by alcoholic potash, and the product ppd. with water. The pp. is recrystallised from alcohol, from which (α)-lactucerol separates first (Hesse, *A.* 234, 245; 244, 268).

Properties.—Crystallises from 90 p.c. alcohol in silky needles (containing 2aq). From chloroform or ether it separates in anhydrous crystals. Insol. water and alkalis. It melts at 162°, but after purification by conversion into its di-acetyl derivative and saponification of the product its melting-point is higher. Conc. H_2SO_4 colours its solution in chloroform red. It absorbs Br with evolution of HBr. It is dextrorotatory; in a 2·3 p.c. solution in chloroform $[\alpha]_D = 76·2$ at 15°. It may be distilled in a current of CO_2.

Acetyl derivative $C_{36}H_{59}AcO$. [202°–207°]. Occurs in lactucarium, and is formed by heating (α)-lactucerol for a short time with Ac_2O at 80°. Small plates, m. sol. cold alcohol, v. sol. ether. Dextrorotatory.

Di-acetyl derivative $C_{36}H_{58}Ac_2O$. [198°–200°]. From (α)-lactucerol and Ac_2O by boiling for 2 hours. Satiny plates. In a 1 p.c. solution in chloroform $[\alpha]_D = 63·6$ at 15°.

Di-propionyl derivative $C_{36}H_{58}(C_3H_5O)_2O_2$. [152°]. Minute needles (from alcohol), v. e. sol. $CHCl_3$ and ether.

Di-benzoyl derivative $C_{36}H_{58}Bz_2O_2$ [156°]. White crystals, insol. water, v. sol. ether and chloroform, sl. sol. alcohol. Saponified by alcoholic potash.

(β)-Lactucerol $C_{36}H_{60}O_2$. $[\alpha]_D = 38$ at 15° in a 4 p.c. solution in chloroform. Occurs as a mono-acetyl derivative in lactucarium, and separated from its (α)-isomeride by crystallisation from alcohol. Long silvery needles (from ether or chloroform). Separates from alcohol as a gelatinous mass (containing 2aq). More soluble in alcohol, and less dextrorotatory than its isomeride.

Acetyl derivative $C_{36}H_{58}Ac_2O$. [230°]. Plates (from alcohol). Less sol. alcohol and ligroïn than its isomeride.

LACTUCIC ACID. Obtained from the juice of *Lactuca canadensis* after separating 'lactucerin,' adding water, ppg. with lead acetate, decomposing the lead salt with H_2S and evaporating (Flowers, *Ph.* [3] 10, 44). Brownish-green amorphous substance, with acrid, bitter taste. Sol. alcohol, insol. petroleum spirit, ether, and chloroform. Ludwig (*J.* 1847, 824) and Walz (*N. Jahr. Pharm.* 15, 118) obtained a substance ($C_{10}H_{58}O_{19}$?) called lactucic acid by triturating lactucarium (1 pt.) with dilute H_2SO_4 (1 pt.), adding alcohol (5 pts. of 84 p.c.), filtering, shaking the filtrate with slaked lime, decolourising with animal charcoal, evaporating, and crystallising the residue from boiling water. Light yellow amorphous mass, gradually becoming crystalline. Its solutions are coloured wine-red by alkalis, and reduce boiling Fehling's solution.

LACTUCIN $C_{60}H_{18}O_{13}$ or $C_{22}H_{26}O_7$ or $C_{22}H_{28}O_8$. S. 1·25 in the cold. Occurs in the juice of common lettuce (*Lactuca sativa*) and of *Lactuca*

altissima (Aubergier, *B. J.* 24, 522; *A.* 44, 299; Walz, *A.* 32, 85; *N. Jahr. Pharm.* 15, 118; Ludwig a. Kromayer, *Ar. Ph.* [2] 111, 1; Kromayer, *Ar. Ph.* [2] 105, 3; Buchner, *Rep. Pharm.* 43, 1; Flowers, *Ph.* [3] 10, 44). Obtained by macerating the dried juice with hot water ($1\frac{1}{2}$ pt.) for four days, pressing the mass, boiling the residue with water, and ppg. the filtrate with lead subacetate, removing excess of lead from the filtrate by H_2S, and evaporating. Pearly scales (from alcohol). M. sol. alcohol and HOAc, sl. sol. ether. Conc. HNO_3 turns it brown. Its solutions are not ppd. by ordinary reagents.

LACTUCOPICRIN $C_{44}H_{61}O_{21}$. An amorphous very bitter substance which remains in the mother-liquor in the preparation of lactucin (Kromayer, *Die Bitterstoffe*, 1861; Flowers, *Ph.* [3] 10, 222). Sol. water and alcohol, its solutions not being ppd. by lead salts.

LACTURAMIC ACID *v.* URAMIDO-PROPIONIC ACID.

LACTYL CHLORIDE is the *chloride* of α-CHLORO-PROPIONIC ACID.

LACTYL-THIO-UREA $CS\left\langle\begin{array}{l}NH.CH.CH_3\\ \quad\ \ |\\ NH.CO\end{array}\right.$.

From thio-urea and α-chloro-propionic ether at 100° (Freytag, *J. pr.* [2] 20, 380). Crystalline.

LACTYL-UREA $C_4H_6N_2O_2$ *i.e.* $CO\left\langle\begin{array}{l}NH.CH.CH_3\\ \quad\ \ |\\ NH.CO\end{array}\right.$. *Methyl-hydantoïn.* [140°] (H.); [145°] (Urech, *B.* 6, 1113). Formed by treating aldehyde-ammonia with crude KCy and hydrochloric acid $CH_3CH(OH)NH_2 + HCN + HCNO = NH_3 + C_4H_6N_2O_2$ (Heintz, *A.* 169, 120). Formed also by heating uramido-propionic acid. Prisms, or cauliflower-like tufts (containing aq); v. sol. water and alcohol, nearly insol. ether. May be sublimed. Tastes bitter. Neutral in reaction. Boiling baryta water converts it into uramido-propionic acid. Heating with barium hydrate at 100°–140° gives alanine. Pure HNO_3 gives a quantitative yield of a nitro-derivative, but no gas is evolved (Franchimont, *R. T. C.* 6, 217).—$AgC_4H_5N_2O_2$, formed by treating lactyl-urea with moist Ag_2O. Insol. water, sol. NH_3Aq. Ppd. as a white powder by adding HNO_3 to its ammoniacal solution.

LÆVULAN $C_6H_{10}O_5$. [250°]. $[\alpha]_D = -221°$. Occurs in an impure condition in the residues obtained from desugarising molasses by Steffen's process (Lippmann, *B.* 14, 1509). White amorphous powder. Sol. hot water, the solution gelatinises on cooling. By long boiling it becomes much more soluble and loses its power of gelatinising. Insol. alcohol. It does not reduce Fehling's solution but produces a blue pp. By HNO_3 it is oxidised to mucic acid. Dilute H_2SO_4 at 120° converts it into levulose.

LÆVULIN $C_{12}H_{20}O_{10}$ (dried at 110°). A substance resembling dextrin, contained in the juice of the tubers of the Jerusalem artichoke (*Helianthus tuberosus*) and of *Dahlia variabilis*, and in oak bark (Ville a. Joulie, *Bl.* [2] 7, 262; Popp, *A.* 156, 181; Dieck a. Tollens, *A.* 198, 228; *B.C.* 1879, 275; Etti, *B.* 14, 1826; Lefranc, *J. Ph.* [5] 2, 216; Reidemeister, *J. Th.* 1881, 68). Prepared by ppg. the juice of artichokes with lead acetate, filtering, removing excess of lead by H_2S, neutralising with $MgCO_3$, filtering and evaporating. The residue is extracted with alcohol, until it is optically inactive. It is then extracted with absolute alcohol, which leaves inulin undissolved, and ppd. with ether.

Properties.—Amorphous deliquescent mass; optically inactive, but becomes lævorotatory on boiling with dilute HCl, being split up into lævulose and glucose. V. sol. water and dilute alcohol, sl. sol. absolute alcohol, insol. ether. Has an insipid taste. Turns brown at 140° forming caramel. Not ppd. by lead subacetate. Reduces Fehling's solution after long boiling. Dilute HNO_3 gives oxalic acid and saccharic acid. Alkalis do not turn it brown. First hydrolysed by yeast and then undergoes alcoholic fermentation. Lævulin prevents the ppn. of ferric and cupric salts by alkalis. $AgNO_3$ gives a white pp. blackened on heating.—$K_2C_{12}H_{18}O_{10}$: ppd. by adding alcoholic KOH to its alcoholic solution. — $Ba_2C_{12}H_{16}O_{10}$ aq: amorphous. — $Pb_2C_{12}H_{16}O_{10}$ aq: amorphous; ppd. by adding an alcoholic solution of lead subacetate to an alcoholic solution of lævulin.

LÆVULINIC ACID *v.* β-ACETYL-PROPIONIC ACID.

LÆVULOSE *v.* SUGAR.

LANTHANUM. La. At. w. 138·2. Mol. w. unknown. S.G. 6·163. Melts between M.P. of Sb (450°) and that of Ag (950°) (Hillebrand a. Norton, *P.* 156, 466). S.H. ·04485 (H. a. N., *P.* 158, 71). S.V.S. 22·4. Chief lines in emission-spectrum 5183, 4921, 4920 in the green; 4824, 4655, 4558 in the blue; 4522, 4330, 4268 in the indigo; 4238, 4196, 4086, 4077 in the violet (Thalén). In 1803 Klaproth separated a new earth from a Swedish mineral; the earth was examined by Hisinger and Berzelius and called by them *ceria* (from the planet *Ceres* then recently discovered). In 1839 Mosander showed that ceria contained two oxides (*P.* 46, 648): the name ceria was retained for one, and the other was given the name *lanthana* (λανθάνειν = to be concealed). In 1841 Mosander discovered that lanthana was a mixture of two oxides (*v. P.* 60, 297); one of these he called lanthana and the other didymia (δίδυμος = twofold).

Occurrence.—As silicate, with silicates of Ce and Di, in *cerite*, *gadolinite*, *orthite*, &c. (Rammelsberg, *P.* 107, 631). *Lanthanite*, from Bethlehem in Pennsylvania, U.S., is a carbonate of La and Di (Lawrence Smith, *Am. S.* [2] 18, 378). La-containing minerals occur in small quantities in a few localities.

Preparation.—The mixed oxides of Ce, La, and Di are separated from *cerite* by treatment with H_2SO_4, &c., as described under CERIUM (vol. i. p. 723); the oxides are dissolved in HNO_3Aq, the solution is evaporated to dryness the residue is heated to full redness until pale yellow, and then treated with boiling dilute HNO_3Aq in which nitrates of La and Di dissolve while basic Ce nitrate remains insoluble. There are various ways of separating La from Di in the nitric acid solution. The hydrated oxides may be obtained by ppn. with NH_3Aq; the pp. is dissolved in H_2SO_4Aq, and the mixed sulphates are obtained by crystallisation; the sulphates are dried and powdered; 1 part is dissolved in small successive portions in 6 parts

water at 2°–3°; the solution is then heated to c. 40° when $La_2(SO_4)_3$ separates nearly free from $Di_2(SO_4)_3$. The $La_2(SO_4)_3$ may be purified by re-solution in ice-cold water and heating to 40°, the operations being repeated until the sulphate is perfectly white and shows no Di lines in the spectrum. Or the solution of $La_2(SO_4)_3$ may be ppd. by oxalic acid, the pp. strongly heated, dissolved in HNO_3Aq, and fractionally ppd. by NH_3Aq; the ppn. must be effected from very dilute solutions by means of very dilute NH_3Aq; the first third of the pp. contains most of the Di oxide; ppn. is continued so long as the pp. shows Di lines in the spectrum. This method gives good results when comparatively much La is present (Mosander, *l.c.*; Bunsen a. Jegel, *P.* 155, 377), but it is slow and laborious. Marignac (*J. pr.* 48, 406) adds excess of HNO_3Aq to the solution of the nitrates of La and Di, heats, and adds oxalic acid; the pp. dissolves; when crystallisation begins the solution is allowed to cool, and is then poured off from the pp. which is rich in Di oxalate; these operations are repeated; a very acid solution of La salt is finally obtained from which NH_3Aq ppts. $La_2O_3.xH_2O$. This method is recommended when much Di is present with little La.

The method of Von Welsbach (*Sitz. W.* 92 [2nd part], 317) was found very good by Robinson (*priv. comm.*). A large quantity of the mixed nitrates of Ce and La obtained from *cerite* after separating basic Ce nitrate (*v.* vol. i. p. 723) is mixed with the necessary quantity of NH_4NO_3, about $\frac{1}{10}$th part conc. HNO_3Aq is added, and the liquid is evaporated until small crystals appear on the surface, a little water is then added, and crystallisation is allowed to proceed for about 24 hours; the crystals are drained and washed with a little HNO_3Aq which is added to the mother-liquor; the mother-liquor is evaporated and crystallised; the liquor from this is again evaporated, and so on until 6-8 fractions are obtained. The first fraction contains almost all the La. By fractionating the middle fraction, placing the first fractional pp. in the former first fraction, and repeating this process a few times, pure $La(NO_3)_3$ is obtained. For other methods of separating La salts from salts of Ce and Di *v.* Hermann, *J. pr.* 82, 385; Erk, *Z.* [2] 7, 100; Cleve, *Bl.* [2] 21, 196, 246.

La_2Cl_6 is obtained by dissolving the pp. of $La_2O_3.xH_2O$ (obtained as described above) in HClAq, adding NH_4Cl, evaporating to dryness, and heating strongly in a covered crucible. By reducing La_2Cl_6 by heating with K and washing out KCl in alcohol, metallic La is obtained. Hillebrand a. Norton obtained approximately pure La by electrolysing La_2Cl_6 covered with a fused mixture of KCl and NaCl, using a thick iron wire as negative electrode and a battery of 4 Bunsen's cells (*P.* 156, 466; *cf.* Bunsen, *P.* 155, 633).

Properties and Reactions.—White metal; fairly malleable and ductile; rather harder than Ce. Oxidises rapidly in dry air, but burns only at temperature considerably higher than that at which Ce burns. Decomposes cold water slowly, hot water rapidly. Easily dissolved by acids, including cold conc. HNO_3, which scarcely acts on Ce.

The atomic weight of La has been determined (1) by converting the oxide into the sulphate and *vice versâ* (Rammelsberg, *P.* 55, 65; Marignac, *A. Ch.* [3] 27, 228; [4] 30, 67; Holzmann, *J. pr.* 75, 348; Czudnowicz, *J. pr.* 80, 33; Hermann, *J. pr.* 82, 395; Zschiesche, *J. pr.* 104, 174; Erk, *Z.* [2] 7, 106; Cleve, *Bl.* [2] 31, 196; Brauner, *C. J.* 41, 75; Crookes, *Pr.* 38, 414; (2) by analysing La iodate (Holzmann, *J. pr.* 75, 349); (3) by estimating Cl in La chloride (Hermann, *J. pr.* 82, 395); (4) by converting La carbonate into oxide (Hermann, *l.c.*); (5) by determining S.H. of La (Hillebrand a. Norton, *P.* 158, 71); (6) by considering the chemical relations of La with other elements in the light of the periodic law.

The at. w. of La was taken for many years as c. 92·2; the oxide was formulated LaO and the chloride $LaCl_2$. Mendelejeff (*v. C. N.* 41, 49) proposed to multiply the usually accepted at. w. by 2, and to regard the oxide as LaO_2; by doing this he placed La in Group IV. along with Ce. As the properties of La salts were not much known when Mendelejeff's memoir was published, he did not strongly press the arguments in favour of the position assigned by him to La. Fuller investigation showed that the usually accepted at. w. of La should be increased by one half, that the oxide should be regarded as similar to the oxides of the earth-metals (M_2O_3), and that La should be placed in Group III. along with Al, Ga, Sc, &c. (*v.* EARTHS, METALS OF THE, vol. ii. p. 424).

La is distinctly metallic in its chemical relations; it forms the oxide La_2O_3 and there are indications of the existence of a higher oxide; the chloride is La_2Cl_6 or $LaCl_3$. La forms several salts of the form LaX_3, $X = NO_3, \frac{SO_4}{2}, \frac{PO_4}{3}$, &c.; a few double salts and one or two basic salts are known. The investigation of the La compounds shows that this metal is to be placed with the metals of the earths (Group III.); it is more closely related to the even series members of the group (Sc, Y, and Yb) than to the odd series members (Al, Ga, In, Tl). The strongly basic character of La_2O_3 marks the connection of La with the alkaline earths and alkali metals. The examination of La compounds is yet far from complete (*cf.* METALS, RARE).

Detection and Estimation.—Most of the La salts are colourless; the soluble salts have an astringent, sweetish taste; solutions of La salts do not show any absorption-bands. Alkalis, NH_4HS, and KCN, form gelatinous pps. insoluble in excess of pptant. Alkali carbonates ppt. $La_2(CO_3)_3$; $BaCO_3$ forms a pp. without warming; $H_2C_2O_4$ forms a white pp. at first curdy, then crystalline, more soluble in acids than the oxalates of Ce and Di; $Na_2S_2O_3$ does not produce any pp. La salts do not colour beads of borax or microcosmic salt.

La may be estimated as La_2O_3 or $La_2(SO_4)_3$. La_2O_3 is obtained (1) by ppg. with NH_3Aq, washing as rapidly as possible with water containing NH_3 (to prevent formation of La_2CO_3 and partial solution of La), solution in HNO_3Aq, re-ppn. by NH_3Aq, washing with NH_3Aq, and strongly heating; (2) by ppg. $La_2(C_2O_4)_3$ by addition of $H_2C_2O_4$ and standing, washing, and heating to white heat. $La_2(SO_4)_3$ is obtained by ppg. with

NH_3Aq, as above, dissolving in warm dilute H_2SO_4Aq, evaporating to dryness at 100°, and gradually heating to redness.

Lanthanum, arsenate of. $La_2(HAsO_4)_3$; and **arsenite of**, $La_2(HAsO_3)_3$; *v.* Smith, *A.* 191, 331.

Lanthanum, borate of (? $2La_2O_3.B_2O_3$); obtained, along with crystals of La_2O_3, by dissolving La_2O_3 in molten borax (Nordenskjöld, *J. pr.* 85, 431).

Lanthanum, bromide of. $La_2Br_6.14H_2O$, or $LaBr_3.7H_2O$. Colourless crystals, e. sol. water or alcohol; obtained by dissolving $La_2O_3.xH_2O$ in HBrAq and evaporating (Cleve, *Bl.* [2] 39, 151; 43, 56). By the action of Br vapour on La_2O_3, the oxybromide LaOBr is obtained (Frerichs a. Smith, *A.* 191, 331). *Double salts* are described by Cleve (*l.c.*):— $La_2Br_6.2AuBr_3.18H_2O$; $La_2Br_6.3ZnI_2.27H_2O$; also by F. a. S. (*l.c.*); $La_2Br_6.3NiBr_2.18H_2O$; and $La_2Br_6.3ZnBr_2.39H_2O$.

Lanthanum, carbide of. A carbide of La is said to be produced by heating the oxalate or formate in absence of air; it is described as similar to, but more easily acted on by acids than, Ce carbide (Delafontaine, *C. N.* 11, 253).

Lanthanum, chloride of. La_2Cl_6 or $LaCl_3$. A white crystalline mass, e. sol. water or alcohol. Obtained by adding NH_4Cl to a solution of $La_2O_3.xH_2O$ in HClAq, evaporating to dryness, and heating in a closed crucible until all NH_4Cl is volatilised (Hermann, *J. pr.* 82, 406; Hillebrand a. Norton, *P.* 158, 71). Mosander (*P. M.* 23, 241) says that $LaCl_3$ can be obtained by evaporating $La_2O_3.xH_2O$ in HClAq to dryness, and heating the residue in a stream of HCl gas.

By slowly evaporating $La_2O_3.xH_2O$ in HClAq, large colourless triclinic crystals of $LaCl_3.7H_2O$ are obtained. *Double salts* are described by Smith (*A.* 191, 331), and Cleve (*Bl.* [2] 21, 196; 39, 151):—$M.9HgCl_2.24H_2O$; $M.3PtCl_4.24H_2O$, $M.2PtCl_4.26H_2O$; $M.3AuCl_3.21H_2O$, $M.2AuCl_3.20H_2O$ ($M = La_2Cl_6$). Oxychlorides are obtained by heating the hydrated chloride in air, and by the action of Cl on La_2O_3 (*v.* LANTHANUM, OXYCHLORIDES OF).

Lanthanum, chromate of. $La_2(CrO_4)_3.8H_2O$; *v.* Smith, *A.* 191, 355.

Lanthanum, cyanide of. $LaCy_3$; *v.* vol. ii. p. 341.

Lanthanum, fluoride of. $La_2F_6.H_2O$. A gelatinous pp. by adding HFAq to solution of La acetate (Cleve, *Bl.* [2] 39, 151; 43, 56). From solution of La sulphate, Smith obtained a pp. of $La_2F_6.3HF$ (*A.* 191, 331). According to Marignac, H_2SiF_6 ppts. La_2F_6 from La salts (*J. pr.* 48, 406).

Lanthanum, hydroxide of. $La_2O_6H_6$, or LaO_3H_3; may also be regarded as *hydrated oxide* $La_2O_3.3H_2O$. A white gelatinous pp. by adding KOHAq or NaOHAq to solution of a La salt (NH_3Aq ppts. basic compounds). Also produced by action of warm water on La_2O_3. $La_2O_6H_6$ is a strongly basic hydroxide; it turns red litmus blue, decomposes NH_4ClAq on warming with evolution of NH_3, absorbs CO_2 from the air; reacts with acids to form salts

$LaX_3\left(X = NO_3, \frac{SO_4}{2}, \frac{PO_4}{3}, \&c.\right)$. Thomsen gives

the heat of neutralisation with H_2SO_4Aq and HClAq as $[La^2O^6H^6, 3H^2SO^4Aq] = 82,320$; $[La^2O^6H^6, 6HClAq] = 74,970$ (*Th.* 1, 375).

Lanthanum, haloid compounds of. LaF_3, $LaCl_3$, and $LaBr_3$ have been isolated; the formulæ may be written La_2F_6, &c., as none of these compounds has been gasified. All form hydrates, and all combine with haloid compounds of Au and some other heavy metals to form double salts. Oxychlorides and oxybromides, LaOX, are known.

Lanthanum, iodide of. LaI_3 has not been isolated, but the double salt $2LaI_3.3ZnI_2.27H_2O$ is described by Frerichs a. Smith (*A.* 191, 355).

Lanthanum, oxides of. Only one oxide, La_2O_3, is known with certainty; there are indications of the existence of an oxide containing more O.

LANTHANUM SESQUIOXIDE, La_2O_3. Obtained by strongly heating $La_2O_3.xH_2O$, or the oxalate, or any La salt the acid of which is volatilisable. Forms a white, amorphous, infusible powder, S.G. 6·48–6·53 (Cleve, *l.c.*; Nilson a. Pettersson, *B.* 13, 1464). S.H. ·0749 (N. a. P., *l.c.*; *v.* also *Pr.* 31, 46). Diamagnetic (N. a. P., *l.c.*). Combines with water to form $La_2O_3.3H_2O$ (*v.* LANTHANUM, HYDROXIDE OF). Easily sol. in acids. Nordenskjöld (*J. pr.* 85, 431) obtained La_2O_3 in lustrous rhombic crystals, $a:b:c = \cdot5658:1:\cdot6863$, S.G. 5·296, by dissolving the amorphous oxide in borax in a porcelain-oven; the crystals did not directly combine with water, but were easily sol. in acids. The great infusibility of La_2O_3, and its power of emitting white light when strongly heated, render it useful as a light-giver; Von Welsbach has patented an arrangement whereby La_2O_3 is heated in the flame of a Bunsen lamp and emits a clear white light (English Patent, 15,286, July 1886).

LANTHANUM PEROXIDE. According to Mosander (*P. M.* 23, 241) a peroxide of La is ppd. by adding BaO_2 to a neutral La salt; on drying it loses O. Hermann (*J. pr.* 82, 397) says that a peroxide is obtained by heating oxalate, nitrate, or carbonate of La in the air; it dissolves in HClAq with evolution of Cl; heated in H it yields La_2O_3. Zschiesche (*J. pr.* 104, 74) was unable to confirm Hermann's observations. Cleve (*Bl.* [2] 43, 56) by ppg. La salts by alkali and H_2O_2Aq obtained an oxide to which he assigned the composition La_4O_9.

Lanthanum, oxybromide of. LaOBr. Obtained by the action of Br vapour on heated La_2O_3 (Frerichs a. Smith, *A.* 191, 331).

Lanthanum, oxychlorides of. LaOCl and $La_8O_9Cl_6$ ($= 3La_2O_3.La_2Cl_6$). The former is a greyish mass, unchanged by water, obtained by heating La_2O_3 in Cl to 200° (Frerichs a. Smith, *A.* 191, 331; Cleve, *Bl.* [2] 39, 151; 43, 56). The latter is obtained by heating $LaCl_3.7H_2O$ and washing the residue with water (Hermann, *J. pr.* 82, 385).

Lanthanum, salts of. La forms one series of salts, LaX_3 where $X = NO_3, \frac{SO_4}{2}, \frac{PO_4}{3}$, &c. Most of the La salts are colourless; those which are soluble have a sweetish astringent taste. The salts of volatilisable acids yield La_2O_3 when strongly heated. $La_2 3SO_4$ combines with the alkali sulphates, but the products are not alums. A good many double La salts are known; a few basic salts have been isolated. The following are the chief La salts: *arsenate, arsenite, borate,*

bromate, carbonate, chlorate, chromate, hypochlorite, iodate, molybdate, nitrate, perchlorate, periodate, phosphates, phosphite, selenate, selenite, silicate, sulphates, sulphites, thiosulphate, tungstate; *v.* CARBONATES, NITRATES, SULPHATES, &c.

Lanthanum, sulphide of. La_2S_3. Red-yellow, microscopic crystals; obtained by the action of 3 parts Na polysulphide with 1 part La_2O_3, and washing with water (Beringer, *A.* 42, 134). Mosander obtained a greyish powder by heating La_2O_3 in CO_2 laden with CS_2 (*P.* 60, 297); and by a similar reaction Frerichs a. Smith (*A.* **191**, 355) obtained La_2S_3 as a brownish-grey powder, soluble in acids with evolution of H_2S, decomposed by water to LaO_3H_3 and H_2S. Didier (*C. R.* 100, 1461) obtained a similar body by heating La_2O_3 in H_2S gas. M. M. P. M.

LANTHOPINE $C_{23}H_{25}NO_4$. [c. 200°]. A base homologous with papaverine, occurring in opium (Hesse, *A.* 153, 57; *Suppl.* 8, 271; *C. C.* 1870, 168).

Preparation.—The aqueous extract of opium is ppd. by Na_2CO_3, the pp. dissolved in ether, the ethereal solution shaken with dilute HOAc, and the acid solution poured into aqueous NaOH. After 24 hours the ppd. thebaïne and papaverine are filtered off, the filtrate neutralised with HCl, ppd. by NH_3, and shaken with chloroform. The chloroform takes up codeïne, lanthopine, and meconidine, and is then shaken with dilute HOAc, and the solution exactly neutralised by NaOH, when lanthopine is ppd.

Properties. — White powder composed of minute prisms (from $CHCl_3$). Insol. water, nearly insol. alcohol, v. sl. sol. ether and benzene, m. sol. chloroform. When ppd. from solutions by KOH or lime it dissolves in excess of the precipitant. NH_3 gives a pp. insol. excess. It does not give a blue colour with $FeCl_3$. Conc. HNO_3 gives an orange-red colour. H_2SO_4 gives no colour in the cold, but a brownish-yellow colour at 150°.

Salts. The sulphate forms extremely thin needles.—$B'HCl\,6aq$: extremely thin needles, appearing like a jelly when in mass; v. sol. boiling water.—$B'_2H_2PtCl_6\,2aq$: lemon-yellow crystalline powder; insol. water, alcohol, and HClAq.

LANUGINIC ACID. C 41·6 p.c., H 7·3 p.c., N 16·3 p.c., S 3·4 p.c., O 31·4 p.c. An acid produced by the action of boiling baryta-water upon wool (Champion, *C. R.* 72, 330; Knecht a. Appleyard, *B.* 22, 1120). The excess of baryta is removed by CO_2, the acid ppd. by lead acetate, and the pp. decomposed by H_2S. Yellowish porous mass, v. sol. hot water, sl. sol. alcohol, insol. ether. Its aqueous solution ppts. colouring matters as lakes. It also ppts. tannin and most metallic oxides from their acetates. It reacts like a proteïd with Millon's reagent and with phosphotungstic acid.

LAPACHIC ACID $C_{15}H_{14}O_3$ *i.e.* $C_{10}H_4O_2(OH)CH{:}CHPr$. *Oxy-amenyl-naphthoquinone. Taiguic acid.* [138°].

Occurrence.—A yellow colouring matter present in the 'lapacho' wood of a genus of the Bignoniaceæ, several species of which are indigenous to the Argentine Republic and other parts of South America (Siewert, *Report of Argentine Republic*, cap. 15, *Philadelphia*). Occurs also in Greenheart from Surinam (Stein, *J. pr.* 99, 3), and in Bethabarra wood (Greene a. Hooker, *Am.* 11, 267).

Preparation.—The wood (10 kilos.), in the form of saw-dust, is boiled with a moderately-concentrated solution of sodium carbonate (500 grms. crystallised salt in 80 litres water); the extraction is repeated several times. The solution is of a blood-red colour, and the addition of hydrochloric acid precipitates the crude acid together with a red-brown resin, from which it is best purified by frequent solution and recrystallisations from benzene (Paternò, *G.* 9, 505; 12, 337; Arnaudon, *C. R.* 46, 1152). Yield 5 p.c. of pure material.

Properties. — Monoclinic prisms; $a{:}b{:}c = \cdot7206{:}1{:}\cdot6192$; $n = 97\cdot9$ (Panebianco, *G.* 10, 80); v. sol. boiling alcohol, benzene, and ether. It dissolves readily in solutions of the alkalis and alkaline earths, forming red solutions containing salts of the acid. It decomposes carbonates on boiling.

Reactions.—1. Completely oxidised by *chromic acid.*—2. Alkaline $KMnO_4$ gives oxalic acid.—3. Boiling *nitric acid* (S.G. 1·38) yields phthalic acid.—4. Distillation with *zinc-dust* yields iso-butylene, naphthalene, and possibly a homologue of naphthalene.—5. Boiling with HIAq and phosphorus forms amyl-naphthalene (305°) and a little di-(β)-naphthyl, both being perhaps derived from an intermediate naphthyl-amylene. 6. Cold conc. HNO_3 (S.G. 1·49) or H_2SO_4 gives lapachone.—7. *Zinc-dust* and *potash* reduce it to an unstable crystalline hydride, re-oxidised by air to lapachic acid.

Salts.—$NaA'\,5aq$: scarlet radio-crystalline mass. S. (of NaA') 15·1 at 24°. Sol. alcohol.—KA'. S. 33·3 at 24°.—NH_4A' aq: large brick-red crystals.—CaA'_2 aq: amorphous red pp. S. ·224 at 24°.—$BaA'_2\,7aq$: long slender needles (from boiling water). S. ·23 at 26°.—SrA'_2 aq.—PbA'_2: amorphous red pp.; insol. water.—AgA': scarlet powder.—Aniline salt $C_6H_5NH_3A'$: [122°]; orange prisms (from alcohol).—*o*-Toluidine salt $C_6H_4MeNH_3A'$: [135°]; yellow laminæ.—*p*-Toluidine salt: [130°]; orange-yellow laminæ.

Acetyl derivative $C_{15}H_{13}AcO_3$. [83°]. Formed, together with a compound $C_{19}H_{18}O_5$ (?), by heating lapachic acid with NaOAc and Ac_2O (Paternò). Sulphur-yellow prisms; insol. water, sol. alcohol, ether, and benzene. Readily converted by potash into lapachic acid. Br in HOAc converts it into bromo-lapachone. HNO_3 (S.G. 1·48) at 0° forms a nitro- compound $C_{15}H_{12}(NO_2)AcO_3$ [170°]; crystallising in reddish plates. The compound $C_{19}H_{18}O_5$ forms small white acicular prisms [132°]; v. sl. sol. cold alcohol and ether. Boiling alcoholic KOH does not saponify it, but converts it into a compound $C_{30}H_{26}O_6$, which crystallises (from alcohol) in orange needles [141°]. Br does not convert the compound $C_{19}H_{18}O_5$ into bromo-lapachone.

Bromo-lapachone $C_{15}H_{13}BrO_3$ *i.e.* $C_{10}H_4O_2{<}{\scriptstyle\begin{matrix}CHBr\\O\end{matrix}}{>}CHPr$ (?). [140°]. Formed by warming lapachic acid with Br in HOAc (Paternò, *G.* 12, 353). Orange laminæ; v. sol. hot alcohol, sol. HOAc, and benzene, sl. sol. ether, insol. cold aqueous alkalis. HNO_3 oxidises it to phthalic acid.

Lapachone $C_{15}H_{14}O_3$ *i.e.* $C_{10}H_4O_2{<}\genfrac{}{}{0pt}{}{CH_2}{O}{>}CHPr$ (?). [156°]. Formed by the action of H_2SO_4 or cold conc. HNO_3 (S.G. 1·49) on lapachic acid (Paternò, *G.* 12, 337; Hooker a. Greene, *B.* 22, 1723). Silky orange-red needles (from alcohol); insol. water, v. sol. hot alcohol and benzene. HNO_3 oxidises it to phthalic acid. Distillation over red-hot zinc-dust gives naphthalene and isobutylene. Ac_2O has no action. Boiling with NaOAc and Ac_2O forms a compound $C_{26}H_{26}O_5$, crystallising in brown tables with blue reflex; nearly insol. Ac_2O. $NaHSO_3$ forms a white crystalline compound. Combines readily with hydroxylamine and with NH_3. Its molecular weight, found by Raoult's method, agrees with the formula $C_{15}H_{14}O_3$. Lapachone is converted by heating with alkalis into $C_{10}H_4O_2(OH).CH_2.CH(OH)Pr$, which separates from cold alcohol or HOAc in large crystals [125°]; v. sol. most solvents; readily converted into lapachone by dilute HCl, and forming the salts BaA″aq and Ag_2A″aq, both crystallising in red needles.

LARCH FUNGUS. This fungus extracted with 95 p.c. alcohol yields a mixture of at least four different resins (Masing, *Ar. Ph.* [3] 6, 111).

(α) $C_{41}H_{77}O_8$. [125°]. S. (95 p.c. alcohol) ·3 at 14°. Insol. chloroform.

(β) $C_6H_{10}O$. [90°]. S. (95 p.c. alcohol) ·7. Sol. chloroform.

(γ) $C_{16}H_{30}O_5$. Agaricic acid. [272°]. Needles; v. sl. sol. boiling alcohol, insol. chloroform (Jahns, *Ar. Ph.* 221, 269).

(δ) A portion easily soluble in alcohol, and partly ppd. by water, leaving in solution a resin [C 61·9 p.c.; H 8·1 p.c.; O 30·0 p.c.] S. ·17; S. (alcohol) 1·7. The resinous mixture is altered by boiling with milk of lime, the pp. then thrown down by HCl being separated by chloroform into two substances: $C_{39}H_{63}O_4$, insol. chloroform, S. (alcohol) ·6, and $C_{35}H_{52}O_6$, sol. chloroform, S. (alcohol) 2·1.

LARDACEÏN *v.* PROTEÏDS.

LARD OIL. A nearly colourless fatty oil, obtained by pressing hog's lard. S.G. $\frac{20}{4}$ ·9122; μ_D 1·4686 (Long, *Am.* 10, 392).

LARICIC ACID $C_{10}H_{10}O_5$. [153°]. S. 1·14 at 60°. Obtained from the small branches of larch trees (*Pinus larix*) from 20 to 30 years old (Stenhouse, *Pr.* 11, 405). The bark is exhausted with water at 80°, and the extract evaporated and distilled. The distillate is evaporated at 80° and the resulting crystals purified by sublimation. Long monoclinic crystals resembling benzoic acid, usually in twins. Sublimes at 93°. Volatile with steam. Has a bitter astringent taste and powerful odour. Reddens litmus slightly. M. sol. boiling water and alcohol, insol. ether. Nitric acid oxidises it to oxalic acid. Its aqueous solution is ppd. by baryta-water, but not by lead or silver salts. Ferric chloride gives a purple-red colour. The K salt forms flat reddish-brown crystals, decomposed by CO_2.

LARREA RESIN. Occurs on branches of *Larrea mexicana* (Stillmann, *B.* 13, 756). 61·7 p.c. of it dissolves in alcohol, 26·3 in aqueous potash, and 1·4 p.c. consists of a colouring matter soluble in water.

LASERPITIN $C_{24}H_{36}O_7$ (Feldmann, *A.* 135, 336; *Bl.* 1866, i. 457) or $C_{15}H_{22}O_4$ (Külz, *Ar. Ph.* [3] 21, 161). [114°] (F.); [118°] (K.). A bitter principle contained in the root of *Laserpitium latifolium*. Extracted by 80 p.c. alcohol (F.) or by light petroleum (K.). Prisms. Insol. water, sol. benzene, chloroform, ether, and CS_2. May be sublimed. Its alcoholic solution is ppd. by water, but not by alcoholic lead acetate (F.). Insol. dilute acids and alkalis. Conc. H_2SO_4 and conc. HClAq form deep-red solutions (K.). When heated with conc. alcoholic KOH it is resolved into angelic acid and laserin $C_{11}H_{22}O_4$ (F.) or $C_{20}H_{30}O_5$ (K.), a crystalline resin, insol. acids, sol. ether, alcohol, chloroform, and HOAc. Potash-fusion gives methyl-crotonic acid and laserin (K.).

Laserpitin forms an acetate $C_{15}H_{22}O_4HOAc$ crystallising from acetic acid in silky needles (K.).

Acetyl derivative $C_{15}H_{21}AcO_4$. [113°]. From laserpitin, Ac_2O, and dry NaOAc (K.). Colourless needles, insol. water, sol. HOAc, alcohol, ether, and $CHCl_3$.

Bromo-derivative $C_{30}H_{39}Br_5O_8$. [90°]. Formed by the action of Br on a solution of laserpitin in $CHCl_3$ (K.). Needles, sol. alcohol, ether, $CHCl_3$, and HOAc.

Di-nitro- derivative $C_{15}H_{20}(NO_2)_2O_4$aq. [115°]. From laserpitin and HNO_3 (K.). Amorphous mass, insol. water, sol. alcohol, ether, $CHCl_3$, and HOAc.

LAUDANINE $C_{20}H_{25}NO_3$ (Hesse, *A.* 153, 57; 176, 201; *Suppl.* 8, 272). [165°]. S.G. 1·256 (Schröder, *B.* 13, 1075). S. (ether) ·155 at 18°. $[\alpha]_j = -13·5$ in a 2 p.c. chloroform solution at 22·5°.

Preparation.—An aqueous extract of opium is ppd. by lime or Na_2CO_3; the filtrate is shaken with ether; the ethereal solution is shaken with dilute acetic acid; the acetic acid solution is neutralised exactly with NH_3; the ppd. lanthopine is removed by filtration; the filtrate is ppd. by excess of ammonia, and the pp. crystallised from ether. Laudanine separates first from the ethereal solution, and afterwards codamine. The laudanine is dissolved in acetic acid solution, and the solution mixed with excess of NaOH, which ppts. cryptopine. The alkaline filtrate is ppd. by ammonium chloride, and the pp. dissolved in aqueous HOAc; on adding KI laudanine hydro-iodide is ppd., and this is decomposed by ammonia and the free base crystallised from ammonia.

Properties.—Stellate groups of small six-sided prisms (from alcohol). Cannot be sublimed. Tasteless. Lævorotatory. In the crystalline state it is v. sol. benzene, $CHCl_3$, and boiling alcohol, sl. sol. cold alcohol, v. sl. sol. ether. In the amorphous state it is much more soluble. Its salts have a bitter taste. From their solutions caustic potash and ammonia ppt. the base in white amorphous flocks, which soon become crystalline, and dissolve in excess of the precipitant. Chloroform extracts the base from the ammoniacal but not from the potash solution. Conc. H_2SO_4 (containing ferric salt) gives an intense rose-red solution, which at 150° changes to dark violet. Conc. HNO_3 gives an orange-red solution. $FeCl_3$ gives an emerald-green colour. The base is poisonous, its hydrochloride acting physiologically like strychnine.

Salts.—$B'_2H_2SO_4$4aq: concentric groups of

needles; v. e. sol. water, almost insol. dilute H_2SO_4.—B′HCl 6aq: prisms; v. sol. water and alcohol, v. sl. sol. NaClAq. Inactive to light.—B′HBr 2aq: nodules. S. 3·5 at 20°.—B′HI aq: crystalline powder. S. ·2 at 15°, v. sol. boiling water, insol. KIAq.—$B'_2H_2PtCl_6$ 2aq: yellow amorphous pp., v. sol. boiling water. —$B'H_2C_2O_4$ 6aq: concentric groups of delicate needles. [110°]. S. 2·2 at 10°.—$B'C_4H_6O_6$ 3aq: [100°]. S. 4·9 at 15°.

LAUDANOSINE $C_{21}H_{27}NO_4$. [89°]. S. (ether) 5·2 at 16°. $[\alpha]_j$ = 105 in a 2 p.c. alcoholic solution at 22·5°; = 56 in a 2 p.c. chloroform solution at 22·5°.

Preparation.—Obtained from opium by ppg. the aqueous extract with Na_2CO_3, dissolving the pp. in ether, shaking the ethereal solution with dilute HOAc, and pouring the acid solution into aqueous NaOH. The pp. contains a large number of bases, and is warmed with alcohol and dilute HOAc, and partially evaporated at 50°. Papaverine and narcotine are then ppd., and thebaïne and tartrate is ppd. by adding tartaric acid to the filtrate. The filtrate is exactly neutralised with NH_3, and $NaHCO_3$ added. After a week the pp. is collected and extracted with benzene. Cryptopine and protopine separate first from the benzene, and when the filtrate is shaken with $NaHCO_3$ laudanosine separates (Hesse, *A. Suppl.* 8, 321). It is purified by dissolving in acetic acid; ppg. with KI; decomposing the resulting salt with NH_3; and recrystallising from benzene.

Properties.—Needles. More soluble in ether than thebaïne and cryptopine, extremely sol. alcohol and chloroform, v. sol. boiling benzene and ligroïn, insol. water and alkalis. Conc. H_2SO_4 (containing ferric salt) gives a brownish-red solution, which at 150° becomes green, and finally dark greenish-violet. $FeCl_3$ gives no colour. Tastes slightly bitter; its salts have an extremely bitter taste. Its alcoholic solution exhibits a strong alkaline reaction. Dextrorotatory. Its hydrochloride is also dextrorotatory, $[\alpha]_j$ = 108 in a 2 p.c. solution at 22·5°.

S a l t s.—B′HI ½aq: small prisms; v. sl. sol. cold water, v. sol. alcohol.—$B'_2H_2PtCl_6$ 3aq: yellow amorphous pp., insol. cold water. —$B'H_2C_2O_4$ 3aq: prisms, v. e. sol. water.

LAUREL OILS. The essential oil from the leaves of the common cherry-laurel (*Cerasus laurocerasus*) consists of benzoic aldehyde, HCy, a volatile oil (possibly benzyl alcohol) convertible by oxidation into benzoic acid, and minute quantities of an odorous resin (Tilden, *Ph.* [3] 5, 761; *cf.* Leger, *Ph.* [3] 3, 971). The essential oil from the fruits of *Laurus nobilis* contains a lævorotatory terpene $C_{10}H_{16}$ (164°), S.G. $\frac{15}{}$ ·908, a lævorotatory sesquiterpene $C_{15}H_{24}$ (250°), S.G. $\frac{15}{}$ ·925, and lauric acid $C_{12}H_{24}O_2$ (Blas, *A.* 134, 1; Gladstone, *C. J.* 17, 1). The essential oil from the leaves of the Californian laurel (*Oreodaphne californica*) contains terpineol (168°) and umbellol $C_8H_{12}O$ (216°) (Stillmann, *B.* 13, 629).

Laurel-nut oil is a fatty oil, S.G. ·932, derived from *Calophyllum inophyllum* growing in the East (Hooper, *Ph.* [3] 19, 525).

LAURENE *v.* DI-METHYL-ETHYL-BENZENE.

LAURIC ACID $C_{12}H_{24}O_2$. *Dodecoic acid.* Mol. w. 200. [43·6°] (Heintz). (225°) at 100 mm. (Krafft, *B.* 13, 1415). S.G. $\frac{20}{}$ ·883 (Görgey). H. C. 1759720 (Louguinine, *A. Ch.* [6] 11, 222). Occurs as glyceryl ether in the berries of the bay tree (*Laurus nobilis*) (Marsson, *A. Ch.* 41, 33; Blas, *A.* 134, 1), in the fat of pichurim beans (Sthamer, *A.* 53, 393), in the volatile oil of these beans (Müller, *J. pr.* 58, 469), in small quantity in spermaceti (Heintz, *A.* 92, 394), in croton oil (Schlippe, *A.* 105, 14), in the fruit of *Cylicodaphne sebifera* (Gorkom, *Tydschrift af neerl. Indic*, 81, 410), in the so-called Dika bread, the fruit of *Mangifera gabonensis* (Oudemans, *J. pr.* 81, 356), in the *age* of the Mexicans, a fat obtained from *Coccus Axia* (Hoppe, *J. pr.* 80, 102), and in cocoa-nut oil (Görgey, *A.* 66, 303).

According to Schering (*A.* 96, 236) it is among the products of the distillation of cetyl alcohol with potash-lime, but Heintz (*A.* 97, 271) denies this. A dodecoic acid [35°], isomeric with lauric acid, may be obtained by treating the amide of myristic acid with Br and NaOH, and converting the resulting dodecylamine into the nitrile and thence into the amide [97°] of dodecoic acid, and boiling the amide with conc. HClAq (Lutz, *B.* 19, 1433).

Preparation.—Lauric acid may be obtained from fats containing it by saponification followed by fractional precipitation of the acids by barium acetate (Heintz, *A.* 92, 294; *P.* 92, 429, 583; *J. pr.* 66, 1). It may also be obtained from the fat of bay-berries by saponifying, distilling the solid fatty acids under reduced pressure, and rectifying *in vacuo* (Krafft, *B.* 12, 1665).

Properties.—Silky needles united in tufts (from alcohol) or scaly crystalline mass (after fusion). Its alcoholic solution has a slight acid reaction. It is slightly volatile with steam. Insol. water, v. sol. alcohol and ether. Gives di-ennyl ketone $(C_{11}H_{23})_2CO$ when its calcium salt is distilled.

S a l t s.—KA′. Amorphous. S. (alcohol) 4·5 at 15°; 38 at 78° (Oudemans, *C. C.* 1863, 737).—KHA'_2. Crystalline. S. (alcohol) 1·5 at 15°; 400 at 78°.—NaA′. White powder. S. (alcohol) 2·5 at 15°; 14·5 at 78°.—$NaHA'_2$. S. (alcohol) 2 at 15°.—$NH_4HA'_2$. S. (alcohol) 6 at 15°.—BaA'_2: crystalline spangles (from alcohol). S. ·07 at 100°; ·0054 at 15° (Oudemans); ·009 at 17°; 50 at 100° (Görgey). S. (alcohol) ·0187 at 15°; ·1009 at 78° (O.); ·07 in the cold; ·5 at 78° (G.). CaA'_2 aq: S. ·0039 at 15°; ·0547 at 100°. S. (alcohol) ·0719 at 15°, 2·20 at 78° (O.).—SrA'_2 aq: S. ·0272 at 15°; ·036 at 100°. S. (alcohol) ·96 at 15°, ·36 at 78°.—MgA'_2 3aq: S. ·023 at 15°.—PbA'_2. [110°–120°] (Heintz). S. ·0011 at 100°. S. (alcohol) ·0047 at 15°, ·235 at 100°.—CoA'_2 aq.—NiA'_2 aq. NiA'_2 3aq. —CuA'_2: S. ·0023 at 15°, ·0029 at 100°.—AgA′: white powder, consisting of minute slender needles. S. ·0001 at 15°, ·0405 at 100°. S. (alcohol) ·0323 at 15°, ·0824 at 78°.

Ethyl ether EtA′. [–10°]. (269°) at 750 mm. (Delffs, *A.* 92, 278). S.G. $\frac{20}{}$ ·86 (Görgey). V.D. 8·4. (calc. 7·9). From the acid, alcohol, and HCl.

Glyceryl ether $C_3H_5(C_{12}H_{23}O_2)_3$ (Schiff, *B.* 7, 781). *Trilaurin. Laurostearin.* [45°]. H. C. 5707420 (Louguinine, *A. Ch.* [6] 11, 222). Obtained from bay berries by extracting with alco-

hol. Silky needles; sl. sol. cold alcohol, v. sol. ether.

Phenyl ether $A'C_6H_5$: [24½°]; (210° at 15 mm.); pearly plates.

p-Tolyl-ether $A'C_7H_7$: [28°]; (220° at 15 mm.) (Krafft a. Bürger, *B.* 17, 1378).

Amide $C_{11}H_{23}.CO.NH_2$: [102°] (Krafft a. Stauffer, *B.* 15, 1729). From the chloride and NH_3.

Chloride $C_{11}H_{23}.CO.Cl$. [-17°]. (142½° at 15 mm.). Colourless liquid (Krafft, *B.* 17, 1378).

Nitrile $C_{11}H_{23}CN$. [4°]. (198° at 100 mm.). S.G. $\frac{4}{4}$ = ·835; $\frac{15}{4}$ = ·827; $\frac{100}{4}$ = ·767. Formed by distilling lauramide with P_2O_5 (Krafft a. Stauffer, *B.* 15, 1729). Colourless liquid of peculiar odour.

LAURIC ALDEHYDE $C_{11}H_{23}CHO$. [45°]. (143° at 22 mm.). Prepared by the dry distillation of a mixture of calcium laurate and formiate (Krafft, *B.* 13, 1414). White crystalline odourless solid.

LAURIN $C_{22}H_{30}O_3$. *Bay-berry camphor.* A substance discovered by Bonastre (*J. Ph.* 10, 32) in the berries of the bay-tree, and further examined by Marsson (*A.* 41, 329) and Delffs (*A.* 88, 354). It is prepared by boiling the skinned and pounded berries with alcohol of 85 to 90 p.c., filtering at the boiling heat, and leaving the liquid to itself for several days. Laurostearin is then first deposited; and on filtering again and leaving the liquid to evaporate, laurin is deposited in crystals contaminated with a viscid oil, from which they may be freed by pressure between paper and recrystallisation. Dimetric crystals, destitute of taste and smell, insol. water, v. sol. alcohol, even in the cold, sol. ether. The solutions are neutral to test-papers. Laurin does not dissolve in alkalis. Laurin cannot be distilled without decomposition. Its alcoholic solution is not precipitated by acetate of lead or nitrate of silver.

LAUROCERASIN. A name given by Lehmann (*N. R. P.* 23, 440) to amygdalin when extracted from the leaves of the cherry laurel (*Cerasus laurocerasus*) or the bark of the berry-bearing alder (*Rhamnus Frangula*), *v.* AMYGDALIN.

LAURONE $C_{23}H_{46}O$ *i.e.* $(C_{11}H_{23})_2CO$. *Di-ennyl ketone.* [69°]. S.G. $\frac{70}{4}$ = ·802; $\frac{100}{4}$ = ·788. Formed by distilling barium laurate with lime. Shining plates (from alcohol). On reduction it gives tricosane (Overbeck, *P.* 86, 591; *A.* 84, 289; Krafft, *B.* 15, 1712).

LAURONOLIC ACID $C_9H_{14}O_2$ *i.e.* $C_8H_{13}CO_2H$. Formed by distilling camphanic acid, or by heating its barium salt with water at 200°; campholactone is formed at the same time (Woringer, *A.* 227, 7).

Properties.—Oil. Sol. water and ether. Volatile with steam. In presence of HCl some of it changes into the isomeric campholactone. When distilled with water, a great part changes to the campholactone.

Salts.—CaA'_2 3aq. Forms dendritic crystals on the surface of an evaporating solution.—AgA'.

LAUROSTEARIN *v. Glyceryl ether* of LAURIC ACID.

LAUROXYLIC ACID *v.* DI-METHYL-BENZOIC ACID.

LAUTH'S VIOLET *v.* AMIDO-IMIDO-IMIDO-DI-PHENYL SULPHIDE.

LAVENDER OIL. A volatile oil obtained by distilling the flowers of *Lavendula officinalis* with steam. S.G. $\frac{15}{}$ ·875. It contains a lævo-rotatory terpene $C_{10}H_{16}$ (162°) which forms a crystalline hydrochloride and various oxygenated bodies which yield camphor on further oxidation (Dumas, *A. Ch.* 13, 275; Lallemand, *A.* 114, 198; Barth, *Z.* 1867, 509; Bruylants, *J. Ph.* [4] 30, 39). English oil of lavender submitted to fractional distillation yields 30 p.c. of the terpene (176°–186°), and 30 p.c. of oxygenated products (200°–207°) (Shenstone, *Ph.* [2] 13, 207).

LEAD. Pb. At.w. 206·4. Mol. w. not known with certainty, but probably same as at. w. (*v.* p. 124). [330°–335°] (Brigel, *B.* 6, 191; Pictet, *P. M.* [5] 7, 446); [326°] (Riemsdyk, *C. N.* 20, 32; Person, *J.* 1849). (Between 1450° and 1600°) (Carnelley a. Williams, *C. J.* 35, 565). S.G. 11·335 at 0° (Quincke, *P.* 97, 396); 11·37 at 0° (Reich, *J. pr.* 78, 328); 11·345 to 11·358 at 4°, 11·352 to 11·366 at 23° (Schweitzer, *Am. Ch.* 7, 174). S.G. molten 10·37–10·65 (Roberts a. Wrightson, *A. Ch.* [5] 30, 181). For other values for S.G. *v.* Clarke's *Table of Spec. Gravities* [1888], pp. 5–6. S.H. –78° to 11° ·03065 (Regnault, *A. Ch.* [3] 26, 286); S.H. 19° to 48° ·0315 (Kopp, *Tr.* 1865. 71); S.H. molten 340° to 450° ·0402 (Person, *A. Ch.* [3] 24, 129). C.E. 0° to 100° ·00002799 (Matthiessen, *Pr.* 15, 220). T.C. (Ag = 100) 8·5 (Wiedemann a. Franz, *P. M.* [4] 7, 33). Heat of fusion 5858 (Rudberg, *P.* 19, 125); 5369 (Person, *A. Ch.* [3] 24, 129). E.C. (Hg at 0° = 1) 4·8 at 0°, 3·363 at 100° (Lorenz, *W.* 13, 422, 582). Crystallises in regular octahedra. For emission-spectrum of lead *v.* Werther, *J. pr* 88, 180; Cornu, *C. R.* 73, 332; L. de Boisbaudran, *C. R.* 77, 1152; Hartley a. Adeney, *Tr.* 1884. 63.

Occurrence.—Lead occurs native in small quantities (*e.g. v.* Chapman, *P. M.* [4] 31, 176; Kokscharow, *J. M.* 1875. 873; Igelström, *J. M.* 1889 (ii.) 32). *Galena* (PbS) is very widely distributed; the other most important ores of lead are *cerusite* (carbonate), *anglesite* (sulphate), *pyromorphite* (phosphate), and *mimetesite* (arsenate). Small quantities of oxychloride, chromate, molybdate, tungstate, vanadate, &c., of Pb also occur. Lead has been known and used from very early times.

Formation.—1. PbS is roasted in a reverberatory furnace until a portion is oxidised partly to PbO and partly to $PbSO_4$; the doors are then closed, and the PbS, PbO, and $PbSO_4$ react to produce SO_2 and Pb; $PbS + 2PbO = 3Pb + SO_2$; $PbS + PbSO_4 = 2Pb + 2SO_2$.—2. PbS is roasted in a reverberatory furnace, the temperature being gradually increased until a considerable quantity of $PbSO_4$ and a little PbO are produced; the doors are then closed, and the temperature is raised until the mass softens but does not melt. When the PbS and $PbSO_4$ react to produce Pb and SO_2 the residue is again roasted, whereby more $PbSO_4$ is formed, and on raising the temperature with closed doors the $PbSO_4$ and PbS react as before. After a time the quantity of $PbSO_4$ relatively to PbS becomes so great that the chief product of their reaction is PbO ($PbS + 3PbSO_4 = 4PbO + 4SO_2$); coal and wood are then thrown into the furnace, and heating is

continued, when the PbO is reduced to Pb($PbO + C = Pb + CO$); at the same time some of the $PbSO_4$ is partly reduced to PbS, which, reacting with the remaining $PbSO_4$, produces Pb and SO_2 ($2PbSO_4 + 2C = PbSO_4 + PbS + 2CO_2$).—3. PbS is melted with scrap Fe; $PbS + Fe = FeS + Pb$.—4. $PbCO_3$ is strongly heated with C; $PbCO_3 + 2C = Pb + 3CO$.—5. PbO is reduced by heating in H or CO, or with C, KCN, or Na.—6. Zinc is suspended in an acidulated solution of a Pb salt, when Pb is ppd. on the zinc.—7. $PbCl_2$ is mixed with Na_2CO_3, and heated with KCN or C.

Preparation.—1. By melting Pb prepared by one of the foregoing methods, exposing the molten mass to a gentle current of air, blowing water-vapour through the mass, and running off the metal from beneath the film of oxides of Cu, Sb, Fe, &c., nearly pure Pb is obtained.—2. Pb oxalate is strongly heated in a carbon crucible, or is mixed with powdered C and heated.—3. Stas prepared pure lead by the following process (*Chem. Proport.* 324). Commercial Pb acetate was dissolved in water, and digested at 40° to 50° in a leaden vessel with sheets of Pb until all Cu and Ag were ppd.; the filtered liquid was run into almost boiling water, strongly acidulated with H_2SO_4; the ppd. $PbSO_4$ was very thoroughly washed, and then suspended in a solution of NH_4 sesquicarbonate and NH_3 until transformed into $PbCO_3$; the $PbCO_3$ was thoroughly washed, a part of it was decomposed to PbO by heating in a Pt dish, and the rest was almost, but not quite, entirely dissolved in dilute HNO_3Aq; the solution of $Pb(NO_3)_2$ was heated to boiling, and the PbO was added little by little; the last traces of Fe were thus ppd. as oxide; the boiling liquid was filtered and poured into solution of NH_4 sesquicarbonate. In this way pure $PbCO_3$ was obtained. The $PbCO_3$ was dried, and added little by little to pure molten KCN contained in an unglazed porcelain crucible placed within a larger crucible, the space between being filled with powdered Al_2O_3 previously heated and mixed with 5 p.c. melted and powdered borax. The Pb thus obtained was again placed in pure molten KCN, and kept there until the upper surface of the Pb appeared convex and lustrous like pure Hg; after partial cooling the Pb was run off into a mould of polished steel. If a trace of PbO or PbS is present in the molten Pb the surface does not become convex.

Properties.—Almost white, lustrous metal. Ordinary lead is blue-grey; it contains traces of Ag, Cu, Sb, and sometimes Fe and Mn. Very malleable and ductile, but the properties are greatly affected by small quantities of impurities, notably by PbO, which is somewhat soluble in molten Pb. Tenacity very low. Somewhat sonorous. Leaves a mark on paper. Lead is so soft that it can be cut by a knife or scratched by the nail; traces of foreign metals, or of As or S, increase the hardness of Pb. By slowly cooling molten Pb, piercing a hole in the crust by an iron rod, and pouring off the still molten portion, the metal is obtained in regular octahedra often aggregated together similarly to crystals of NH_4Cl (Marx, *S.* 57, 193; Stolba, *D. P. J.* 164, 371). Crystals of Pb are also obtained by hanging a rod of zinc in a slightly acidulated solution of a Pb salt, or by passing an electric current through such a solution. Pb vaporises at high temperatures (1400°–1600°); the vapour is very poisonous. The lustrous surface of Pb quickly tarnishes in ordinary air from formation of a film of oxide (probably Pb_2O). Very finely divided Pb is quickly changed to the suboxide Pb_2O; such finely divided Pb may be obtained by covering a Zn plate with a little $PbSO_4$ made into a paste with water, laying another Zn plate on the top, and placing the whole in NaClAq for 9 or 10 days (*v.* Bolley, *Ph. C.* 1850. 59). Pb is readily changed to PbO on the surface by melting in air. Pb is not changed in dry air, nor when kept under pure water from which all air has been removed; in contact with water and the atmosphere it becomes gradually covered with a white deposit of $2PbCO_3$, PbO_2H_2, and small quantities of a soluble Pb salt are also formed (*v. Reactions*, No. 2). Pb is soluble in HNO_3Aq, and is slowly changed to $PbCl_2$ by the action of HClAq in the air; hot conc. H_2SO_4 forms $PbSO_4$; Pb is oxidised by heating with KNO_3 or $KHSO_4$. Combines with the halogens, also with S, Se, P, and As; forms alloys with many metals.

The atomic weight of Pb has been determined (1) by finding V.D. of $PbCl_2$ (Roscoe, *Pr.* 27, 426), and analyses of this compound (Marignac, *Ar. Sc.* 1, 59, 209; Dumas, *A. Ch.* [3] 55, 196); (2) by syntheses of $Pb(NO_3)_2$ and $PbSO_4$ (Stas, *Rech.* 101; *Chem. Proport.* 329); (3) by converting Pb, PbO, and PbS into $PbSO_4$, and by analysing $PbCO_3$ (Berzelius, *P.* 8, 15; *G. A.* 37, 259, 265; Turner, *A.* 13, 17); (4) by determining S.H. of Pb (Regnault, *A. Ch.* [3] 26, 286).

Lead is metallic in its chemical behaviour. The oxide PbO is strongly basic; it is slightly soluble in water, and the solution turns red litmus blue and absorbs CO_2 from the air; it decomposes hot solutions of NH_4 salts with evolution of NH_3, and it reacts with acids to form salts PbX_2 ($X = NO_3, \frac{1}{2}SO_4$, &c.), $PbCO_3$ is isomorphous with the carbonates of the alkaline earths; on the other hand, PbO dissolves in fairly conc. KOHAq, probably forming a salt PbO_2K_2, and compounds of PbO with CaO and Ag_2O are known. PbO_2 reacts with strong bases, *e.g.* KOH, to form unstable salts, *e.g.* K_2PbO_3; on the other hand, treatment of Pb_3O_4 with conc. H_3PO_4Aq or $H_4C_2O_2Aq$ produces solutions which react as if they contained salts of PbO_2. The greater number of the lead salts correspond with the oxide PbO; $Pb(CH_3)_4$, however, is stable as a gas.

Lead is placed in Series II. of Group IV.; the other odd series members of this group are Si, Ge, and Sn. Pb more nearly resembles Sn than any other member of Group IV.; it is more distinctly metallic than the other elements of the group; the other elements of this group form several compounds MX^{I}_4, whereas most of the Pb compounds belong to the form MX^{I}_2. Pb forms many basic and several double salts (*cf.* CARBON GROUP OF ELEMENTS, vol. i. p. 684; also TIN GROUP OF ELEMENTS, in vol. iv.). In its physical properties Pb resembles Tl; one series of Tl salts, however, is similar to those of the alkali metals, and the other series resembles those of the earth metals (*v.* EARTHS, METALS OF THE, vol. ii. p. 424). The atom of Pb is divalent in the gaseous molecule $PbCl_2$, and tetravalent in the gaseous molecule $Pb(CH_3)_4$.

Ramsay (*C. J.* 55, 521) has determined the lowering of vapour-pressure of Hg produced by dissolving Pb in Hg; the results obtained make it probable that the molecular weight of lead is the same as the atomic weight; this result assumes the accuracy of Van't Hoff's law, that equal volumes of dilute solutions contain equal numbers of molecules of the dissolved substances, and it also regards the molecular weight of liquid Hg as the same as the atomic weight.

Reactions.—1. Unchanged in *dry air*; superficially oxidised (probably to Pb_2O) in *moist air*; oxidised to PbO by *heating in air* or *oxygen*.—2. *Water* quite free from air has no action on Pb at ordinary temperatures (Stalman, *D. P. J.* 180, 366; Böttger, *J.* 1866. 232; but *v.* Müller, *J. pr.* [2] 36, 317). *Water and air* together dissolve a little Pb, and at the same time a deposit of $2PbCO_3.Pb(OH)_2$ is formed. Water charged with CO_2 under a pressure of a few atmospheres dissolves considerable quantities of Pb (perhaps in the form of an acid carbonate). The presence of small quantities of nitrates, especially NH_4NO_3, of soluble alkaline chlorides, and of some other salts, *e.g.* $(NH_4)_2SO_4$, increases the solvent action of water on Pb; the amount of Pb in solution is greater after a few days' action than after many days' exposure to the air. In these reactions the soluble salt of Pb is probably slowly acted on by the CO_2 of the air with formation and ppn. of insoluble $2PbCO_3.Pb(OH)_2$. The presence of alkaline carbonates or of a little Ca silicate in water almost wholly stops the solvent action on Pb; probably the insoluble hydrocarbonate is formed as quickly as Pb is dissolved. The action of water on lead has been examined by Graham, Miller a. Hofmann, Noad (*C. J.* 4, 20), Yorke (*P. M.* [3] 5, 82), Dumas (*C. R.* 77, 1054), Berthelot (*C. R.* 77, 1063), Pattison Muir (*C. N.* 25, 294; 33, 102, 125, 145; 34, 223, 234; 35, 82, 110; *C. J.* 31, 660), Müller (*J. pr.* [2] 36, 317), Carnelley a. Frew (*S. C. I.* 7, 15, 78), and others. Granulated lead slowly decomposes *boiling water*, evolving H (Stolba, *J. pr.* 94, 113).—3. Lead is dissolved by several *acids*; slowly by hot conc. HClAq in contact with air; also slowly by conc. H_2SO_4 (Calvert a. Johnson, *C. J.* 16, 66); rapidly by HNO_3Aq. For account of gaseous products of reaction with HNO_3Aq. *v.* Ackworth a. Armstrong, *C. J.* 32, 54.

Technical applications of lead.—Lead is largely used for vessels and apparatus in which different chemical processes are conducted, *e.g.* for sulphuric acid chambers; water-pipes are usually made of lead. Alloys of lead with tin form solder and pewter; an alloy with As is used for making shot; an alloy with Sb is used as type-metal, and emery wheels and grinding tools used by lapidaries are made of an alloy of Pb and Sb; alloys of Pb with Sn and Bi have low melting-points. Lead oxide, chromate, acetate, and carbonate are all largely used in manufactures.

Detection and Estimation. HClAq ppts. white $PbCl_2$ from solutions of Pb salts; sl. sol. cold water, fairly sol. hot water, nearly insol. dilute HClAq. Dilute H_2SO_4, or a soluble sulphate, ppts. white $PbSO_4$ almost insol. dilute H_2SO_4Aq, quite insol. alcohol. K_2CrO_4Aq ppts. yellow $PbCrO_4$, insol. water. KIAq ppts. yellow PbI_2, sol. boiling water, but reppd. in yellow crystalline spangles on cooling. H_2S ppts. brownish-black PbS, insol. dilute acids, alkalis, or alkaline sulphides; presence of much HCl prevents ppn. from rather dilute solutions of salts of lead; in presence of a little HCl pp. is sometimes red or yellow-red, and consists of xPbS.yPbCl$_2$ (*v. Lead, sulphochloride of*). The H_2S test is said to detect 1 pt. of lead in 100,000 pts. of water; the H_2SO_4 test 1 pt. in 20,000; and the K_2CrO_4 test 1 pt. in 70,000. Pb may be estimated as $PbSO_4$ by ppn. with dilute H_2SO_4Aq adding about 2 vols. of alcohol, washing with alcohol, drying and calcining.

Supposed allotropic form of lead. When lead is deposited on the negative electrode by passing a current through a neutral or acid solution of a lead salt, and the current is continued for some hours, the lead becomes the colour of copper (Wöhler, *A. Suppl.* 2, 135). After washing the red leaflets thus obtained with water and alcohol, they retain their colour on exposure to the air, and are not acted on by dilute HClAq or cold dilute HNO_3Aq, or alkalis, but are readily dissolved by hot HNO_3Aq; heated in H they melt above 200° and become ordinary lead. Wöhler regarded the red substance either as an allotropic form of lead, or as a hydride of lead; Stolba (*J. pr.* 94, 113) suggested that the red colour was due to a film of oxide on the surface of the lead (*v.* also Schützenberger, *C. R.* 86, 1265).

Lead, alloys of. Lead alloys with many metals; the alloys are produced by fusing together the constituent metals; some of them are definite compounds, in these cases either of the constituents is generally soluble in the compound.

Alloys with bismuth, and with bismuth and other metals. Pb and Bi may be alloyed in all proportions; malleability is diminished by adding more than an equal weight of Bi. By fusing together 70 p.c. Pb, 15 p.c. Bi, and 15 p.c. Sb an alloy is obtained which expands on cooling. An amalgam of Pb (4 pts.) Bi (2 pts.), and Hg (1 pt.) may be melted by rubbing pieces of it together. Alloys of Pb with Bi and Sn are known as *fusible alloy*; the M.P. varies from c. 90° to c. 170°; all these alloys are said to solidify at 98°. (For M.P. and solidification-points of these alloys *v.* Dallo, *C. C.* 1865. 831; for expansion and S.H. *v.* Spring, *A. Ch.* [5] 7, 178, also Wiedemann, *W.* 3, 237; for thermal conductivity *v.* Wiedemann a. Franz, *P.* 89, 514; 108, 399; *cf.* also vol. i. p. 511.)

Britannia metal is composed of equal parts of brass, Sn, Sb, and Bi; *Queen's metal* of 1 pt. Pb, 1 pt. Bi, 1 pt. Sb, and 9 pts. Sn. Alloys of Pb with Bi, Sn, and Ag are very fusible, melting as low as 45°; the alloy often used for tinning the inside of glass globes, tubes, &c. is made by fusing together 1 pt. Pb, 1 pt. Sn, 2 pts. Bi, and adding 10 pts. Ag.

Alloys with copper *v.* vol. ii. p. 254.

Alloys with mercury. Pb easily amalgamates with Hg, by rubbing together Pb filings with Hg or by adding Hg to molten Pb. An amalgam containing 33 p.c. Pb is liquid; an amalgam of equal parts Pb and Hg can be crystallised. Contraction occurs during the amalgamation.

Alloys with potassium and sodium. Prepared either by directly heating the metals together or by fusing PbO with an alkaline flux, *e.g.* with cream of tartar. When distilled with EtI, MeI, &c., compounds of Pb with Et, Me, &c. are obtained.

Alloys with tin. These metals may be alloyed in all proportions; the S.G. of the alloy is always a little less than that calculated from the S.G. of the constituents. There are no indications of the formation of definite compounds (*v.* Laurie, *C. J.* 55, 677). These alloys are very easily ignited and burnt. The two commonest alloys of Pb and Sn are *solder* and *pewter*. *Fine solder* contains 1 pt. Pb and 2 pts. Sn; *common solder*, equal pts. Pb and Sn; *coarse solder*, 2 pts. Pb and 1 pt. Sn. The M.P. varies from c. 340° for 1 pt. Pb and 2 pts. Sn, to 370° for equal parts Pb and Sn, and 440° for 2 pts. Pb and 1 pt. Sn; by increasing the relative quantity of Pb the M.P. rises until the alloy of 25 pts. Pb to 1 pt. Sn melts at c. 560°; by increasing the relative quantity of Sn, above 2 pts. to 1 of Pb, the M.P. also slightly rises until the alloy of 6 pts. Sn to 1 pt. Pb melts at c. 380°. *Pewter* is an alloy of c. 80 pts. Pb with 20 pts. Sn. According to Rudberg (*P.* 18, 240) when Pb and Sn are melted together and allowed to cool, the thermometer always shows a stationary point at 187°; he thinks that a compound $PbSn_3$ is always formed, that this alloy has a fixed solidification-point lower than that of Pb (326°) or Sn (228°), and that the heat produced by the solidification of this alloy acting on the excess of Pb or Sn causes fluctuations in the final solidification-point of the whole mixture (*v.* also Pohl, *W.A.B.* 1850. 402; Riche, *C.R.* 55, 143; Wertheim, *P. Ergänzbd*, 2, 75; Matthiessen, *P.* 130, 62). It seems that the amount of Pb in pewter vessels for domestic use should not exceed 18 p.c., else Pb may be dissolved out by the action of dilute acids, *e.g.* vinegar.

Alloys with tin and copper. *Bell-metal* is an alloy of 4·3 p.c. Pb, 80 p.c. Cu, 10·1 p.c. Sn, and 5·6 p.c. Zn. A little Pb is sometimes added to Cu and Sn in making *bronze*.

Alloys with palladium. A crystalline, greyish-white, brittle alloy is obtained by fusing granulated Pb with rather more than its own weight of Pd foil, and removing excess of Pb by the action of acetic acid and CO_2. The alloy has the composition Pd_3Pb; S.G. 11·225 (Bauer, *B.* 3, 691; 4, 449).

Alloys with platinum. An alloy having the composition PtPb is formed by fusing 3 pts. Pb with 1 pt. Pt, and exposing the product to the prolonged action of CO_2, O, and acetic acid vapour (Bauer, *B.* 3, 691; 4, 449). Steel-grey, crystalline; fairly fusible; S.G. 15·736. Bauer (*l.c.*) also describes an alloy $PtPb_2$.

Alloys with zinc. Pb and Zn alloy in all proportions; all the Zn is removed by heating very strongly. Alloying Pb with Zn increases the hardness of the Pb. Alloys of Pb, Zn, and Sn solidify at 168°; when the ratio is 2Pb:Zn:9Sn the alloy solidifies at 168° only, but other alloys show also two higher points.

Lead also alloys with *chromium* and *manganese*.

Lead, antimonate of; *v.* vol. i. p. 286.

Lead, antimonides of. Pb and Sb may be melted together in all proportions; the alloys are crystalline; most of them are formed with expansion. Ordinary *type metal* consists of 83 pts. Pb and 17 pts. Sb (*v.* Riche, *C. R.* 55, 143; Matthiessen, *P.* 110, 28; Calvert a. Johnson, *P. M.* [4] 18, 354; H. v. d. Planitz, *B.* 7, 1664; Rollmann, *P.* 84, 277).

Lead, arsenates of; *v.* vol. i. p. 308.

Lead, arsenides of. Pb melted with As takes up c. 16 p.c. of the latter; the alloys are brittle and very fusible; some, but not all, of the As is expelled by heating. *Shot-metal* is an alloy of Pb with not more than 3 p.c. As.

Lead, arsenites of; *v.* vol. i. p. 306.

Lead, borates of; *v.* vol. i. p. 530.

Lead, borofluoride of. $Pb(BF_4)_2[=PbF_2.2BF_3]$. Prismatic crystals; obtained by dissolving PbO in excess of HBF_4Aq and evaporating to a syrup. Crystallises with difficulty; partially decomposed by water or alcohol (Berzelius, *P.* 2, 113; *cf.* Borofluorides, vol. i. p. 526).

Lead, bromide of. $PbBr_2$. Mol. w. not certain; but from analogy of $PbCl_2$ is probably 365·9(=$PbBr_2$). Melts at c. 499° (Carnelley, *C. J.* 33, 278); boils at c. 861° (Carnelley a. Williams, *C. J.* 33, 283). S.G. ppd. $PbBr_2$ 6·572 at 19·2° (Clarke's *Table of Specific Gravities* [1888] 32). H.F. $[Pb,Br^2]=64{,}450$; $[Pb,Br^2,Aq]=54{,}410$ (*Th.* 3, 337). Obtained by digesting PbO or $PbCO_3$ with HBrAq, or by ppg. the solution of a Pb salt by HBrAq or a soluble bromide. Obtained in well-formed, colourless, rhombic needles by slowly evaporating a solution of Pb in alcohol containing Br (Hjortdahl, *Z. K.* 3, 302). Sl. sol. cold, more sol. hot, water; more sol. acids. From the solution in hot conc. HBrAq (72 p.c. HBr), Ditte says that white lustrous needles, $PbBr_2.3H_2O$, crystallise (*C. R.* 92, 718); and that the compound $5PbBr_2.2HBr.10H_2O$ is obtained by passing HBr into the solution of $PbBr_2$ in HBrAq. After melting, $PbBr_2$ solidifies to a yellow, horn-like mass. Heated in air, a yellow mass remains containing the *oxybromide* Pb_2OBr_2 (=$PbBr_2.PbO$); the same oxybromide is obtained by digesting $PbBr_2$ with $Pb(C_2H_3O_2)_2Aq$. A compound of $PbBr_2$ with $PbCl_2$ has been obtained, also compounds of $PbBr_2$ with PbI_2, and with $Pb(CNS)_2$ (*v. Lead, bromochloride of*; *Lead, iodobromides of*; and *Lead, bromosulphocyanides of*). André (*A. Ch.* [6] 3, 104) describes several *double compounds* of $PbBr_2$ with NH_4Br.

Lead, brom-iodides of; *v. Lead, iodobromides of.*

Lead, bromochloride of. $PbBr_2.PbCl_2$ (=PbBrCl). White needles, observed by Iles in a blast furnace where lead carbonate ores had been reduced (*C. N.* 43, 216); crystallisable from water; S.G. 5·741.

Lead, bromosulphocyanides of. $PbBr_2.Pb(CNS)_2$; brownish crystals, by digesting the constituents together, and then crystallising from boiling water. By acidifying with HBrAq, the salt $8PbBr_2.Pb(CNS)_2$ is produced (Grissom a. Thorp, *Am.* 10, 229).

Lead, chlorides of. Only one chloride of lead, $PbCl_2$, has been isolated; but there is strong proof of the existence of the tetrachloride, $PbCl_4$, in solutions of PbO_2 in HClAq.

Lead chloride, $PbCl_2$. (*Lead dichloride*

Plumbous chloride. Horn-lead.) Mol. w. 277·14. S.G. 5·805 at 15° (Stolba, *J. pr.* 97, 503); 5·88 (Brügelmann, *B.* 17, 2359). V.D. 137·1 at c. 1080° (mean of 4) (Roscoe, *Pr.* 27, 426). Melts at 498°, and boils between 861° and 954° (Carnelley, *C. J.* 33, 278; and C. a. Williams, *C. J.* 35, 564). Crystallises in rhombic system; $a:b:c = \cdot5943:1:\cdot5949$ (Schabus, *W. A. B.* 1850. 456). H.F. $[Pb,Cl^2] = 82,770$; $[Pb,Cl^2,Aq] = 75,970$ (*Th.* 3, 337).

Occurrence.—As *cotunite*; found in the crater of Vesuvius after the eruption of 1822, mixed with NaCl and $CuSO_4$.

Formation.—1. By heating Pb in a stream of Cl; combination occurs slowly.—2. By dissolving Pb in hot HClAq in contact with air; $PbCl_2$ separates on cooling.—3. By adding solution of a chloride, *e.g.* NaClAq, to a conc. solution of a Pb salt.—4. By dissolving PbS in hot HClAq and crystallising.

Preparation.—PbO or $PbCO_3$ is boiled with dilute HClAq, and HClAq is added little by little until all is dissolved; the liquid is allowed to cool, and the $PbCl_2$ which separates is repeatedly crystallised from boiling water.

Properties.—Large, white, rhombic crystals (*v. supra*), which melt at 498° and boil between 861° and 954° (*v. supra*). V.D. at c. 1080° agrees with the formula $PbCl_2$. Sl. sol. cold water, S. = ·95 at 16·5°, solution contains ·9414 p.c. $PbCl_2$ (Bell, *C. N.* 16, 69); addition of 1 p.c. HCl diminishes S. to ·347, and with 14 p.c. HCl, S. = ·09. If more than 14 p.c. HCl is present S. increases; S. in HClAq S.G. 1·162 = 2·9 (Bell, *l. c.*). According to Field (*C. J.* [2] 11, 575) $PbCl_2$ is less soluble in NaClAq containing 5 p.c. NaCl than in water (S. = ·23); but the values of S. for water and conc. NaClAq are about the same. The considerably greater solubility of $PbCl_2$ in conc. than in dilute HClAq is supposed by Ditte to be due to the formation of a compound of $PbCl_2$ and HCl which is decomposed by water (*C. R.* 92, 718). Ditte gives the following table:—

HCl in 100 pts. H_2O	$PbCl_2$ dissolved in 1000 pts. of the liquid in col. 1				
	at 0°	20°	40°	55°	80°
0	8	11·8	17	21	31
5·6	2·8	3	4·6	6·5	12·4
10	1·2	1·4	3·2	5·5	12
18	2·4	4·8	7·2	9·8	19·8
21·9	4·7	6·2	10·4	12·9	23·8
31·5	11·9	14·1	19	24	38
46	29·8	30 (at 17°)	—	—	—

$PbCl_2$ is readily dissolved by boiling water, but almost all crystallises out on cooling. Insol. alcohol 94 p.c.; somewhat sol. in more dilute. Fairly sol. $NaC_2H_3O_2Aq$, $Na_2S_2O_3Aq$, and some other salt solutions. After melting and cooling, $PbCl_2$ appears as a horn-like mass (hence the name *horn-lead* formerly used).

Reactions.—1. Heated in the *air* until white fumes cease to come off, a light-yellow oxychloride Pb_2OCl_2 (= $PbCl_2.PbO$) is formed (*v. Lead, oxychlorides of*).—2. Recently ppd. $PbCl_2$ when digested with cold *neutral lead acetate* produces an oxychloride $2Pb_2OCl_2H_2O$ (Brandes, *A.* 10, 273).—3. The oxychloride $Pb_2OCl_2.H_2O$ is obtained by partially ppg. $PbCl_2Aq$ by *lime water*.—4. By adding *caustic potash* to $PbCl_2$ suspended in water, the oxychloride $PbCl_2.2PbO$ is said to be formed (Ditte, *C. R.* 94, 1180).—5. According to Berzelius, the product of the action of *ammonia* on $PbCl_2$ is $PbCl_2.3PbO.4H_2O$.—6. Heated in *carbon monoxide*, $COCl_2$ and Pb are produced.—7. Heated, not too strongly, in *phosphoretted hydrogen*, HCl, P, and Pb are formed.—8. Oxidised by *alkaline hypochlorites* to PbO_2.—9. Long-continued passage of Cl into $PbCl_2$ suspended in water most probably produces $PbCl_4$, PbO_2 being simultaneously ppd. (*v.* Fisher, *C. J.* 35, 284).

Combinations.—1. $PbCl_2$ absorbs *ammonia gas*, forming $2PbCl_2.3NH_3$ according to H. Rose. All the NH_3 is readily given off on warming.—2. Combines with *lead monoxide*, when the two are heated together, to form oxychlorides $xPbCl_2.yPbO$ (*v. Lead, oxychlorides of*).—4. With *lead carbonate* forms $PbCl_2.PbCO_3$; obtained by boiling together the two salts; or by the action of CO_2 on $PbCl_2$ under pressure (Miller, *C. J.* [2] 8, 37).—5. With *lead acetate* to form $PbCl_2.Pb(C_2H_3O_2)_2$; obtained by mixing freshly ppd. $PbCl_2$ with $Pb(C_2H_3O_2)_2$ and enough glacial acetic acid to form a viscid mass, which soon solidifies, and removing excess of acid by pressure (Carius, *A.* 127, 87).—6. With *lead phosphate*, forms $PbCl_2.Pb_3(PO_4)_2.H_2O$ and $PbCl_2.2Pb_3(PO_4)_2$, or according to Gerhardt (*A. Ch.* [3] 22, 505) $PbCl_2.Pb_2H_2(PO_4)_2$. The former is produced by pouring boiling $PbCl_2Aq$ into excess of boiling Na_2HPO_4Aq; the latter by pouring the Na phosphate into the $PbCl_2$ solution (Heintz, *P.* 73, 122). *Pyromorphite* $PbCl_2 3Pb_3(PO_4)_2$ occurs native.—7. Combines with *lead bromide* to form $PbCl_2.PbBr_2$, with *lead iodide* to form $PbCl_2.PbI_2$, with *lead fluoride* to form $PbCl_2.PbF_2$, and with *lead sulphocyanide* to form $PbCl_2.Pb(CNS)_2$ (*v. Lead bromochloride, Lead iodobromides, Lead chlorofluoride,* and *Lead chlorosulphocyanide*).—8. Probably combines with *chlorine* to form $PbCl_4$, when Cl is passed into $PbCl_2$ dissolved in considerable excess of HClAq, or when Cl is passed into $PbCl_2Aq$ mixed with $CaCl_2$ (*v. Lead tetrachloride*). — 9. André (*A. Ch.* [6] 3, 104) describes various *double compounds* of $PbCl_2$ with NH_4Cl.

LEAD TETRACHLORIDE. (*Plumbic chloride.*) No other chloride of lead except $PbCl_2$ has been isolated, but there is considerable evidence in favour of the existence in HCl solution of tetrachloride $PbCl_4$.

If a considerable quantity of HClAq is added to $PbCl_2$, and Cl is passed in, the $PbCl_2$ dissolves to a reddish-brown liquid; on warming Cl is evolved; addition of water causes ppn. of PbO_2.

A mixture of $PbCl_2Aq$ with $CaCl_2Aq$ absorbs much Cl and forms a deep-yellow liquid, which may be preserved unchanged in a closed vessel, but is decomposed in an open vessel giving $PbCl_2$ and Cl; a few drops of this liquid added to a large quantity of water gives a pp. of $PbCl_2$ and PbO_2; alkalis and alkaline carbonates ppt. PbO_2; $MnCl_2Aq$ ppts. MnO_2 and $PbCl_2$; Fe, Cu, Zn, gold leaf, and finely divided Pt, are soluble in the liquid with separation of $PbCl_2$; it rapidly oxidises many organic bodies, $PbCl_2$ being ppd.

(Sobrero a. Salmi, *A. Ch.* [3] 29, 165; Nicklès, *A. Ch.* [4] 10, 323).

PbO_2 dissolves in cold fairly conc. HClAq. From this yellow solution, alkalis, alkaline carbonates, oxides and carbonates of Ba, Mg, Zn, &c., and alkaline borates and acetates, ppt. PbO_2. The solution smells of Cl, and is decomposed by heat with evolution of Cl and ppn. of $PbCl_2$. If the HClAq is saturated with PbO_2 the addition of water ppts. PbO_2. Fisher (*C. J.* 35, 282) determined the ratio of Pb ppd. from this solution by water as PbO_2 to Cl given off by decomposing the solution with ppn. of $PbCl_2$. The ratio was almost exactly Pb:2Cl; now this is the ratio required on the hypothesis that the decomposition by water proceeds as shown in equation (1), and the decomposition to $PbCl_2$ and Cl proceeds as shown in equation (2)—

(1) $PbCl_4 + 2H_2O = PbO_2 + 4HCl$
(2) $PbCl_4 = PbCl_2 + Cl_2$.

Fisher proved that the whole of the Pb in solution is thrown down by water as PbO_2. A yellow liquid with properties the same as those of the liquid just described is obtained by treating Pb_3O_4 with a considerable quantity of HClAq (Fisher, *l.c.*).

By the method described above, Sobrero a. Salmi (*l.c.*) obtained a double salt $PbCl_4.9NaCl$, and Nicklès (*l.c.*) obtained $PbCl_4.16CaCl_2$. Evaporation *in vacuo*, over conc. KOHAq, of a solution of PbO_2 in HClAq produces crystals of $PbCl_2$ containing some $PbCl_4$, according to Bendant a. Daguin (*Ann. M.* [5] 4, 239; *v.* also Nikolukine, *J. R.* 1885. 207, abstract in *C. J.* 50, 123).

Lead, chlorobromide of; *v. Lead, bromochloride of.*

Lead, chlorocarbonate of; *v. Lead chloride, Combinations* No. 4.

Lead, chlorocyanide of; *v. Lead cyanochloride of.*

Lead, chlorofluoride of. $PbCl_2.PbF_2$ (= PbFCl). Obtained by ppg. boiling $PbCl_2$Aq by KFAq, or $Pb(C_2H_3O_2)_2$Aq by a solution of 2 parts NaF with 3 parts NaCl (Berzelius). A white powder, slightly soluble in water without decomposition.

Lead, chloriodides of; *v. Lead, iodochlorides of.*

Lead, chlorophosphate of; *v. Lead chloride, Combinations* No. 6.

Lead, chlorosulphide of; *v. Lead, sulphochloride of.*

Lead, chlorosulphocyanide of, $PbCl_2.Pb(CNS)_2$; by digesting the constituents together, and crystallising from boiling water; slowly changed to PbO_2H_2 by NH_3Aq (Grisson a. Thorp, *Am.* 10, 229).

Lead, chromates of; *v.* vol. ii. pp. 155 and 157.

Lead, cyanides of. None has been isolated, but an *oxycyanide*, and also *ferri-* and *ferrocyanides*, are known; *v.* vol. ii. pp. 341, 339, and 335.

Lead, cyanochloride of. $PbCl_2.2PbCy_2$; by digesting $PbCl_2$ with KCyAq (Grisson a. Thorp, *Am.* 10, 229).

Lead, ferricyanide of; *v.* vol. ii. p. 339.

Lead, ferrocyanide of; *v.* vol. ii. p. 335.

Lead, fluochloride of; *v. Lead, chlorofluoride of.*

Lead, fluoride of. PbF_2. Pb is not acted on by HFAq, PbO_2H_2, or $PbCO_3$, dissolves in HFAq, and on evaporating, and heating to remove HF, PbF_2 remains. PbF_2 is also ppd. on adding $Pb(C_2H_3O_2)_2$Aq to HFAq. A white powder; slightly soluble in water; sol. in HNO_3Aq (Berzelius). Gunz (*A. Ch.* [6] 3, 5) gives H.F. of PbF_2 as $[PbO^2H^2,2HF] = 24,300$.

Lead, hydroxides of; *v. Lead, oxides and hydrated oxides of.*

Lead, iodide of. PbI_2. Mol. w. not certainly known, but from analogy of $PbCl_2$ probably 459·46 (= PbI_2). S.G. 6·12; 5·6247 molten at 383° (Rodwell, *T.* 1882. 1144). Melts c. 383°, and boils between 861° and 954° (Carnelley, *C. J.* 33, 277; C. a. Williams, *C. J.* 37, 126). For expansion of PbI_2 *v.* Rodwell, *Pr.* 32, 23. H.F. $[Pb,I^2] = 39,800$ (*Th.* 3, 337).

Preparation.—Solution of $Pb(NO_3)_2$ is added to solution of FeI_2; the pp. is washed with cold water and dried. KI or CaI_2 may be used instead of FeI_2. If $Pb(C_2H_3O_2)_2$Aq is added to KIAq oxyiodides are formed when excess of Pb salt is added, and soluble double iodides are formed if excess of KI is present; to prevent both results the solution of $Pb(C_2H_3O_2)_2$ should be acidified either with HNO_3 or $C_2H_4O_2$.

Properties and Reactions.—Golden-yellow crystals; hexagonal, $a:c = 1:1·3018$ (Nordenskjöld). Melts when heated to a brown-red liquid, and solidifies to a yellow mass. Heated in the air I is evolved, and oxyiodides (*q.v.*) are formed. S. cold water ·03; boiling water ·515. Decomposed by Cl. Zn or Fe boiled with PbI_2 under water forms ZnI_2 or FeI_2, and ppts. Pb. $Na_2S_2O_3$ in excess forms Pb sulphite and NaI (Michaelis a. Koethe, *B.* 6, 999). NH_3Aq added to boiling PbI_2Aq ppts. $3PbO.PbI_2.2H_2O$. Dry PbI_2 is unchanged by light; when moist and exposed to direct sunshine, in contact with the air, it is slowly changed to $PbCO_3$ and PbO_2 with separation of I; this change is hastened by all substances which absorb I (Schmid, *P.* 127, 493). PbI_2 is somewhat soluble in conc. solution of alkali iodides, but is ppd. on dilution.

Combinations.—1. Absorbs *ammonia*, forming a white compound $PbI_2.2NH_3$.—2. With *lead monoxide* forms various oxyiodides $xPbI_2.yPbO$ (*v. Lead, oxyiodides of*).—3. By dissolving PbI_2 in warm *iodhydric acid* solution, and allowing to cool, white lustrous needles of $PbI_2.2HI = H_2PbI_4$ separate. This compound may be called *iodo-plumbhydric acid* or *iodo-plumbic acid*; it is decomposed by water; gives off HI *in vacuo*; according to Berthelot, the crystals contain $10H_2O$ (*C. R.* 91, 1024).—4. PbI_2 combines with *potassium iodide* to form various double salts, one of which, $PbI_2.2KI$, seems best regarded as the K salt of H_2PbI_4. Yellow, lustrous leaflets of $PbI_2.KI$ are obtained by dissolving the constituent salts in the ratio PbI_2:KI in boiling water, and allowing to cool; by dissolving this salt in warm KIAq and cooling, the salt $PbI_2.4KI$ is said to be obtained in white needles (Boullay, *A. Ch.* [2] 34, 366). Remsen (*Am.* 11, No. 5) asserts that the process described by Boullay does not result in production of $PbI_2.4KI$, and that the salt formed with most ease when PbI_2 and KI react under different conditions is $PbI_2.KI.H_2O$ (*cf.* Ditte, *C. R.* 92, 1341).—5. By mixing a boiling solution of KI

and NH_4Cl with $Pb(C_2H_3O_2)_2Aq$, taking care that no permanent pp. was formed, and cooling, Völkel obtained clear yellow lustrous needles of $PbI_2.2NH_4Cl$ (*P.* 62, 252); decomposed by water with separation of PbI_2. By saturating hot NH_4ClAq with PbI_2, cooling, pouring off from $PbI_2.2PbCl_2$ which separates, and evaporating, Poggiale (*C. R.* 20, 1180) obtained $PbI_2.4NH_4Cl.2H_2O$; decomposed by water with separation of PbI_2.—6. PbI_2 combines with *silver iodide*. For properties of the $PbI_2.AgI$ produced *v.* Rodwell (*Pr.* 32, 540); Bellati a. Romanese (*Pr.* 34, 104).—7. Compounds with *lead bromide* are formed by crystallising PbI_2 from HBrAq (*v. Lead, iodobromides of*).—8. Compounds with *lead chloride*, $PbI_2.PbCl_2$(= PbICl) and $PbI_2.2PbCl_2$, are known (*v. Lead, iodochlorides of*).—9. By boiling $PbCO_3$ repeatedly with PbI_2Aq, Poggiale (*C. R.* 20, 1184) obtained $PbI_2.PbCO_3$.—10. $PbI_2.Pb(C_2H_3O_2)_2$ was obtained by Carius (*A.* 127, 87) similarly to the $PbCl_2$ compound (*v. Lead chloride, Combinations* No. 5).

Lead, iodobromides of. By crystallising PbI_2Aq from HBrAq, Grisson a. Thorp obtained the compounds (1) $PbBr_2.PbI_2$, (2) $3PbBr_2.PbI_2$, (3) $6PbBr_2.PbI_2$ (*Am.* 10, 229).

Lead, iodocarbonate of; *v. Lead, iodide of, Combinations* No. 9.

Lead, iodochlorides of. The compound PbClI (= $PbCl_2.PbI_2$) is obtained, in sulphur-yellow prisms, by cooling a solution of PbI_2 in boiling HClAq (Labouré, *J. Ph.* [3] 4, 328). According to Engelhardt the compound contains more PbI_2 than required by the above formula (*J. pr.* 67, 293). By saturating hot NH_4ClAq with PbI_2, and allowing to cool, Poggiale obtained yellow needles of $PbI_2.2PbCl_2$ (*C. R.* 20, 1180).

Lead, iodosulphocyanide of, $PbI_2.3Pb(CNS)_2$; formed with some difficulty by digesting the constituents and crystallising from hot water (Grisson a. Thorp, *Am.* 10, 229).

Lead, oxides and hydroxides (or hydrated oxides) of. Five oxides of lead have been isolated, viz., Pb_2O, PbO, Pb_2O_3, Pb_3O_4, and PbO_2; one or more oxides intermediate between Pb_3O_4 and PbO_2 perhaps exist. Two hydrates of PbO, viz. $2PbO.H_2O$ and $3PbO.H_2O$ are known; the hydrates $Pb_2O_3.3H_2O$ and $PbO_2.H_2O$ have also been isolated. The most stable oxide is PbO; Pb_2O is easily oxidised to PbO by heating in air, and Pb_2O_3, Pb_3O_4, and PbO_2 are reduced to PbO when strongly heated. PbO reacts with acids as a basic oxide, forming salts PbX_2, $X = NO_3$, Cl, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c.; it decomposes NH_4 salts, evolving NH_3, and combines with CO_2 to form $PbCO_3$. PbO also reacts with strongly basic oxides as an acidic oxide forming unstable *plumbites, e.g.* K_2PbO_2. PbO_2 reacts as an acidic peroxide; with KOH and NaOH it forms fairly stable *plumbates*, $M^I_2PbO_3$; with most acids it forms salts of PbO, but it appears capable of dissolving without reduction in glacial acetic and phosphoric acids. The reactions of Pb_2O_3 and Pb_3O_4 indicate that these oxides are compounds of the form $xPbO.yPbO_2$. As none of the oxides of Pb has been gasified the molecular weight of none is known with certainty.

Lead suboxide, Pb_2O. The grey pellicle which forms on the surface of lead exposed to the air consists of Pb_2O, according to Berzelius. Pb_2O is prepared by heating PbC_2O_4 in a retort to near 300° as long as any gas is given off; $2PbC_2O_4 = Pb_2O + CO + 3CO_2$; the residue is allowed to cool in the retort (Dulong, *S.* 17, 229; Pelouze, *J. pr.* 25, 486). Pb_2O is a black powder; S.G. 9·772 (Playfair a. Joule, *C. S. Mem.* 3, 83); heated in air it burns to PbO; heated out of contact with air, PbO and Pb are produced. Moist Pb_2O rapidly absorbs O from the air, forming white $PbO.xH_2O$. Dilute acids resolve Pb_2O into PbO, which dissolves, and Pb; saturated $Pb2NO_3Aq$ produces a similar resolution, but Pb_2O is wholly soluble in dilute $Pb2NO_3Aq$. This oxide was at one time supposed to be a mixture of PbO and Pb; but this is disproved by the facts that when the oxide is rubbed with Hg, either dry or under water, no Pb is removed, and that PbO is not removed from it by boiling with Pb acetate solution.

Lead protoxide PbO. (*Plumbous oxide. Litharge. Massicot.*) Mol. w. unknown, as oxide has not been gasified. S.G. 9·277 at 17·5° (Herapath, *P. M.* 64, 321); 9·25 (Playfair a. Joule, *C. S. Mem.* 3, 84); 9·17 to 9·88 (Ditte, *C. R.* 94, 1310); 8·74 to 9·29 (Geuther, *A.* 219, 60). H.F. [Pb,O] = 50,300; heats of neutralisation [PbO,2HClAq] = 56,830; [PbO,HNO³Aq] = 24,250 to form basic nitrate (*Th.* 3, 337). Crystallises in rhombic forms $a:b:c$ = ·666:1: ·971 (Nordenskjöld, *P.* 114, 619; *v.* also Mitscherlich, *P.* 49, 403; *J. pr.* 19, 451; Grailich, *W. A. B.* 28, 282; Marx, *J. pr.* 3, 217). PbO is dimorphous according to Ditte (*C. R.* 94, 1310).

Occurrence.—As *lead-ochre*, in small quantities in Mexico, Baden, Virginia, and a few other localities.

Formation.—1. By heating Pb to low redness in presence of air; if the temperature is kept below the melting-point of the PbO, the oxide is obtained as a yellowish powder, known commercially as *massicot*; if the PbO is melted during the preparation, the oxide solidifies to a scaly reddish solid known as *litharge*.—2. By heating Pb with KNO_3.—3. By strongly heating red lead in air.—4. By strongly heating 'white lead' on an iron plate.—5. By adding boiling Pb acetate solution to boiling KOHAq; pp. is crystalline (Winkelblech, *A.* 21, 21; *J. pr.* 10, 227).—6. By slowly pouring Pb acetate solution into CaOAq at 80° until a crystalline crust appears, then adding a little more, and allowing to cool (Brendecke, *R. P.* 55, 318).—7. By adding $PbSO_4$, made into a paste with water, to boiling NaOHAq (Wichmann, *C. C.* 1860. 334). For modifications of these processes *v.* Payen, *J. pr.* 13, 485; Behrens, *B. J.* 24, 134.—8. According to Yorke (*P. M.* [3] 5, 82), crystals of PbO are produced by placing Pb in a vessel of water exposed to the air. The reaction of steam with Pb at white heat produces PbO.

Preparation.—1. Basic Pb nitrate is heated in a Pt crucible until completely decomposed (the neutral salt melts before decomposition is complete). Berzelius recommends the following procedure. Equal weights of PbO and $Pb2NO_3$ are kept in boiling water until the PbO is wholly transformed into basic nitrate; the basic salt is dissolved in boiling water, the solution is filtered hot and allowed to cool; the basic nitrate which separates is subjected to the action of the boiling solution as long as any solid separates on cooling.

A small quantity of the basic nitrate is made into a paste with water, the inside of a Pt crucible is covered with this paste, and the crucible is dried; the rest of the salt is strongly pressed while moist, then dried, and broken into smaller pieces, which are placed in the crucible, which is then heated until the decomposition is completed. The PbO formed from the pieces of basic nitrate in the middle of the crucible is pure; the outer layers of PbO contain a little Pt.—2. PbO is prepared in crystalline form by dissolving PbO, prepared as in 1, in hot KOHAq or NaOHAq and allowing to cool. The colour and S.G. of the crystals vary with the conditions. Ditte (*C. R.* 94, 1310) obtained a greenish crystalline mass (S.G. 9·1699) by heating KOHAq c. 13 p.c. with $PbO.xH_2O$; using 25 p.c. KOHAq he obtained sulphur-yellow lustrous crystals (S.G. 9·2089); brownish needles (S.G. 9·8835) were obtained by using 30 p.c. KOHAq and allowing to cool; KOHAq 18·5 p.c., saturated with $PbO.xH_2O$ when hot, gave deep green, almost black, crystals on cooling (S.G. 9·5605); saturated KOHAq boiled with $PbO.xH_2O$ gave deep rose-coloured crystals of PbO (S.G. 9·4223), differing in form from the usual crystals, and becoming yellow when strongly heated (*cf.* Mitscherlich, *J. pr.* 19, 451; Calvert, *B. J.* 24, 135; Becquerel, *A. Ch.* [2] 51, 105).

Properties.—PbO is a yellow to reddish-yellow crystalline solid; the colour and S.G. of the oxide when well crystallised seem to vary with the conditions of formation, *v. Preparation*, No. 2. Melts between 585° and 630° to a clear dark-red liquid. According to Leblanc (*B. J.* 26, 193) molten PbO absorbs O, which it gives off on solidifying. PbO is sl. sol. water; 1 part dissolves in c. 7000 water; the solubility is affected by the state of aggregation of the PbO (*cf.* Bineau, *C. C.* 1855. 877); if the solution is exposed to the air CO_2 is absorbed, and the Pb ppd. as basic carbonate; the PbO is also removed by filtration through paper (Yorke, *P. M.* [3] 5, 82). Heated to between 300° and 450° in air, PbO is oxidised to Pb_3O_4, but at higher temperatures Pb_3O_4 is deoxidised to PbO. PbO is soluble in warm conc. KOHAq or NaOHAq. Geuther (*A.* 219, 56) says that two varieties of PbO exist, one yellow and the other red; the yellow crystallises in rhombic, the red in hexagonal, forms.

Reactions.—1. *Heated in air* Pb_3O_4 is formed at c. 300°–450°; at a somewhat higher temperature PbO is re-formed.—2. Heated in *hydrogen*, or *carbon monoxide*, reduction to Pb occurs at a little above 100°; PbO is also reduced to Pb by heating with C, Na, or KCN.—3. Reacts with most *acids* to form salts PbX_2, X = NO_3, Cl, $\frac{1}{2}SO_4$, &c.; absorbs CO_2 from the air forming $PbCO_3$.—4. Decomposes *alkali salts* with separation of the alkali.—5. Dissolves in warm fairly conc. *potash* or *soda* solution, probably with formation of *plumbites* $K_2(Na_2)PbO_2$.—6. Dissolves in *molten potash* forming K_2PbO_2 which, on long-continued heating in air, is oxidised to K_2PbO_3 (Carnegie, *C. N.* 60, 113) (*v.* PLUMBATES under LEAD PEROXIDE, p. 132).—7. Dissolves also by boiling with *milk of lime*: on evaporating in absence of air a compound separates in needles, probably $CaPbO_2$.—8. Molten PbO dissolves *silica*, easily forming glass-like silicates; these silicates readily dissolve CaO, Al_2O_3, &c.—9. Heated in *chlorine*, *bromine*, or *iodine* vapour, the compound $PbCl_2$, $Pb_7Br_{11}O_2$, or $Pb_9I_4O_6$, is formed; heated with Cl and air, Br and air, or I and air, the product is $Pb_8Cl_{16}O$, $Pb_9Br_7O_2$, or $Pb_9I_2O_8$ (Cross a. Sigiura, *C. J.* 33, 405).—10. By boiling excess of PbO with conc. *calcium chloride* solution, filtering, and washing with alcohol the pp. that forms on cooling, André (*C. R.* 104, 359) obtained $2PbO.CaO.CaCl_2.4H_2O$; by using *strontium chloride* he obtained $2PbO.SrCl_2.5H_2O$. 11. PbO does not react with *phosphorus trichloride* at 160°, but when heated together over a flame, PbO and PCl_3 react violently forming $PbCl_2$, $Pb(H_2PO_3)_2$, and P (Michaelis, *J. pr.* [2] 4, 449).—12. Dissolves in *magnesium chloride* solution; on filtering and evaporating, the oxychloride $3PbO.PbCl_2.H_2O$ separates (Voigt, *Chem. Zeitung*, 13, 695).

HYDRATES OF LEAD MONOXIDE.—1. $3PbO.H_2O$; obtained by adding c. 400 grams KOH to 1000 cc. water containing freshly ppd. PbO in suspension (Ditte, *C. R.* 94, 1310); also by adding basic Pb acetate solution to NH_3Aq at 20°–25°, and digesting the pp. under the liquid for some time (Payen, *A. Ch.* [4] 8, 302; Behrens, *B. J.* 24, 134). This hydrate forms lustrous octahedral crystals; S.G. 7·592 at 0° (Ditte, *C. R.* 94, 1310); loses some H_2O at 130°, and is entirely dehydrated at 145°; c. sol. caustic alkali solutions.—2. $2PbO.H_2O$. By ppg. $Pb(C_2H_3O_2)_2Aq$ by KOHAq or NaOHAq, and digesting with excess of pptant.; if $Pb(NO_3)_2$ is used some basic nitrate is always formed (Schaffner, *A.* 51, 175). The hydrates of PbO readily absorb CO_2 from the air; they also combine with NH_3 to form $PbO.H_2O.2NH_3$ and $8PbO.2NH_3.H_2O$ (Calvert, *C. R.* 23, 480).

Plumbites. Although PbO is a markedly basic oxide, it nevertheless dissolves in alkali solutions to form unstable salts of the form $M^I_2PbO_2$; these salts, *plumbites*, have not been much investigated; according to Carnegie (*C.N.* 60, 113) K plumbite is formed by dissolving PbO in molten KOH, and on long-continued heating in air it is oxidised to plumbate K_2PbO_3. The Ag salt is produced by adding NaOHAq to a mixture of a Pb and a Ag salt; Wöhler gives the formula $Ag_2O.2PbO$. Krutwig (*B.* 15, 1264) obtained a yellow salt, $Ag_2PbO_2.2H_2O$, by adding $AgNO_3Aq$ to alkaline $Pb(NO_3)_2Aq$, and washing with hot KOHAq and then with hot water; the salt soon became black in the air.

LEAD SESQUIOXIDE. Pb_2O_3. (*Plumbo-plumbic oxide.*) Mol. w. unknown, as oxide has not been gasified. A reddish-yellow powder resembling PbO; Debray describes Pb_2O_3 as greenish-brown (*C. R.* 86, 513). Debray (*l.c.*) prepares this oxide by heating PbO_2 to 350°, or by heating PbO or better $PbCO_3$ to the same temperature in a stream of air or O; Carnelley a. Walker (*C. J.* 53, 85) say that PbO_2 is changed to Pb_2O_3 at 280°–290°, and that Pb_2O_3 gives off O at c. 370°. According to Jacquelain (*J. pr.* 53, 153) Pb_2O_3 may be obtained by pouring a solution of red lead, Pb_3O_4, in glacial acetic acid into very dilute NH_3Aq, separating the pp. quickly, washing it with hot water containing a very little acetic acid, and drying at 100°. Winkelblech (*A.* 21, 21) obtained this oxide by pouring NaOHAq into $Pb(C_2H_3O_2)_2Aq$ until the pp. dissolved, and then

adding cold NaClOAq, taking care to avoid excess which would produce PbO_2. Debray asserts that this method yields only a mixture of PbO and PbO_2. Pb_2O_3 is not decomposed by heat until c. 360°, but a little above this temperature it gives off O, leaving Pb_3O_4; heated to c. 530°, PbO is produced (Carnelley a. Walker, *C.J.* 53, 85). Pb_2O_3 is resolved by acids into PbO_2 and a salt of PbO; Winkelblech's statement that Pb_2O_3 is dissolved unchanged by HClAq, from which solution it may be ppd. again by alkalis, is denied by Hausmann (*A.* 91, 235). Pb_2O_3 is reduced to PbO by $H_2C_2O_4$Aq or $H.CO_2H$Aq.

Hydrate of lead sesquioxide. $Pb_2O_3.3H_2O$. Obtained by adding PbO to conc. K_2PbO_3Aq, as a red curdy pp. (Seidel, *J. pr.* [2] 20, 200). The solution of K_2PbO_3 is obtained by dissolving pure PbO_2 in molten KOH with a very little water, and then dissolving the fused mass in a small quantity of water.

Red oxide of lead. Pb_3O_4. (*Diplumbo-plumbic oxide. Red lead. Minium.*) Mol. w. unknown, as oxide has not been gasified. S.G. 9·096 at 15° (Herapath, *P. M.* 64, 321).

Occurrence.—*Minium* is found mixed with other lead ores in Yorkshire, Anglesey, Virginia, the Eifel, &c.

Formation.—By heating PbO in air to low redness (not above 450°) for some time, and cooling slowly.—2. By adding PbO in KOHAq to K_2PbO_3Aq, washing the pp. with hot water, and heating it.—3. Finely divided ppd. Pb exposed to air in presence of water and a little NH_3Aq is slowly changed to Pb_3O_4 mixed with Pb carbonate (Schönbein, *J. pr.* 74, 323).

Preparation.—1. A mixture of 1 pt. $KClO_3$, 4 pts. PbO (prepared by heating $PbCO_3$), and 8 pts. KNO_3 is heated; the mass melts, and PbO_2 is formed and on continued heating is changed to Pb_3O_4; the fused mass is treated with water and the residue is boiled with dilute KOHAq, to dissolve unchanged PbO, washed and dried (Levol, *J. pr.* 22, 38).—2. 5 to 6 pts. $Pb(NO_3)_2$ are dissolved in water, and KOH is added until the pp. which forms is dissolved, to this liquid is added 1 pt. PbO_2 and the whole is boiled for some time; unchanged PbO_2 is decomposed by digesting with $H_2C_2O_4$Aq, and the PbC_2O_4 formed is dissolved in KOHAq; the residue is washed and dried (Levol, *l.c.*).—3. Commercial red lead usually contains some PbO; this may be removed by digestion with dilute acetic acid, or better with lead acetate solution. Löwe (*D.P.J.* 271, 472) recommends to digest 1 pt. commercial red lead with 10-15 pts. of a 10 p.c. solution of $Pb(NO_3)_2$, for some time at a gentle heat, then to boil, and finally wash well.

Properties.—A scarlet crystalline-granular powder; when heated it becomes brighter red and then violet; at c. 500°-530° decomposition to PbO and O occurs. S.G. according to different observers varies from 8·91 to 9·1 (*v.* Clarke's *Specific Gravity Tables.* [2nd ed.], p. 47). Insol. water; reacts with dilute acids to form salts of PbO, and PbO_2 which remains undissolved; with conc. H_2SO_4, or HClAq, gives salts of PbO and O or Cl. Dissolves completely in glacial acetic acid forming a liquid which acts as an energetic oxidiser (*v. Reactions*, No. 6). Pb_3O_4 is readily reduced to PbO, *e.g.* by SO_2Aq or HNO_2Aq.

Reactions.—1. *Heated* to c. 500°-530°, gives PbO and O.—2. Reduced to PbO by *easily oxidised bodies*, *e.g.* SO_2Aq, HNO_2Aq, solution of sugar.—3. With *stannous chloride* gives $PbCl_2$ and $SnCl_4$.—4. Dissolves in considerable quantity of conc. cold *hydrochloric acid* to form a yellow liquid from which alkalis, alkaline carbonates, borates, and acetates, and oxides and carbonates of Ba, Mg, Zn, &c. ppt. PbO_2; on heating, the solution decomposes to $PbCl_2$ and Cl; this solution almost certainly contains $PbCl_4$, on warming Cl is evolved and $PbCl_2$ ppd. (Fisher, *C. J.* 35, 282; *v. Lead tetrachloride*, p. 126). Dilute HClAq forms $PbCl_2$, H_2O, and PbO_2. Warm HClAq in excess evolves Cl and ppts. $PbCl_2$.—5. *Dilute sulphuric, nitric*, or *acetic acid*, and other *dilute acids* ppt. PbO_2 and form sulphate, &c. of PbO. Hot conc. H_2SO_4 forms $PbSO_4$ and O.—6. Pb_3O_4 dissolves in *glacial acetic acid*; this solution is strongly oxidising, *e.g.* it converts SO_2Aq to SO_3Aq, As_2O_3Aq to As_2O_5Aq, PbS to $PbSO_4$, Pb, Hg, and Cu to oxides, separates I from KI (Schönbein, *J. pr.* 74, 315); when dropped into dilute NH_3Aq a pp. of Pb_2O_3 is produced (Jacquelain, *J. pr.* 53, 153; *v. Lead sesquioxide*, p. 129). According to Jacquelain (*loc. cit.*) a solution of Pb_3O_4 in glacial acetic acid at 40° gives crystals of $PbO(OC_2H_3O)_2$ on cooling; these crystals may be kept under acetic acid but are resolved into PbO_2 and $H_4C_2O_2$ on warming or treating with water. Schönbein (*J. pr.* 74, 315) says that conc. acetic acid dissolves about 9 p.c. of Pb_3O_4 when shaken for 15 mins. with excess of the finely powdered oxide; the solution is easily decomposed by heat or dilution, but is stable at c. −18°; by careful addition of H_2SO_4, $PbSO_4$ is ppd. and an acetate corresponding to PbO_2 remains in solution; this solution deposits PbO_2, slowly at ordinary temperatures, quickly when heated; addition of KOHAq does not ppt. Pb_3O_4, but a mixture of PbO and PbO_2.—7. Pb_3O_4 dissolves in conc. *phosphoric acid*; the solution reacts similarly to that of Pb_3O_4 in acetic acid. By using a *mixture of phosphoric and sulphuric acids*, a solution is obtained containing only the phosphate corresponding to PbO_2, and free from PbO (Jacquelain, *J. pr.* 53, 152; *v. Lead peroxide*, p. 131).—8. Conc. solutions of *arsenic* and *tartaric acids* dissolve Pb_3O_4; the solutions resemble those in acetic and phosphoric acids, but are more easily decomposed.

Composition and constitution of red lead.—When PbO is heated in air, O is slowly and continuously absorbed; when c. 1·76 p.c. O has been absorbed the product is red, but absorption of O continues, and some specimens of red lead contain 2·67 p.c. O in excess of that contained in the PbO (Jacquelain, *J. pr.* 53, 151). An absorption by PbO of 1·79 p.c. O corresponds with the formation of Pb_4O_5; the formation of Pb_3O_4 requires 2·39 p.c. Older analyses of red lead led to the supposition that it was Pb_2O_3 (Dumas, *B. J.* 13, 113). Careful syntheses and analyses have, however, shown that a definite red-coloured oxide exists having the composition Pb_3O_4. At the same time the analyses of commercial red leads made by Mulder (*J. pr.* 50, 438) and Jacquelain (*J. pr.* 53, 151) show that the percentage of O above that required to form PbO varies from 1·16 to 2·67. Several samples of red lead agreed in composition with the formula Pb_4O_5,

others approached Pb_3O_7 (*cf.* Löwe, *D. P. J.* 271, 472). It is still doubtful whether a series of oxides exists of the form $xPbO.yPbO_2$, x varying from 1 to 3 or 4 and y from 1 to 2 or 3, or whether only two such oxides are definite bodies, viz. $PbO.PbO_2(=Pb_2O_3)$ and $2PbO.PbO_2(=Pb_3O_4)$.

Red lead, Pb_3O_4, may be regarded either as $2PbO.PbO_2$ or as $PbO.Pb_2O_3$; the reaction of Pb_3O_4 with acids, the synthesis of Pb_3O_4 by the action of PbO in KOHAq on $K_2PbO_3(=K_2O.PbO_2)$, and the fact that PbO_2 is acidic towards some oxides, point to the constitution $2PbO.PbO_2$ rather than $PbO.Pb_2O_3$.

Lead peroxide. PbO_2. (*Brown oxide of lead. Puce oxide of lead. Lead dioxide.*) Mol. w. unknown, as oxide has not been gasified. S.G. 8·902 at 16·5° (Herapath, *P. M.* 64, 321); 8·756 to 8·897 (Playfair a. Joule, *C. S. Mem.* 3, 84); 9·045 (Wernicke, *P.* 141, 109).

Occurrence.—As *plattnerite*, at Leadhills, in hexagonal prisms.

Formation.—1. By boiling a Pb salt with a filtered solution of bleaching powder.—2. By digesting red lead with dilute HNO_3Aq, and washing the residue.—3. By mixing solutions of Pb acetate (4 pts.) with soda crystals ($3\frac{1}{2}$ pts.), and passing Cl into the mixture: $2\frac{1}{2}$ pts. PbO_2 are obtained; $PbCl_2$ is not formed (Wöhler, *J. pr.* 90, 383; *cf.* Geuther, *A.* 96, 382).—4. By heating PbO with $KClO_3$ to less than red heat and washing the mass with water.—5. By boiling $PbO.xH_2O$ with K_3FeCy_6Aq in presence of KOH ($2K_3FeCy_6Aq + 2KOHAq + PbO = 2K_4FeCy_6Aq + PbO_2 + H_2O$; Overbeck, *Ar. Ph.* [2] 85, 5).—6. By fusing PbO with KOH for some time (Becquerel, *A.Ch.* 51, 504). Carnegie (*C. N.* 60, 113) obtained $PbO_2.H_2O$ by long-continued fusion of PbO in KOH, solution in water, and careful neutralisation by dilute H_2SO_4Aq (*v. Hydrates of lead peroxide, infra*).—7. By oxidising PbO by an alkaline solution of $KMnO_4$ (Reynoso, *C. R.* 32, 646).—8. By electrolysing strongly alkaline solutions of Pb salts, the hydrate $PbO.H_2O$ (*q.v.*) is deposited on the positive electrode (Becquerel, *A.Ch.* [3] 8, 405). By slowly electrolysing a solution of 1 pt. $Pb(NO_3)_2$ in 8 pts. water, Wernicke obtained PbO_2 (*P.* 141, 109).—9. PbO_2 is obtained, mixed with PbO, by shaking basic Pb acetate with H_2O_2Aq (Schönbein, *J. pr.* 75, 88).

Preparation.—1. Very finely powdered Pb acetate is subjected to the action of a boiling filtered solution of bleaching powder, the liquid being poured off, and fresh solution added from time to time, until no trace of Pb is found in solution; the residue is washed with hot water, and dried at a low temperature (Böttger, *J. pr.* 73, 493).—2. Fehrmann (*B.* 15, 1882) recommends to add a filtered solution of bleaching powder to conc. $PbCl_2Aq$ at 50° to 60°, until a few drops of the supernatant liquid cease to show a brown colour when filtered, and to wash the pp. out of contact with air.

Properties.—A dark puce-brown powder; black according to Fehrmann (*B.* 15, 1882). The native compound forms metal-like, lustrous, iron-black, hexagonal crystals; S.G. 9·392 to 9·448 (Breithaupt, *J. pr.* 10, 508). When heated, PbO_2 gives Pb_3O_4 and O, and at a higher temperature it is resolved into PbO and O. Readily parts with O to oxidisable bodies, *e.g.* rubbed with P or S vivid combustion occurs; sugar and gallic acid &c. are ignited by trituration with PbO_2. Acids generally react with PbO_2 to form salts of PbO; cold conc. HClAq seems to produce $PbCl_4$, and solutions of Pb_3O_4 in glacial acetic and phosphoric acids probably contain salts corresponding with PbO_2 (*v. Reactions*, No. 9). PbO_2 reacts with strongly basic oxides as an acidic oxide to form plumbates $M^I_2PbO_3$ (*v. infra, Plumbates*). On account of its readiness to part with O, PbO_2 is largely used for forming a surface on which to strike 'safety' matches.

Reactions.—1. *Heated*, easily goes to Pb_3O_4 and O, and at a higher temperature to PbO and O.—2. Readily gives up $\frac{1}{2}$ of its O to *easily oxidised bodies*, either at the ordinary temperature or by slightly heating; *e.g.* when PbO_2 is rubbed with an equal weight of $H_2C_2O_4$, H_2O, CO_2, and $PbCO_3$ are formed; PbO_2 rubbed with $\frac{1}{8}$ pt. sugar or $\frac{1}{6}$ pt. tartaric acid oxidises these rapidly, causing ignition; P is oxidised and ignited when rubbed with PbO_2 (*v.* Böttger, *A.* 34, 94).—3. *Sulphur dioxide* is rapidly absorbed by PbO_2 with rise of temperature and production of SO_3. 4. *Potassium iodide* is decomposed with liberation of I.—5. PbO_2 reacts with a dilute solution of *potassium ferrocyanide* to form K_3FeCy_6 provided the KOH produced in the reaction is neutralised by CO_2; with conc. *potassium ferricyanide* solution in presence of KOH, K_4FeCy_6 is formed.—6. By digesting PbO_2 with *ammonia solution*, PbO, H_2O, and NH_4NO_3 are produced. 7. Not acted on by cold *nitric* or *sulphuric acid*; with hot conc. H_2SO_4 gives $PbSO_4$ and O.—8. Cold conc. *hydrochloric acid* in excess dissolves PbO_2, producing a yellow liquid which evolves Cl on heating and gives a pp. of $PbCl_2$; alkalis, alkaline carbonates, and alkaline earth oxides and carbonates ppt. PbO_2 from this solution; the solution almost certainly contains $PbCl_4$ (*v. Lead tetrachloride*, p. 126). Hot HClAq evolves Cl and forms $PbCl_2$.—9. A basic acetate derived from PbO_2 is said by Jacquelain (*J. pr.* 53, 152) to be obtained by dissolving *red lead* in *glacial acetic acid* at 40° and cooling; J. gives the formula $PbO(C_2H_3O_2)_2$ to the crystals which form. These crystals may be preserved unchanged under acetic acid; on drying between paper, or on adding water, they are resolved into PbO_2 and acetic acid. Similar salts derived from PbO_2 are obtained by dissolving *red lead* in very conc. *phosphoric* and *arsenic acids*, but the salts are very unstable (J. *l.c.*; *cf. Red oxide of lead, Reactions*, No. 6, p. 130).—10. Heated with *phosphorus trichloride*, $PbCl_2$, $POCl_3$, and $Pb(H_2PO_3)_2$ are formed (Michaelis, *J. pr.* [2] 4, 449).—11. Heated in *chlorine*, *bromine*, and *iodine*, the compounds Pb_4Cl_7O, $Pb_7Br_{11}O_2$, and $Pb_{11}I_5O_7$, respectively, are obtained; heated in *chlorine and air*, *bromine and air*, and *iodine and air*, the products are $Pb_{12}Cl_{21}O_4$, $Pb_4Br_5O_2$, and $Pb_{11}I_4O_{10}$, respectively (Cross a. Sigiura, *C. J.* 33, 405).—12. PbO_2 reacts with *alkalis* to form compounds in which PbO_2 forms the negative radicle; *e.g.* the salt K_2PbO_3 may be obtained from a solution in conc. hot KOHAq (*v. infra, Plumbates*).

Hydrates of lead peroxide. (1) $PbO_2.H_2O$. This hydrate is formed, as a brown pp., by dis-

solving PbO in molten KOH, heating in air for a considerable time, dissolving the K_2PbO_3 produced in cold water, and *exactly neutralising* by dilute H_2SO_4Aq (Carnegie, *C. N.* 60, 113). It is also probably obtained, at the positive electrode, by the electrolysis of strongly alkaline solutions of Pb salts (Becquerel, *A. Ch.* [3] 8, 405). By electrolysing an alkaline solution of Pb-Na tartrate, Wernicke (*P.* 141, 109) obtained a lustrous blue-black film, which had the composition $PbO_2.H_2O$, S.G. 6·267. (2) According to Carnelley a. Walker (*C. J.* 53, 85), ppd. PbO_2 after drying in the air for 10 days has very nearly the composition $3PbO_2.H_2O$; at 230° this hydrate is changed to PbO_2.

Plumbates.—PbO_2 reacts with acids as a basic peroxide forming salts corresponding with PbO; in some cases unstable salts derived from PbO_2 appear to be produced (*v. supra*, *Lead peroxide*, *Reactions* 8 and 9). PbO_2 also reacts with alkalis as an acidic oxide to form salts $M^I_2PbO_3$ known as *plumbates*. Fremy (*C. R.* 15, 1109) obtained colourless crystals of $K_2PbO_3.3H_2O$ by dissolving PbO_2 in boiling very conc. KOHAq, adding a little water, and placing over H_2SO_4. Seidel (*J. pr.* [2] 20, 200) obtained the salt by adding PbO_2 to molten KOH containing a little water, dissolving the fused mass in water, and evaporating over H_2SO_4 *in vacuo*. The crystals form quadratic octahedra, $a:c = 1:1·2216$; they are decomposed by water with separation of PbO_2. A corresponding Na salt is known. Solutions of these salts are said to yield pps. of plumbates when added to solutions of various metallic salts. K_2PbO_3 is also produced by dissolving PbO in molten KOH and heating in air (Becquerel, *A. Ch.* 51, 504; Carnegie, *C. N.* 60, 113). According to Crum (*A.* 55, 213) a plumbate of Ca is obtained by digesting $Pb(NO_3)_2$ for some hours at 57° with excess of CaO and bleaching powder.

Lead, oxybromides of. Several oxybromides of Pb are known. The compound $PbO.PbBr_2$ is formed by heating $PbBr_2$ in air so long as white fumes are evolved; also by digesting $PbBr_2$ with solution of Pb acetate. By heating PbO in Br vapour, Cross a. Sigiura obtained $Pb_7Br_{11}O_2$; and by heating the same oxide in a mixture of Br and air they obtained $Pb_6Br_7O_2$ (*C. J.* 33, 405); from PbO_2 they obtained $Pb_7Br_{11}O_2$ by heating in Br.

Lead, oxychlorides of. $PbCl_2$ and PbO very readily combine when heated together to form oxychlorides from which HNO_3Aq dissolves out PbO.

$PbCl_2.PbO$: occurs native as *matlockite*, S.G. 7·21 (Greg, *P. M.* [4] 2, 120; Rammelsberg, *P.* 75, 141); formed by heating $PbCl_2$ in air until fumes are no longer evolved; also by digesting freshly ppd. $PbCl_2$ with cold Pb acetate solution (the oxychloride thus formed is $(PbCl_2.PbO)_2.H_2O$ according to Brandes, *A.* 10, 273); also (with H_2O) by partial ppn. of $PbCl_2Aq$ by CaOAq, thus prepared it is used as a pigment (*Pattinson's white lead*).

$PbCl_2.2PbO$: occurs native as *mendipite*, in yellow-white trimetric prisms, S.G. 7 to 7·1; formed, according to Ditte (*C. R.* 94, 1180), by gradually adding KOHAq to $PbCl_2$ suspended in water, or by adding KClAq to $PbO.xH_2O$.

$PbCl_2.3PbO$: the hydrate with $4H_2O$ is formed by adding NH_3Aq to $PbCl_2Aq$ (Berzelius); also by mixing NaCl with PbO, making into a paste with water, and allowing to stand; the product of this reaction, when washed and heated, gives a yellow powder, known as *Turner's yellow*, which is probably $PbCl_2.3PbO$. The hydrate $PbCl_2.3PbO.H_2O$ was obtained by Voigt (*Chem. Zeitung*, 13, 695) by dissolving PbO in $MgCl_2Aq$, filtering, and evaporating.

$PbCl_2.7PbO$: a lustrous, golden-yellow, crystalline mass, obtained by melting together 1 pt. pure NH_4Cl and 10 pts. pure PbO, pouring off from a little Pb (formed by the reducing action of NH_3 set free by the PbO acting on NH_4Cl), and allowing to cool; known as *Cassel yellow*.

By heating PbO in a mixture of Cl and air, Cross a. Sigiura obtained $Pb_8Cl_{16}O$ (*C. J.* 33, 405), by heating PbO_2 in Cl the product was Pb_4Cl_7O, and by heating PbO_2 in a mixture of Cl and air the compound $Pb_{12}Cl_{21}O_4$ was obtained.

According to André (*A. Ch.* [6] 3, 104) $PbCl_2.PbO$, $PbCl_2.2PbO$, and $PbCl_2.3PbO$ are obtained by ppg. $PbCl_2$ by KOHAq.

Lead, oxycyanide of; *v.* vol. ii. p. 341.

Lead, oxyiodides of. Several oxyiodides of lead are known. $PbI_2.PbO.H_2O$ is formed by adding KIAq to excess of Pb acetate solution and digesting the pp. in the liquid; it is a yellowish-white powder, insol. water (Brandes, *A.* 10, 269; *cf.* Ditte, *C. R.* 92, 145). Other oxyiodides, described by Kühn (*Ph. C.* 1847. 593) and Denot (*J. Ph.* 20, 1) are $PbI_2.2PbO.H_2O$, $PbI_2.3PbO.2H_2O$, and $PbI_2.5PbO$. Cross a. Sigiura (*C. J.* 33, 405) describe the oxyiodides $Pb_{11}I_4O_{10}$, $Pb_9I_2O_8$, $Pb_{11}I_5O_7$, and $Pb_9I_4O_6$, obtained by heating PbO_2, and PbO, in I and air, and in I only.

Lead, phosphide of. No phosphide of Pb has been isolated with certainty. Pelletier (*A. Ch.* [2] 13, 114) said that Pb takes up c. 15 p.c. P when P is thrown on to melted Pb, or when Pb filings are strongly heated with glacial phosphoric acid, or $PbCl_2$ with P; but the experiments of Cloud (in Percy's laboratory) make it doubtful whether Pb and P combine. According to H. Rose (*P.* 24, 326) a brown pp., consisting of a phosphide of Pb, is obtained by passing PH_3 into Pb acetate solution.

Lead, salts of. *Compounds formed by replacing the H of acids by Pb.* Pb forms one series of well-marked salts, PbX_2, where X = Cl, NO_3, $\frac{1}{2}SO_4$, $\frac{1}{2}CO_3$, $\frac{1}{3}PO_4$, $\frac{1}{3}AsO_4$, &c. $PbCl_4$ very probably exists in a solution of PbO_2, or Pb_3O_4, in cold conc. HClAq; and $PbO(C_2H_3O_2)_2$ is said to have been isolated; these two salts belong to the series PbX_4, corresponding with the oxide PbO_2. Very many basic salts of Pb are known, and a considerable number of double salts. The formulæ of the Pb salts are determined from analyses, comparison with the salts and compounds of Sn, Ge, and Si, and from the vapour densities of $PbCl_2$ and $PbMe_4$. The following are the chief salts of lead (*v.* Carbonates, Nitrates, Sulphates, &c.): *Antimonate*, *arsenate* and *-ite*, *borate*, *bromate*, *carbonates*, *chlorate* and *-ite*, *chromates*, *dithionate*, *hypophosphite*, *iodate*, *molybdate*, *nitrates* and *-ites*, *pentathionate*, *perchlorate*, *periodates*, *phosphates* and *-ite*, *sulphates* and *-ite*, *selenate* and *-ite*, *silicates*, *thiosulphate*, *trithionate*, *tungstates*, *uranate*, *vanadates*.

Lead, selenide of, PbSe. Occurs native as *clausthalite* in the Hartz, &c., the Pb being sometimes partly replaced by Co, Cu, Hg, Ag, &c.; S.G. 7 to 8·8 (H. Rose, *P.* 2, 416; 3, 281; Stromeyer, *P.* 2, 403; Kersten, *P.* 46, 265). PbSe is produced by heating the constituents in the ratio Pb:Se; it forms a porous, grey, soft mass (Berzelius); melted under borax small regular crystals are obtained, S.G. 8·154 (Little, *A.* 112, 212). Heated in air Se is vaporised, then a little PbSe, and a residue of basic selenite of Pb is left; cold HNO_3Aq dissolves Pb, leaving Se.

Lead, selenocyanide of, $Pb(SeCy)_2$; *v.* vol. ii. p. 348.

Lead, silicofluoride of, $Pb(BF_4)_2$. Long prismatic crystals; by dissolving PbO in HBF_4Aq and evaporating to a syrup; partially decomposed by water or alcohol (Berzelius, *P.* 2, 113).

Lead, sulphides of. Besides PbS, which is a well-marked compound, two subsulphides, Pb_4S and Pb_2S, probably exist; there are also indications of the formation of a persulphide.

LEAD SULPHIDE. (*Lead monosulphide. Plumbous sulphide.*) PbS.

Occurrence.—Native as *galena*; crystallised in monometric octahedra, and cubic and rhombic dodecahedra; S.G. 7·25 to 7·7 (*v.* Neumann, *P.* 23, 1).

Preparation.—1. By mixing S with molten Pb.—2. By heating PbO with excess of S.—3. By the action of H_2S or an alkaline sulphide on Pb salts.—4. By passing CS_2 over Pb heated a little above redness, crystals of PbS are formed (Pb thiocarbonate seems to be also produced) (Gautier a. Hallopeau, *C. R.* 108, 111).—5. Well-formed crystals of PbS are obtained by passing H_2S into a solution of c. 3 grams $Pb(NO_3)_2$ in 250 c.c. 10 p.c. HNO_3Aq at c. 15°; if only c. 1 p.c. HNO_3 is present the pp. is amorphous (Muck, *Z.* [2] 4, 241).—6. Crystalline PbS is produced by the action of PbO on thio-urea (Reynolds, *C. J.* 45, 162). Addition of H_2S to a Pb salt in presence of HClAq sometimes produces a red pp. of $3PbS.PbCl_2$; on warming and passing in more H_2S, PbS is formed.—7. Winssinger (*Bl.* [2] 49, 452) obtained an aqueous solution of colloidal PbS by ppg. by H_2S a very dilute solution of a Pb salt, and dialysing; the solution was reddish-brown.

Properties.—Lead-grey crystalline solid, as prepared by fusion of Pb and S; S.G. 7·505 (Karsten, *S.* 65, 394). A brown-black powder, as prepared by ppn. by H_2S: S.G. 6·924 at 4° (Playfair a. Joule, *C. J.* 1, 137), 6·77 (Schneider, *J. pr.* [2] 2, 91). Melts at full red-heat out of contact with air, and is said to sublime unchanged. Insol. in dilute acids, caustic alkalis, and alkaline sulphide solutions.

Reactions.—1. *Heated in air* evolves SO_2 and forms Pb and $PbSO_4$ and some PbO (Descotils, *A. Ch.* [2] 55, 441).—2. Heated with *lead monoxide* forms Pb and SO_2; Pb and SO_2 are also produced by heating with *lead sulphate*; if little PbS is heated with much $PbSO_4$ the chief products are PbO and SO_2 (*v.* LEAD; *Formation*, Nos. 1 and 2, p. 122).—3. Melted with *scrap iron* FeS and Pb are formed.—4. Heated in *steam* gives H_2S, and at first PbO and afterwards Pb.—5. Heated with *alkaline carbonates* half the Pb of the PbS is separated.—6. Boiled with dilute *nitric acid* $Pb(NO_3)_2$, S, and NO are produced; *fuming nitric acid* forms $PbSO_4$ and S, and sometimes $Pb(NO_3)_2$.—7. *Conc. hydrochloric acid* forms $PbCl_2$ and H_2S.—8. *Aqua regia* forms $PbCl_2$ and $PbSO_4$.—9. Slowly reacts with *chlorine* to form $PbCl_2$ and S_2Cl_2.—10. By long *fusion with potash and nitre* Pb_3O_4 is produced (Carnegie, *C. N.* 60, 113).—11. Heated with lead, subsulphides (*q.v.*) Pb_4S and Pb_2S are formed.

Combinations.—With *lead chloride* to form the sulphochloride (*q.v.*) $3PbS.PbCl_2$.

LEAD SUBSULPHIDES. Pb_4S and Pb_2S. Said to be formed by heating together PbS and Pb in the proper proportions (*v.* Bredberg, *P.* 17, 274). Pb_2S is also formed, according to Berthier (*A. Ch.* [2] 22, 240), by heating $PbSO_4$ in a crucible lined with charcoal.

LEAD PERSULPHIDE. Addition of K pentasulphide to solution of a Pb salt gives a blood-red pp. which is quickly changed, even in the liquid in which it is produced, into PbS and S. Berzelius gives the formula PbS_5 to the persulphide.

Lead, sulphochloride of. $3PbS.PbCl_2$. Obtained as a red pp. by passing a little H_2S into a dilute Pb solution acidified by HCl; Renisch (*J. pr.* 13, 130) obtained the compound by passing H_2S into a solution of 1 part Pb acetate in 200 parts water to which 20 parts HClAq, S.G. 1·168, were added. Also produced as a yellowish-red solid by digesting freshly-ppd. PbS with $PbCl_2Aq$. Decomposed by H_2S with formation of PbS. Boiling water partly dissolves out $PbCl_2$.

Lead, sulphocyanide of. $Pb(SCy)_2$; *v.* vol. ii. p. 350. Combines with $PbBr_2$ and $PbCl_2$; *v.* *Lead bromosulphocyanide*, and *Lead chlorosulphocyanide*, pp. 125, 127.

Lead, thiocarbonate of. $PbCS_3$. Formed by adding solution of an alkali thiocarbonate to a Pb salt (*cf.* THIOCARBONATES, vol. i. p. 703).

M. M. P. M.

LEAD, WHITE. White lead is a hydrocarbonate of Pb varying in composition; *v.* vol. i. p. 699.

LEAD ORGANIC DERIVATIVES.

Lead trimethyl salts. *Chloride* $PbMe_3Cl$. Formed by the action of boiling aqueous HCl on $PbMe_4$ (Cahours, *A. Ch.* [3] 62, 257; *A.* 122, 48). Long needles resembling $PbCl_2$. May be sublimed. M. sol. boiling water and alcohol. Converted into $PbCl_2$ by long boiling with HClAq.

Bromide $PbMe_3Br$. More soluble than the chloride.

Iodide $PbMe_3I$. Obtained by adding iodine to $PbMe_4$ till the odour becomes permanent. White mass, crystallising from water in long colourless needles which may be sublimed. Sl. sol. water, v. sol. alcohol. On distillation with solid KOH it yields $PbMe_3OH$, a strong basic oil smelling like oil of mustard solidifying in prisms.

Lead tetra-methyl, $PbMe_4$. (110°) (B.). V.D. 9·52 (calc. 9·25). S.G. $\frac{0}{}$ 2·034. From MeI and an alloy of lead (5 pts.) and sodium (1 pt.), or, better, from $PbCl_2$ and $ZnMe_2$ (Cahours). Colourless liquid, having a camphor-like odour, insol. water, sol. alcohol and ether (Cahours). According to Butlerow it smells like strawberries or mould. It does not unite directly with chlorine or iodine, but is decomposed thereby, *e.g.*

$PbMe_4 + I_2 = PbMe_3I + MeI$. Acids convert it into CH_4 and a salt of $PbMe_3$.

Di-plumbic hexa-ethide, Pb_2Et_6. *Lead tri-ethyl*. S.G. $\frac{0}{}$ 1·471. Formed by adding sodium (1 pt.) to molten lead (3 pts.) and mixing the cooled and powdered alloy with EtI in flasks provided with inverted condensers. When the first violent action has ceased the product is freed from EtI by distilling at 100°, and the residue extracted with ether (Klippel, *J. pr.* 81, 287; *cf.* Löwig, *J. pr.* 60, 304; *A.* 88, 318),

Properties. — Yellowish mobile oil, insol. water, v. sol. alcohol and ether. Decomposed on distillation. By exposure to light, or by prolonged boiling with water, it decomposes with separation of metallic lead. When exposed to the air in ethereal solution it absorbs O and CO_2 with formation of $(PbEt_3)_2O$ and $(PbEt_3)_2CO_3$. It combines with iodine forming $PbEt_3I$.

Lead triethyl salts. *Chloride* $PbEt_3Cl$. Obtained by adding $BaCl_2$ to a solution of $(PbEt_3)_2SO_4$ in alcohol, or by treating $(PbEt_3)_2O$, $(PbEt_3)_2CO_3$, or $PbEt_4$ with HCl. Beautiful long needles, giving off a pungent odour when heated, presently decomposing with separation of $PbCl_2$ and metallic lead.—$PbEt_3HgCl_3$: white nacreous scales (from hot alcohol). — $(PbEt_3Cl)_2PtCl_4$: copper-red crystals, sl. sol. water, m. sol. alcohol and ether.

Bromide $PbEt_3Br$. Long needles (from ether).

Iodide $PbEt_3I$. From Pb_2Et_6 and iodine, or from $(PbEt_3)_2SO_4$ and KI. Sol. ether and very unstable, the ethereal solution quickly depositing PbI_2.

Cyanide $PbEt_3Cy$. From $PbEt_3Cl$ and KCy in alcoholic solution at 100°. Prisms (from ether).

Hydroxide $PbEt_3(OH)$. From the chloride by treatment with moist Ag_2O or by distillation with KOH. Needles, sl. sol. water, v. sol. alcohol and ether. Has strong alkaline reaction and caustic taste. Saponifies fats; ppts. ferric, cupric, and argentic oxides from their salts. Ppts. alumina and zinc oxide, the pp. dissolving in excess of the precipitant. Expels NH_3 from its salts. Absorbs atmospheric CO_2. Fumes with HCl. When heated it gives off white vapours which powerfully excite sneezing.

Carbonate $(PbEt_3)_2CO_3$. Small hard crystals, nearly insol. water, sl. sol. alcohol and ether. Has a burning taste.

Nitrate $PbEt_3NO_3$: unctuous crystalline mass, decomposed by heat with slight detonation. V. sol. alcohol and ether.—$(PbEt_3)_2SO_4$: from the oxide and H_2SO_4. White crystalline pp., nearly insol. water, alcohol, and ether, v. sol. alcohol mixed with H_2SO_4 or HCl, from which solution it separates in octahedra.

Phosphate $(PbEt_3)_3PO_4$: stellate groups of crystals, v. sol. water, alcohol, and ether.

Sulphocyanide $PbEt_3SCy$: crystals, sol. water, alcohol, and ether.

The formate $PbEt_3CHO_2$, acetate $PbEt_3C_2H_3O_2$, butyrate $PbEt_3C_4H_7O_2$, oxalate $(PbEt_3)_2C_2O_4aq$, tartrate $PbEt_3C_4H_5O_6$ (dried at 100°), and benzoate are crystalline.

Lead tetrethide, $PbEt_4$. Mol. w. 323 (c. 200°); (152° at 190 mm.) (B.). S.G. 1·62.

Preparation.—$PbCl_2$ is added to $ZnEt_2$ as long as reaction occurs. The $PbEt_4$ is distilled with steam. $2ZnEt_2 + 2PbCl_2 = 2ZnCl_2 + 2PbEt_2$ and then $2PbEt_2 = Pb + PbEt_4$ (Buckton, *P. M.* [4] 18, 212; 17, 232; *A.* 109, 218; 112, 220; Frankland a. Lawrance, *C. J.* 35, 244).

Properties.—Oil, not decomposed by water or by gaseous NH_3, CO_2, CO, C_2N_2, NO, O, or H_2S. Partially decomposes at 200°.

Reactions.—1. Gaseous SO_2 reacts forming diethyl sulphone and lead ethyl sulphinate: $PbEt_4 + 3SO_2 = Et_2SO_2 + (EtSO_2)_2Pb$. — 2. *Iodine* forms $PbEt_3I$ and EtI.—3. Conc. HCl forms $PbEt_3Cl$ and ethane.

Di-plumbic hexa-isoamylide, $Pb_2(C_5H_{11})_6$. Prepared like the corresponding Pb_2Et_6, using isoamyl iodide (Klippel). Oil, with irritating vapour. Detonates with HNO_3.

Lead tri-isoamyl salts. *Chloride* $Pb(C_5H_{11})_3Cl$: from the oxide and HCl. White needles.

Iodide $Pb(C_5H_{11})_3I$: from $Pb_2(C_5H_{11})_6$ in ether by adding iodine. [100°]. Needles, insol. water.—$Pb(C_5H_{11})_3HgI_3$: golden laminæ, insol. water, sl. sol. alcohol and ether.—*Hydroxide* $Pb(C_5H_{11})_3OH$, viscid mass, insol. water, sol. alcohol and ether. Feebly alkaline, ppts. ferric, but not cupric and silver salts.

Lead tetra-phenyl $Pb(C_6H_5)_4$. [225°]. S.G. $\frac{20}{}$ 1·530. Prepared by boiling 500 g. of an 8 p.c. alloy of sodium and lead with 500 g. of bromobenzene and 20 c.c. of acetic ether for sixty hours (Polis, *B.* 20, 716, 3331. Small needles or dimetric prisms; $a:c = 1:·381$. Decomposes at 270°. V. sl. sol. alcohol, ether, and HOAc, m. sol. benzene, $CHCl_3$ and CS_2. Heated with HClAq at 230° it yields $PbCl_2$, benzene, and chloro-benzene.

Lead diphenyl salts. *Chloride* $PbPh_2Cl_2$. Formed by passing chlorine into a solution of lead tetra-phenyl in CS_2, or by ppg. $PbPh_2(NO_3)_2$ with KCl. White powder, insol. alcohol and ether; v. sl. sol. benzene.

Bromide $PbPh_2Br_2$. From lead di-phenyl nitrate and KBr. White powder, which decomposes before fusion.

Iodide $Pb(C_6H_5)_2I_2$. [c. 103°]. Formed by adding iodine to a solution of lead tetraphenyl in chloroform (Polis). Golden plates, sol. chloroform, benzene, and alcohol.

Nitrate $Pb(C_6H_5)_2(NO_3)_2$ 2aq. Obtained by gradually adding lead tetra-phenyl to boiling HNO_3 (S.G. 1·4). Small lustrous plates (from water). V. sol. hot water and alcohol. Detonates when heated. Boiling its aqueous solution produces a pp. of the basic salt $Pb(C_6H_5)_2(NO_3)(OH)$ as a white powder which detonates when heated.

Oxide $Pb(C_6H_5)_2O$. Obtained by boiling the nitrate with aqueous NaOH (Polis, *B.* 20, 3332). White powder, insol. alcohol, ether, and benzene.

Oxy-cyanide $Pb(C_6H_5)_2Cy(OH)$. From the nitrate in aqueous solution and KCy. White powder, insol. water, alcohol, and ether.

Sulphocyanide $Pb(C_6H_5)_2(SCy)_2$. Formed by adding ammonium sulphocyanide to an aqueous solution of the acetate. White powder, insol. water and ordinary solvents.

Phosphate $(PbPh_2)_3(PO_4)_2$. Formed by adding sodium phosphate to an aqueous solution of the nitrate. White pp., insol. usual solvents.

Oxy-carbonate $(PbPh_2OH)_2CO_3$. Ppd. as

a white insoluble powder by adding Na_2CO_3 to solutions of salts of lead diphenyl.

Chromate $Pb(C_6H_5)_2CrO_4$. From the nitrate and $K_2Cr_2O_7$. Yellow pp., insol. water.

Sulphide $Pb(C_6H_5)_2S$. From the acetate and H_2S. Yellow prisms, sl. sol. alcohol; v. sol. benzene. Decomposes between 80° and 90°.

Formate $Pb(C_6H_5)_2(CHO_2)_2$ aq. From lead tetra-phenyl and concentrated formic acid. Needles. Melts above 200°, with decomposition.

Acetate $Pb(C_6H_5)_2(C_2H_3O_2)_2$ 2aq. From lead tetra-phenyl and glacial HOAc (Polis, *B.* 20, 3333). Prisms, v. sol. water containing acetic acid. Melts at 193° when anhydrous.

Lead tetra-*p*-tolyl $Pb(C_7H_7)_4$. [240°]. S.G. $\frac{20}{}$ 1·433. Prepared by heating a mixture of 8 p.c. sodium lead alloy (300 g.), *p*-bromo-toluene (120 g.), toluene (40 g.), and acetic ether (4 c.c.) for thirty hours in an oil-bath. Repeated crystallisation of the product from benzene and alcohol yields lead tetra-tolyl and di-*p*-tolyl (A. Polis, *B.* 21, 3424). Small needles. Decomposes at 254°. More sol. benzene, CS_2 and $CHCl_3$ than lead tetra-phenyl. When heated with HCl at 200° it gives $PbCl_2$ and chloro-toluene. Cold conc. HNO_3 causes decomposition with blackening, but on adding lead tetra-tolyl to boiling nitric acid (S.G. 1·4) the products are lead di-tolyl nitrate $Pb(C_7H_7)_2(NO_3)_2$ and nitro-toluene.

Lead di-*p*-tolyl salts.

Chloride $Pb(C_7H_7)_2Cl_2$. Formed by passing Cl into a solution of lead tetra-tolyl in CS_2. White powder, insol. alcohol and ether, sl. sol. $CHCl_3$, benzene, and CS_2. Decomposed when heated. Converted into the corresponding nitrate by $AgNO_3$ in alcoholic solution.

Bromide $Pb(C_7H_7)_2Br_2$. From $Pb(C_7H_7)_4$ in CS_2 and bromine. Resembles the chloride.

Iodide $Pb(C_7H_7)_2I_2$. From $Pb(C_7H_7)_4$ and iodine, both dissolved in CS_2. Yellow powder, more sol. chloroform and CS_2 than the chloride or bromide.

Nitrate $Pb(C_7H_7)_2(NO_3)_2$ 2aq. Prepared as above. White powder composed of very slender needles; sol. water, containing HNO_3, sl. sol. alcohol. Detonates when heated.

Oxy-nitrate $Pb(C_7H_7)_2(OH)(NO_3)$. Formed by heating the nitrate with water, or by adding ammonia to a solution of the nitrate in dilute HNO_3. White amorphous powder.

Chromate $Pb(C_7H_7)_2CrO_4$. Insol. yellow powder, ppd. by adding $K_2Cr_2O_7$ to a solution of the acetate.

Sulphide $Pb(C_7H_7)_2S$. Formed by passing H_2S into a solution of the acetate. Transparent yellow plates (from alcohol-benzene), sl. sol. alcohol and ether, v. sol. benzene, CS_2 and $CHCl_3$. Begins to turn brown at 90° and melts at 98°. It is decomposed by light.

Formate $Pb(C_7H_7)_2(CHO_2)$. Formed from $Pb(C_7H_7)_4$ and formic acid. Beautiful white needles, which at 233° blacken and decompose.

Acetate $Pb(C_7H_7)_2(C_2H_3O_2)_2$ 2aq. [183·5°]. Formed by adding $Pb(C_7H_7)_4$ to boiling HOAc. Small white needles, more sol. dilute HOAc than the corresponding phenyl compound.

LECANORIC ACID $C_{16}H_{14}O_7$. (*a*)-*Orsellic acid. Diorsellic acid.* [153° cor.]. S. ·01 at 100° (Schunck). S. (80 p.c. alcohol) ·7 at 15° (Schunck), S. (ether) 4 at 20° (Hesse); 1·25 at 15° (Schunck). Discovered by Schunck in 1842 and extracted from several lichens of the genera *Lecanora*, *Variolaria*, and *Roccella* (Schunck, *A.* 41, 157; 54, 261; 61, 72; Rochleder a. Heldt, *A.* 48, 1; Stenhouse, *A.* 68, 61; 70, 218; Strecker, *A.* 68, 108; Laurent a. Gerhardt, *A. Ch.* [3] 24, 315; Robiquet, *A. Ch.* 42, 236; Hesse, *A.* 139, 22). Obtained by exhausting the lichens with ether, dissolving the greenish-white crystalline residue left on evaporation in milk of lime, ppg. the filtrate with H_2SO_4, washing the pp. with water, and recrystallising it from hot alcohol (Hesse). Stellate needles (containing aq). Almost insol. cold water. Decomposed by heat with evolution of CO_2. A solution of barium lecanorate is not decomposed by CO_2. $FeCl_3$ colours its alcoholic solution dark purple-red. An ammoniacal solution of lecanoric acid forms white pps. with lead subacetate and with $AgNO_3$, but the silver salt is quickly reduced. An alcoholic solution gives no pp. with alcoholic solutions of lead acetate, $HgCl_2$, or $AgNO_3$, but with cupric acetate it gives an apple-green pp. When a solution of lecanoric acid is boiled it gives orsellic acid $C_{16}H_{14}O_7 + H_2O = 2C_8H_8O_4$. A solution of barium lecanorate yields, on boiling, first barium orsellate, and finally orcin $C_7H_8O_2$ and $BaCO_3$. An alcoholic solution yields, on boiling, orsellic ether. An ammoniacal solution acquires, on exposure to air, a splendid purple colour, through formation of orceïn. Bleaching-powder gives a red tint, quickly changing to brown.

Salt.—BaA'': small stellate needles.

Di-bromo-lecanoric acid $C_{16}H_{12}Br_2O_7$. [179°]. From lecanoric acid and Br in ether (Hesse). White crystals (from alcohol), insol. water. $FeCl_3$ colours its alcoholic solution violet. Gives off CO_2 on fusion.

Tetra-bromo-lecanoric acid $C_{16}H_{10}Br_4O_7$. [157°]. From lecanoric acid and excess of Br in ether. Pale yellow prisms (from alcohol), v. sol. alcohol, ether, and alkalis. $FeCl_3$ colours its alcoholic solution purple. Boiling baryta-water decomposes it.

LECITHIN $C_{44}H_{82}O_9PN$ (Von Lippmann, *B.* 20, 3201); $C_{44}H_{90}O_9PNaq$ (Diaconoff). *Protagon.* Occurs in the eggs and milt or soft roe of the carp and herring, the yolk of poultry eggs, the brain of man, sheep, and domestic fowl, bile of pigs, men, and oxen, retina of oxen, blood, yeast, milk, butter, radicles of sprouting lupin seeds, maize, peas, wheat, beet-root, &c. (Gobley, *J. Ph.* [3] 9, 1, 83, 161; 11, 409; 12, 5; 17, 401; 18, 107; 19, 406; 21, 241; 30, 241; 33, 161; Strecker, *A.* 123, 356; *Z.* [2] 4, 437; Kodweiss, *A.* 59, 261; Diaconoff, *Z.* [2] 4, 154; Liebreich, *A.* 134, 29; Cahn, *H.* 5, 215; Hoppe-Seyler, *H.* 2, 427; 3, 378; *J.* 1866, 698, 744; Hermann, *Z.* 1866, 250; Schmidt-Mülheim, *J. Th.* 1883, 166; Schulze a. Barbieri, *J. pr.* [2] 27, 358; *H.* 13, 365; Heckel a. Schlagdenhauffen, *C. R.* 103, 388; Copeman a. Winston, *J. Physiol.* 10, 213).

Preparation.—1. Yolk of egg is extracted with alcohol-ether, and an alcoholic solution of platinic chloride is added. A compound of lecithin and platinic chloride is ppd., and this is agitated with Ag_2O, the filtrate freed from silver by H_2S and evaporated (Strecker).—2. Brain is

exhausted with ether, and the residue extracted with absolute alcohol at 40°. The alcoholic extract is cooled at 0° and filtered, and the pp. of lecithin and cerebrin collected, washed with alcohol, and treated with ether. The ethereal solution of lecithin is evaporated (Diaconoff).—3. Beet-root is extracted with ether-alcohol, the ether evaporated and the residue dissolved in alcohol and ppd. by platinic chloride. The pp. is decomposed by H_2S (Lippmann).

Properties.—Hygroscopic wax-like substance, which swells up in water and is v. sol. alcohol, ether, chloroform, and oils. Boiling with baryta-water produces glycero-phosphoric acid, neurine, and a fatty acid (stearic, oleïc, or palmitic). According to Diaconoff lecithin from brain may be separated by dissolving in alcohol and cooling to −10°, into a stearo-lecithin which separates and an oleo-lecithin which remains in solution. According to Strecker the decomposition by baryta may be represented thus:—

$$C_{2n+8}H_{4n+18}O_9NP + 3H_2O =$$
$$2C_nH_{2n}O_2 + C_3H_9PO_6 + C_5H_{15}NO_2$$
or
$$C_{2n+8}H_{4n+14}O_9NP + 3H_2O =$$
$$2C_nH_{2n-2}O_2 + C_3H_9PO_6 + C_5H_{15}NO_2\ ;$$

thus stearo-lecithin would be $C_{44}H_{90}O_9NP$, while oleo-lecithin would be $C_{44}H_{86}O_9NP$ and might be written

$$(C_{18}H_{33}O_2)_2C_3H_5O.PO(OH).O.C_2H_4.N(CH_3)_3.OH.$$

The particular lecithin examined by Strecker appeared, however, to be $C_{42}H_{84}O_9NP$ or to contain one oleyl and one palmityl radicle in place of the two oleyls in the above formula. That the neurine is not present as a base appears from the observation that lecithin is hardly attacked by dilute (10 p.c.) sulphuric acid (Gilson, *H.* 12, 585). The neurine salt of di-stearyl-glycero-phosphoric acid appears therefore not to be a true lecithin (*v.* Glycerin). According to Lippmann the base obtained by boiling beet-root lecithin with baryta is sometimes neurine and sometimes betaïne. The presence of lecithin enables a solution of glucose to absorb oxygen from the air in the same way as an alkaline solution of that sugar (Nencki a. Sieber, *J. pr.* [2] 26, 17).

Salts.—The hydrochloride is a waxy mass.—$(C_{42}H_{83}O_8PN)_2PtCl_6$: yellow flocculent pp. v. sol. ether, chloroform, and benzene, but ppd. from these solutions by alcohol (Strecker).—$CdCl_2$ gives a pp. in a solution of lecithin in ether-alcohol.

LEDITANNIC ACID $C_{15}H_{20}O_8$. Occurs in the leaves of the marsh wild rosemary (*Ledum palustre*) (Willigk, *A.* 74, 363; Rochleder a. Schwartz, *A.* 74, 366; *Z.* 1866, 382; Thal, *J.* 1883, 1401). Prepared by ppg. the alcoholic decoction of the leaves with water, and the filtrate with lead acetate. The pp. is dissolved in dilute HOAc, filtered, heated to boiling, and ppd. with lead subacetate. The pp. is suspended in water and decomposed by H_2S, and the filtrate evaporated in a current of CO_2. Reddish powder, v. sol. water and alcohol. $FeCl_3$ colours its aqueous solution dark green. Lead acetate and $SnCl_4$ give yellow pps. Boiling dilute H_2SO_4 forms ledixanthin but no sugar.

Ledixanthin $C_{[illegible]}H_{[illegible]}O_4$ is a reddish-yellow powder, v. sol. alkalis. Its alcoholic solution gives a reddish-brown pp. with lead acetate. On dry distillation it yields pyrocatechin.

LEDUM OIL. An oil obtained by steam distillation from the leaves of *ledum palustre.* According to Willigk (*Sitz. W.* 9, 302) it consists of a terpene and of an oxygenated oil $C_{50}H_{24}O_3$. Grassmann (*Rep. Pharm.* 38, 53) obtained a volatile oil (1 pt.) and ledum-camphor (2 pts.). Fröhde (*J. pr.* 82, 181) found the oil to be acid and to contain a terpene (160°) and an oxygenated oil (241°). According to Trapp (*Russ. Zeit. Pharm.* 1874, 289) the oil when recently prepared is yellowish, viscid, lighter than water, and possesses a pungent odour; when exposed to air the greater part solidifies to a crystalline mass soluble in alcohol. The solution of this solidified oil (ledum camphor) in H_2SO_4 is turned violet by HNO_3. Ivanoff (*Russ. Zeit. Pharm.* 1876, 577) found ledum oil to consist of a white crystalline mass saturated with oil. By repeated crystallisation from alcohol white prisms of $C_5H_8O_2$ were obtained. These were insol. water, v. sol. alcohol, ether, chloroform, and benzene, melted at 101°, boiled at 174°, and were dextrorotatory in alcoholic solution. According to Hjelt a. Collan (*B.* 15, 2500) ledum camphor melts at 101°, and has a vapour density 12·33 corresponding with the formula $C_{25}H_{44}O_2$ (calc. 13·02), and sublimes in long white needles. Rizza (*J. R.* 19, 319) gives the following properties for ledum camphor, $C_{15}H_{26}O$ [101°]; (292° i. V.); V.D. 8·10; and states that Ac_2O at 150° converts it into a sesquiterpene $C_{15}H_{24}$ (264°), S.G. $\frac{0}{}$ ·935.

LEGUMIN *v.* Proteïds.

LEKENE C_xH_y. [79°]. S.G. = ·939. Forms the chief constituent of ozokerit or mineral-wax, from which it is isolated by distilling the wax *in vacuo,* dissolving the distillate in benzene, and precipitating with absolute alcohol (Beilstein a. Wiegand, *B.* 16, 1547). White glistening crystals. S. (96 p.c. alcohol at 16°) = ·0105; S. (benzene at 15°) = ·8; sparingly sol. in most other cold solvents, e. sol. hot benzene and chloroform, insol. acetone. It decomposes on distillation under ordinary pressure, but can be distilled *in vacuo.* It is very stable towards oxidising agents.

LEMON OIL. Obtained by pressure from the peel of the fruit of *citrus medica.* Contains a terpene $C_{10}H_{16}$ (166°) (Blanchet a. Sell, *A.* 6, 281; Soubeiran a. Capitaine, *A.* 34, 317) or (175°) (Regnault, *J.* 1863, 70; *A.* 52, 171). S.G. ·85 at 15°-22°. The terpene is dextrorotatory, $[\alpha]_D$ = 109° (Kanonnikoff, *Bn.* 3, 299). According to Wallach (*A.* 227, 290) oil of lemon contains pinene and hesperidene (*cf.* Deville, *A.* 71, 348; Oppenheim, *B.* 5, 628). In examining the essential oil obtained by steam distillation from lemon peel, Tilden (*Ph.* [3] 9, 654) found the S.G. to be ·852 at 20°, and the rotation + 59° in a column 100 mm. long. In this oil he found terebenthene $C_{10}H_{16}$, citrene $C_{10}H_{16}$ (constituting 70 p.c. of the whole), cymene (6 p.c.), a dextrorotatory body $C_{10}H_{18}O$ resembling terpineol (over 200°), a compound ether $C_{10}H_{17}AcO$ decomposed by heat into HOAc and $C_{10}H_{16}$, and $C_{14}H_{14}O_6$ [116°] Tilden a. Dick, *C. J.* 57, 32). The citrene (176°) forms a terpene hydrate when treated with HNO_3. Conc. H_2SO_4 converts it into an inactive hydrocarbon (176°). Bouchardat a. Lafont (*C. R.* 101, 383) find in essence of lemon a terpene $C_{10}H_{16}$ (178°) with a rotatory power + 105° which yields

a solid inactive hydrochloride. Flavitzky (*Bl.* [2] 35, 171) found in a commercial sample of lemon oil ($[\alpha]_D = +60°$) a lævorotatory terpene (165°); S.G. $\frac{20}{}$ ·857; $[\alpha]_D = -29·8°$ which formed a lævorotatory hydrochloride $[\alpha]_D = -25·9°$, but this was possibly an adulterant. The oil from the peel of *citrus bigamalia* contains a terpene (178°) S.G. $\frac{15}{}$ ·852 which is strongly dextrorotatory, and forms a crystalline hydrochloride $C_{10}H_{16}2HCl$ (De Luca, *J.* 1857, 481).

LEPARGYLIC ACID *v.* Azelaïc acid.

LEPIDEN AND ITS DERIVATIVES. Most of these complex compounds were first described by Zinin.[1] It is only recently that light has been thrown on their constitution.

$$\textbf{Lepiden} \quad C_{28}H_{20}O \quad = \quad \begin{array}{c} C_6H_5.C - C.C_6H_5 \\ \| \qquad \| \\ C_6H_5.C \quad C.C_6H_5 \\ \diagdown \diagup \\ O \end{array}$$

(*Tetraphenylfurfuran*) (Zinin, *Z.* 1867, 313; Japp a. Klingemann, *B.* 21, 2934 *n.*; *cf.* Dorn, *A.* 153, 358). Formed, along with benzil and oily matters, when benzoïn is heated with $1\frac{1}{2}$ times its weight of conc. hydrochloric acid (saturated at 8°) for 7–8 hours at 130°. The product is washed with ether, which removes the oil and benzil, after which it is recrystallised from boiling glacial acetic acid (Zinin). Also formed when bidesyl (hydro-oxylepiden), or isobidesyl, is heated with conc. hydrochloric acid for 2–3 hours at 130°–140° (Magnanini a. Angeli, *B.* 22, 855):

$$\begin{array}{cc} C_6H_5.CH - CH.C_6H_5 \\ | \qquad\quad | \\ C_6H_5.CO \quad CO.C_6H_5 \end{array} = \begin{array}{c} C_6H_5.C - C.C_6H_5 \\ \| \qquad \| \\ C_6H_5.C \quad C.C_6H_5 \\ | \qquad | \\ OH\,OH \end{array}$$

$$= \begin{array}{c} C_6H_5.C - C.C_6H_5 \\ \| \qquad \| \\ C_6H_5.C \quad C.C_6H_5 \\ \diagdown \diagup \\ O \end{array} + H_2O.$$

—Laminæ [175°]. Volatilises at 220°. Insol. water, sol. 170 pts. of boiling alcohol, 52 pts. of ether at 17°, 28 pts. of boiling glacial acetic acid, 8 pts. of cold benzene. Boiling alcoholic potash is without action on it. Nitric acid or chromic acid oxidises it to 'acicular oxylepiden' $C_{28}H_{20}O_2$. Chlorine has the same action; but bromine converts it into dibromlepiden. With phosphorus pentachloride it yields dichlorlepiden.

Chlorlepiden $C_{28}H_{19}ClO$. By treating an alcoholic solution of dichlorlepiden with sodium amalgam for 24 hours (Dorn, *A.* 153, 355).—Large needles [143°–146°], insol. ether, sl. sol. alcohol, v. sol. benzene.

Dichlorlepiden $C_{28}H_{18}Cl_2O$. Cannot be obtained by passing chlorine into a boiling solution of lepiden, as under these circumstances 'acicular oxylepiden' is formed (Zinin, *J. R.* 7, 333). By heating together equal weights of lepiden and phosphorus pentachloride (Zinin, *J. R.* 5, 22).—Needles [169°], sol. 20 pts. boiling glacial acetic acid, 66 pts. boiling alcohol (95 p.c.), v. sol. ether.

A dichlorlepiden described by Dorn (*A.* 153, 355), and stated by him to melt at 156°, is probably identical with the foregoing.

Isodichlorlepiden $C_{28}H_{18}Cl_2O$. Formed, together with hydrodichloroxylepiden, by boiling an acetic acid solution of 'acicular dichloroxylepiden' [202°] (Zinin, *J. R.* 7, 331), or of 'sparingly soluble dichloroxylepiden,' with zinc-dust (Zinin, *J. R.* 7, 194).—Needles [166°], sol. 174 pts. boiling alcohol (95 p.c.), 12·5 pts. boiling glacial acetic acid, sol. ether. Oxidation converts it back into 'acicular dichloroxylepiden.'

Pentachlorlepiden $C_{28}H_{15}Cl_5O$. By heating oxylepiden with excess of a mixture of phosphorus pentachloride and oxychloride for half-an-hour at 200° (Dorn, *A.* 153, 355).—Indistinct crystals [186°], v. sl. sol. alcohol, ether, and glacial acetic acid, v. sol. benzene.

Hexachlorlepiden $C_{28}H_{14}Cl_6O$. By heating dichloroxylepiden with the foregoing mixture for 1 hour at 200° (Dorn).—Yellow amorphous substance [80°–90°], v. sol. alcohol, ether, and benzene.

Octochlorlepiden $C_{28}H_{12}Cl_8O$. By heating dichloroxylepiden with the foregoing mixture for 7 hours at 210° (Dorn).—Orange-yellow amorphous substance [97°], v. sol. alcohol, ether, and benzene.

Dibromlepiden $C_{28}H_{18}Br_2O$. Prepared by heating a solution of lepiden in acetic acid with bromine (Zinin, *Z.* 1867, 315). Formed, along with hydrodibromoxylepiden, when 'acicular dibromoxylepiden' is treated with zinc and acetic acid (Zinin, *J. R.* 7, 330).—Laminæ (from acetic acid) [190°] (Zinin), [185°] (Berlin); sol. 480 pts. alcohol (94 p.c.), 44 pts. boiling, and 66 pts. cold, acetic acid, 50 pts. ether.

Oxylepiden $C_{28}H_{20}O_2$. Zinin has prepared three isomeric oxylepidens, which he distinguishes as 'acicular oxylepiden,' 'tabular oxylepiden,' and 'octahedral oxylepiden.'

1. '*Acicular oxylepiden*' (*dibenzoylstilbene*) $\begin{array}{c} C_6H_5.C{=}C.C_6H_5 \\ | \qquad | \\ C_6H_5.CO\ CO.C_6H_5 \end{array}$ (Magnanini a. Angeli, *B.* 22, 854; *cf.* Japp a. Klingemann, *C. S. Pr.* 1889, 136). By oxidising lepiden with nitric acid (Zinin, *Z.* 1867, 314). By treating thionessal $C_{28}H_{20}S$ (Berlin, *A.* 153, 131) or tolallyl sulphide $C_{28}H_{20}S_2$ (Dorn, *A.* 153, 352) with hydrochloric acid and potassium chlorate. By digesting benzoïn with dilute sulphuric acid (Limpricht a. Schwanert, *B.* 4, 337). In order to prepare it, 1 pt. of lepiden is suspended in 10 pts. of boiling glacial acetic acid, and a mixture of 1 pt. of acetic acid with 3 pts. of nitric acid (S.G. 1·5) is added (Zinin, *l.c.*).—Yellow needles [220°], insol. water, almost insol. ether, sol. 200 pts. of boiling alcohol (94 p.c.) and 22 pts. boiling glacial acetic acid, v. sol. benzene. When heated to 340° it is converted into 'tabular oxylepiden' along with a little 'octahedral oxylepiden.' Chromic anhydride in acetic acid solution oxidises it to dioxylepiden $C_{28}H_{20}O_3$. Zinc and acetic acid reduce it to lepiden. Heating with hydriodic acid has the same effect (Dorn), also distillation with zinc-dust (Berlin). In the formation of lepiden by reduction, the oxylepiden is probably first converted into hydro-oxylepiden, which then parts with water, yielding lepiden

[1] Zinin's work appeared for the most part in the *Journal of the Russian Chemical Society.* The author of the present article is indebted, for his account of this portion of the subject, to Beilstein's *Handbuch der organischen Chemie.*

(*v. supra*). Sodium amalgam, acting on the acetic acid solution, reduces it to hydro-oxylepiden $C_{28}H_{22}O_2$ (Zinin). When heated with benzoïn it is reduced to lepiden, whilst the benzoïn yields benzil (Limpricht a. Schwanert, *B.* 4, 338). Alcoholic ammonia at 200° converts it into a mixture of two imides of the formula $C_{28}H_{21}NO$—one derived from 'acicular,' the other from 'tabular,' oxylepiden—whilst with methylamine it yields a methylimide $C_{29}H_{23}NO$ [161°] (Klingemann a. Laycock, *private communication*). Heating with phosphorus pentachloride converts it into dichlorlepiden.

2. '*Tabular oxylepiden*' (*tetraphenylcrotolactone*)

$$\begin{array}{c} (C_6H_5)_2\,C - C.C_6H_5 \\ \mid \quad\;\; \Vert \\ CO \quad C.C_6H_5 \\ \diagdown \;\; \diagup \\ O \end{array}$$

(Japp a. Klingemann, *C. S. Pr.* 1889, 137). By heating 'acicular oxylepiden' to 340° and recrystallising the product, first from ether and afterwards from alcohol. Tabular crystals are deposited first, then microscopic octahedra of the third modification (Zinin, *J. R.* 5, 16). Tabular crystals [136°], insol. water, sol. 14·5 pts. boiling alcohol (95 p.c.), and in its own weight of boiling glacial acetic acid. Dissolves readily in hot alcoholic potash solution (distinction from 'octahedral oxylepiden'), forming a salt of oxylepidenic acid $C_{28}H_{22}O_3$ (*infra*). Zinc and acetic acid are without action on it; but sodium and boiling amyl alcohol reduce it to tetraphenylbutyrolactone $C_{28}H_{22}O_2$. Alcoholic ammonia at 200° converts it into an imide $C_{28}H_{21}NO$; with alcoholic methylamine at 150° it yields the methylamide of oxylepidenic acid $C_{28}H_{21}O_2(NHCH_3)$. When heated with phosphorus pentachloride at 200° it forms chloroxylepiden $C_{28}H_{19}ClO_2$.

3. '*Octahedral oxylepiden.*' Only 2 p.c. of this compound is formed when 'acicular oxylepiden' is heated to 340°. Most readily obtained by boiling 'acicular oxylepiden' with an alcoholic solution of caustic potash or caustic soda. Four parts of 'acicular oxylepiden' are boiled for 12–15 hours with 60 parts of alcohol (95 p.c.) and 3 parts of caustic soda, employing a reflux condenser. The product is washed successively with alcohol, water, and ether, and is finally recrystallised from boiling acetic acid (Zinin, *J. R.* 7, 186; *J.* 1875, 409).—Yellowish, microscopic octahedra [232°]. Sol. 76 parts boiling glacial acetic acid, almost insol. alcohol. When heated to incipient boiling it is totally converted into 'tabular oxylepiden.' Boiling the acetic acid solution with zinc reduces it to hydro-oxylepiden, part of which loses water, yielding lepiden. A solution of chromic anhydride in acetic acid oxidises it to isodioxylepiden $C_{28}H_{20}O_3$. Alcoholic potash is without action on it.

As regards the constitution of 'octahedral oxylepiden,' it is probable that this compound is a stereometric isomeride of 'acicular oxylepiden,' the latter representing the *maleoid*, the former the *fumaroid* form of dibenzoyl-stilbene:

$$\begin{array}{c} C_6H_5.CO.C.C_6H_5 \\ \Vert \\ C_6H_5.CO.C.C_6H_5 \end{array} \qquad \begin{array}{c} C_6H_5.CO.C.C_6H_5 \\ \Vert \\ C_6H_5.C.CO.C_6H_5 \end{array}$$

'Acicular oxylepiden' [220°] (Maleoid dibenzoylstilbene). 'Octahedral oxylepiden' [232°] (Fumaroid dibenzoylstilbene)

(Japp a. Klingemann, *C. S. Pr.* 1889, 138). Both yield on reduction the same hydro-oxylepiden (bidesyl)

$$\begin{array}{c} C_6H_5.CO.CH.C_6H_5 \\ \mid \\ C_6H_5.CO.CH.C_6H_5 \end{array}$$

which may be converted by dehydration into lepiden.

The three oxylepidens yield by destructive distillation the same so-called *isolepiden* $C_{27}H_{20}O$ (*infra*).

Chloroxylepiden $C_{28}H_{19}ClO_2$. By heating 'tabular oxylepiden' with a mixture of phosphorus pentachloride (1 part) and phosphorus trichloride ($\frac{1}{2}$ part) at 180°–200° (Zinin, *J. R.* 5, 21.—Crystals [185°]; sol. 22·8 parts boiling glacial acetic acid.

Dichloroxylepiden $C_{28}H_{18}Cl_2O_2$. 'Acicular dichloroxylepiden' is obtained by heating lepiden with four times its weight of phosphorus pentachloride and treating the product with water (Zinin, *J. R.* 5, 23). By the oxidation of dichlorlepiden [169°] (Zinin, *J. R.* 7, 332; *J.* 1876, 426).—Needles [202°]; sol. 146 parts cold, 13·7 parts boiling acetic acid, 90 parts boiling ether. When boiled with zinc and acetic acid it yields a mixture of hydrodichloroxylepiden and isodichlorlepiden [166°].

When the foregoing 'acicular dichloroxylepiden' is heated to near its boiling-point it is converted into a mixture of two new isomeric dichloroxylepidens, which may be separated by the difference in their solubility in ether. 'Readily soluble dichloroxylepiden,' which forms the chief product, is very soluble in alcohol, ether, and acetic acid, and is deposited from these solutions as a soft resin. Alcoholic caustic potash converts it into a salt of dichloroxylepidenic acid $C_{28}H_{22}Cl_2O_3$. The other isomeride, 'sparingly soluble dichloroxylepiden,' is best prepared by boiling 4 parts of 'acicular dichloroxylepiden' with three parts of caustic soda and 40 parts of alcohol for from 20 to 24 hours. It forms a granular powder consisting of microscopic prisms [230°]; almost insol. alcohol and ether, sol. 36 parts boiling glacial acetic acid. Boiling with acetic acid and zinc converts it into isodichlorlepiden [166°] (Zinin, *J. R.* 7, 191).

These three compounds, as their mode of formation and reactions denote, are to be regarded as dichlor-substitution products of 'acicular,' 'tabular,' and 'octahedral' oxylepiden respectively.

A fourth *dichloroxylepiden* has been obtained by Dorn (*A.* 153, 353) by treating *dichlorthionessal* $C_{28}H_{18}Cl_2S$ with hydrochloric acid and potassium chlorate.—Small needles [178°]; readily sol. alcohol, benzene, and glacial acetic acid. Not attacked by alcoholic potash at 150°. Zinc and acetic acid convert it into a dichlorlepiden [156°] (*v. supra*); whilst with hydriodic acid at 100° it yields dichlorlepiden, lepiden, and oxylepiden (?).

Dibromoxylepiden $C_{28}H_{18}Br_2O_2$. Three dibromoxylepidens, corresponding with the first three of the foregoing dichloroxylepidens, have also been described by Zinin (*J. R.* 7, 329; *J.* 1876, 425). In their modes of preparation, properties, and reactions, they resemble the chlorine compounds. 'Acicular dibromoxylepiden' is obtained either by brominating 'acicular oxylepi-

den' or by oxidising dibromlepiden in acetic acid solution with nitric acid. Needles [222°]; sol. 40 parts boiling acetic acid. Heated above its melting-point it yields two isomeric dibromoxylepidens—'readily soluble dibromoxylepiden,' which is resinous, v. sol. alcohol, ether, and acetic acid, and is converted by alcoholic caustic potash into a salt of dibromoxylepidenic acid $C_{28}H_{26}Br_2O_3$, and 'sparingly soluble dibromoxylepiden.' This latter is more easily obtained by boiling the acicular modification with a quantity of alcoholic potash insufficient to dissolve it. Crystallises from alcohol in lemon-yellow rhombic tables [239°]; almost insol. ether, sol. 66 parts boiling acetic acid and 1,000 parts boiling alcohol (95 p.c.). Heated above its melting-point it is converted into 'readily soluble dibromoxylepiden (Zinin, *J. R.* 7, 329; *J.* 1876, 425).

Both 'acicular' and 'sparingly soluble' dibromoxylepiden, when reduced with zinc and acetic acid, yield the same hydrodibromoxylepiden (dibrombidesyl), part of which undergoes dehydration, forming dibromlepiden [190°].

Hydro-oxylepiden (*Bidesyl*)

$$C_{28}H_{22}O_2 = \begin{array}{ll} C_6H_5.CH & \!\!\!-\,CH.C_6H_5 \\ \quad\;\; | & \;\;\;| \\ C_6H_5.CO & \;\;CO.C_6H_5 \end{array}$$

(Magnanini a. Angeli, *B.* 22, 853). Formed, along with lepiden, by the action of zinc and acetic acid on 'octahedral oxylepiden,' or of sodium amalgam on 'acicular oxylepiden.' The product of the reaction is ppd. with water and treated with ether, which dissolves only the lepiden (Zinin, *J. R.* 7, 188; *J.* 1875, 409). By the action of desyl bromide, $C_6H_5.CHBr.CO.C_6H_5$, on sodium-deoxybenzoïn, or of iodine on sodium-deoxybenzoïn:

$$2\begin{array}{l} C_6H_5.CHNa \\ \quad\;\; | \\ C_6H_5.CO \end{array} + I_2 = \begin{array}{ll} C_6H_5.CH & \!\!\!-\,CH.C_6H_5 \\ \quad\;\; | & \;\;\;| \\ C_6H_5.CO & \;\;CO.C_6H_5 \end{array} + 2NaI$$

(Knövenagel, *B.* 21, 1358).—Long flat needles (from acetic acid); [251°] (Zinin); [254°–255°] (Knövenagel; also Magnanini a. Angeli). Almost insol. cold alcohol and ether, sol. 112 pts. boiling acetic acid, sol. hot benzene. Heated with hydrochloric acid at 130°–140° it parts with water, yielding lepiden (Magnanini a. Angeli, *B.* 22, 855).

Tetraphenylbutyrolactone

$$C_{28}H_{22}O_2 = \begin{array}{ll} (C_6H_5)_2C & \!\!\!-\,CH.C_6H_5 \\ \qquad | & \;\;| \\ \qquad CO & CH.C_6H_5 \\ \qquad \diagdown & \!\!\diagup \\ \qquad\;\; O & \end{array}.$$

By treating a solution of 'tabular oxylepidene' (tetraphenylcrotolactone) in boiling amyl alcohol with sodium (Klingemann a. Laycock, *private communication*).—Microscopic, white needles [221°], sol. boiling, sl. sol. cold, alcohol.

Hydrodichloroxylepiden $C_{28}H_{20}Cl_2O_2$. Formed, along with dichlorlepiden, when 'sparingly soluble dichloroxylepiden' is boiled for a long time with zinc and acetic acid, or, more readily, by boiling an alcoholic solution of 'acicular dichloroxylepiden' with sodium amalgam, keeping the liquid acid with acetic acid (Zinin, *J. R.* 7, 195; *J.* 1875, 413).—Flat needles (from acetic acid) [261°], insol. alcohol and ether, sol. 205 pts. boiling acetic acid.

Hydrodibromoxylepiden $C_{28}H_{20}Br_2O_2$. By the action of zinc and acetic acid on 'acicular' or 'sparingly soluble' dibromoxylepiden (Zinin, *J. R.* 7, 330; *J.* 1876, 425).—Slender needles, v. sl. sol. alcohol and ether, sol. 172 pts. boiling acetic acid.

Dioxylepiden $C_{28}H_{20}O_3$. By warming 25 pts. of 'acicular oxylepiden,' suspended in 20 pts. of acetic acid, with a solution of 12-15 pts. of chromic anhydride dissolved in 150 pts. of acetic acid (Zinin, *Z.* 1871, 483).—Rhombic tables [157°], sol. 24 pts. boiling alcohol (95°). Reducing agents are without action on it. By further action of chromic anhydride it yields benzil and benzoic acid. Alcoholic potash hydrolyses it into deoxybenzoïn and benzoic acid:

$$C_{28}H_{20}O_3 + 2KHO = C_{14}H_{12}O + 2C_6H_5.CO_2K.$$

Isodioxylepiden $C_{28}H_{20}O_3$. By boiling 'octahedral oxylepiden' with a solution of chromic anhydride in acetic acid (Zinin, *J. R.* 7, 190; *J.* 1875, 410).—Laminæ [164°], sol. 10 pts. boiling alcohol, less sol. ether, sol. 4 pts. boiling acetic acid. Boiling alcoholic potash is without action on it (distinction from foregoing isomeride).

Oxylepidenimide $C_{28}H_{21}NO$. By heating 'acicular oxylepiden' with alcoholic ammonia for 5 hours at 200°; it yields a mixture of oxylepidenimide and the isomeric tetraphenylpyrrholone. The oxylepidenimide is separated by means of its greater solubility in alcohol (Klingemann a. Laycock, *private communication*).—Yellow prisms (from benzene) [180°–182°]. Heated to 310° it changes into tetraphenylpyrrholone (*v. infra*).

Oxylepiden-methylimide $C_{28}H_{20}O(N.CH_3)$. By heating 'acicular oxylepiden' with an alcoholic solution of methylamine for 2 hours at 200° (K. a. L.).—Small pale-yellow plates [161°] from alcohol; well-shaped crystals from carbon bisulphide. V. sol. benzene, readily sol. carbon bisulphide, moderately sol. boiling alcohol.

Oxylepidenic acid (*Benzoyl-triphenyl-propionic acid*)

$$C_{28}H_{22}O_3 = \begin{array}{ll} (C_6H_5)_2C & \!\!\!-\!\!-\!\!-\,CH.C_6H_5 \\ \qquad | & \quad\;\;| \\ \quad COOH & \;CO.C_6H_5 \end{array}$$

(Japp a. Klingemann, *C. S. Pr.* 1889, 138). The potassium salt is formed when 'tabular oxylepiden' is dissolved in hot alcoholic potash (Zinin, *J. R.* 5, 18).—The acid crystallises in laminæ, v. sol. ether, sol. 3·5 pts. boiling alcohol (95 p.c.), insol. water. Melts at 196°, breaking up into 'tabular oxylepiden' and water:

$$\begin{array}{ll} (C_6H_5)_2C & \!\!\!-\!\!-\!\!-\,CH.C_6H_5 \\ \qquad | & \quad\;\;| \\ \quad COOH & \;CO.C_6H_5 \end{array} = \begin{array}{ll} (C_6H_5)_2C & \!\!\!-\,C.C_6H_5 \\ \qquad | & \;\;\| \\ \qquad CO & C.C_6H_5 \\ \qquad \diagdown & \!\!\diagup \\ \qquad\;\; O & \end{array} + H_2O.$$

The so-called *isoxylepidenic acid* described by Zinin (*J.* 1877, 397) is identical with the foregoing (Japp a. Klingemann, *C. S. Pr.* 1889, 139).

Tetraphenylpyrrholone

$$C_{28}H_{21}NO = \begin{array}{ll} (C_6H_5)_2C & \!\!\!-\,C.C_6H_5 \\ \qquad | & \;\;\| \\ \qquad CO & C.C_6H_5 \\ \qquad \diagdown & \!\!\diagup \\ \qquad\;\; NH & \end{array}.$$

Formed, along with the isomeric oxylepidenimide, when 'acicular oxylepiden is heated with alcoholic ammonia at 200°. By heating oxylepidenimide to 310°. As sole product when 'tabular oxylepiden' is heated with alcoholic ammonia at 200° (Klingemann a. Laycock).—Small pale-yellow plates [208°], sparingly sol. alcohol.

Oxylepiden-methylamide

$$C_{29}H_{25}NO_2 = \begin{array}{ccc}(C_6H_5)_2C & \text{———} & CH.C_6H_5 \\ | & & | \\ CO.NCH_3 & & CO.C_6H_5\end{array}$$

. Formed when 'tabular oxylepiden' is heated with an alcoholic solution of methylamine at 150°: $C_{28}H_{20}O_2 + NH_2CH_3 = C_{29}H_{25}NO_2$ (Klingemann a. Laycock).—Yellowish laminæ [267°] from acetic acid; short needles from alcohol. Sl. sol. boiling alcohol, more sol. boiling acetic acid. Decomposed by distillation *in vacuo* into methyl-tetraphenylpyrrholone (prismatic crystals [158°] from benzene) and water:

$$\begin{array}{ccc}(C_6H_5)_2C & \text{———} & CH.C_6H_5 \\ | & & | \\ CO.NCH_3 & & CO.C_6H_5\end{array}$$

$$= \begin{array}{c}(C_6H_5)_2C\text{—}C.C_6H_5 \\ |\quad\;\; \| \\ CO\;\; C.C_6H_5 \\ \diagdown\diagup \\ N.CH_3\end{array} + H_2O.$$

The compound thus formed appears to be isomeric, not identical, with oxylepiden-methylimide (K. a. L.).

Dichloroxylepidenic acid $C_{28}H_{20}Cl_2O_3$. By dissolving 'readily soluble dichloroxylepiden' in boiling alcoholic potash (Zinin, *J. R.* 7, 191; *J.* 1875, 411).—Rhombic laminæ [182°], from acetic acid. Sol. 16 pts. boiling acetic acid. Heated to 200° it parts with 1 mol. water, and is reconverted into 'readily soluble dichloroxylepiden.'

Dibromoxylepidenic acid $C_{28}H_{20}Br_2O_3$. By dissolving 'readily soluble dibromoxylepiden' in boiling alcoholic potash (Zinin, *J. R.* 7, 330; *J.* 1876, 425).—Six-sided laminæ from acetic acid.

So-called isolepiden and its derivatives.—Under the name of *isolepiden*, Zinin (*J. R.* 5, 20) has described a compound which he obtained by the destructive distillation of oxylepiden, and which he regarded as isomeric with lepiden. Japp a. Klingemann have, however, shown (*C. S. Pr.* 1889, 139) that this compound has the formula $C_{27}H_{20}O$, instead of $C_{28}H_{20}O$, and that it is formed from oxylepiden with elimination of carbonic oxide according to the equation

$$C_{28}H_{20}O_2 = C_{27}H_{20}O + CO.$$

The name 'isolepiden' is consequently inappropriate, but will be retained here, as the constitution of the compound is unknown, and a systematic name cannot be given. The formulæ of the various hydro- 'isolepidens' and oxy- 'isolepidens' described by Zinin must also be written with 27 instead of with 28 atoms of carbon, although these compounds have not yet been re-investigated.

Isolepiden $C_{27}H_{20}O$ (Japp a. Klingemann, *l.c.*). By the destructive distillation of oxylepiden (Zinin, *J. R.* 5, 20; *cf.* preceding paragraph). The three oxylepidens all yield this compound on distillation; but in reality it is only 'tabular oxylepiden' which yields it, as the other two oxylepidens are previously transformed into 'tabular oxylepiden' at the temperature of the reaction. The distillate is washed with ether and then recrystallised, first from alcoholic potash, afterwards from alcohol. The ether extracts a little 'tabular oxylepiden,' which is carried over undecomposed (Japp a. Klingemann, *C. S. Pr.* 1889, 139).—Isolepiden forms yellow tabular crystals [150°]. Decomposes on redistillation. Sol. 18 pts. boiling alcohol (95 p.c.), and in 2 pts. boiling acetic acid (Zinin, *J.* 1877, 394). Not attacked by alcoholic potash. It is reduced by zinc-dust and acetic acid to dihydro-isolepiden $C_{27}H_{22}O$, and by sodium amalgam to tetrahydro-isolepiden $C_{27}H_{24}O$. Oxidising agents convert it into oxy-isolepiden, and ultimately into a mixture of benzophenone and benzil.

Dihydro-isolepiden $C_{27}H_{22}O$. By reducing a solution of isolepiden in from 5 to 6 pts. of acetic acid with zinc-dust. The product is poured into water, and the pp. is washed with ether and recrystallised from alcohol (Zinin, *J.* 1877, 394).—Small rectangular prisms [182°]. Sol. 12·5 pts. boiling alcohol (95 p.c.), v. sl. sol. ether.

Tetrahydro-isolepiden $C_{27}H_{24}O$. By the action of sodium amalgam on a boiling alcoholic solution of isolepiden (Zinin). Separates from ether as a soft resinous mass which soon becomes crystalline [132°]. Readily sol. alcohol and acetic acid, less sol. ether. Chromic anhydride oxidises it in acetic acid solution, even in the cold, to dihydro-isolepiden.

Oxyisolepiden $C_{27}H_{20}O_2$. Three pts. of isolepiden are dissolved in 40 pts. of acetic acid, and oxidised with a solution of 3 pts. of chromic anhydride in 30 pts. of acetic acid (Zinin, *J.* 1877, 395).—Short slender needles [161°]. Sol. 40 pts. boiling, and 600 pts. cold, alcohol, and in 4 pts. boiling acetic acid. Boiling alcoholic potash is without action on it. Zinc and acetic acid reduce it to dihydro-isolepiden. Excess of chromic acid oxidises it, in acetic acid solution, to benzophenone as chief product, together with benzil and benzoic acid.

Oxy-isolepiden, like oxylepiden, may be converted into isomeric compounds. Thus, when it is boiled with a quantity of alcohol or alcoholic potash insufficient to dissolve it, it is transformed into *cuneiform oxy-isolepiden* [162°]. When this is heated above its melting-point, or when ordinary oxy-isolepiden is distilled, *tabular oxy-isolepiden*, a third isomeride, is formed. Rhombic tables [152·5°] from acetic acid. Sol. 13·5 pts. boiling acetic acid, 80 pts. boiling alcohol. F. R. J.

LEPIDINE *v.* (*Py.* 1)-METHYL-QUINOLINE.

LEUCANILINE is described under TRI-AMIDO-DI-PHENYL-TOLYL-METHANE.

Para-leucaniline is described as TRI-AMIDO-TRI-PHENYL-METHANE.

LEUCAURIN *v.* TRI-OXY-TRI-PHENYL-METHANE.

LEUCATROPIC ACID $C_{17}H_{32}O_5$. [74°]. Occurs in belladonna (Kunz, *Ar. Ph.* [3] 23, 722). Minute satiny needles. Insol. cold, m. sol. boiling water, and alcohol.

LEUCEÏNES *v.* PROTEÏDS.

LEUCIC ACID. Described as OXY-HEXOIC ACID.

LEUCINDIGO *v.* INDIGO.

LEUCINE $C_6H_{13}NO_2$ *i.e.* $CH_3.CH_2.CH_2.CH_2.CH(NH_2).CO_2H$. *a-Amido-n-hexoic acid.* Mol. w. 131. [170°] (Schwanert). S.G. $\frac{18}{}$ 1·293 (Engel a. Vilmain, *Bl.* [2] 24, 279). S. 2·2 at 18° (Schulze, *H.* 9, 254); 3·7 in the cold (Zollikofer). S. (alcohol of S.G. ·828) ·152 in the cold (Mulder). S. (96 p.c. alcohol) ·096 in the cold (K.). S. (98 p.c. hot alcohol) ·125 (K.). $[\alpha]_D = +14·1°$ in a 15 p.c. HCl solution; $= +5·6°$ in a 25 p.c. solution in NH_3Aq (Reese, *A.* 242, 11). Discovered by Proust (*A. Ch.* [2] 10, 40) as a product of the putrefaction of cheese, and called 'caseous oxide.' Braconnot

(*A. Ch.* [2] 13, 119) found it among the products of the action of H_2SO_4 on animal substances. Mulder (*J. pr.* 16, 290) showed the two substances thus obtained were identical.

Occurrence.—In old cheese (Proust), in fresh calf's liver (Liebig, *Chem. Briefe*, ed. 3, 453), in diseased but not in healthy human liver (Frerichs a. Städeler, *J.* 1854, 675; 1856, 702; 1858, 550), in the tissue of the lungs (Cloetta, *A.* 92, 289), in the thymoid and thyroid glands, and in the pancreas (Gorup-Besanez, *A.* 98, 7; Radziejewsky, *Z.* 1866, 416), in the brain of oxen (W. Müller, *A.* 103, 131), in the pancreas of oxen (Scherer, *J.* 1859, 610), in the liver and urine in cases of typhus, smallpox, leucæmia, and poisoning by phosphorus (Salkowsky, *J. Th.* 1880, 457; Valentiner, *J.* 1854, 675; Sotnitschewsky, *H.* 3, 391), in the stomachs and intestines of the pupæ of butterflies (Schwarzenbach, *J.* 1857, 538), in *Agaricus muscarius* (Ludwig, *J.* 1862, 516), in the juice of vetches germinated in the dark (Gorup-Besanez, *B.* 7, 146; *cf.* Cossa, *G.* 5, 314), in *chenopodium album* in young pumpkin plants (Schulze a. Barbieri, *B.* 11, 1233), and in beet-root molasses (Lippmann, *B.* 17, 2837).

Formation.—1. In the putrefaction of proteïds and gelatin (Bopp, *A.* 69, 20) and by boiling these substances with dilute H_2SO_4, or by fusing them with potash (Hinterberger, *Sitz. W.* 9, 450; *A.* 71, 75; Zollikofer, *A.* 82, 174; Gossmann, *A.* 91, 130; Leyer a. Köller, *A.* 83, 332; Schlossberger, *Z.* 1860, 424; Erlenmeyer a. Schöffer, *Z.* 1859, 315; Hochstetter, *J. pr.* 29, 36; Ritthausen a. Kreusler, *J. pr.* [2] 3, 307).—2. In the pancreatic digestion of gelatin (Nencki, *B.* 7, 1593; Jeanneret, *J. pr.* [2] 15, 353).—3. By acting on α-bromo-hexoic acid with ammonia (Hüfner, *J. pr.* [2] 1, 6; *Z.* [2] 4, 391, 616).

Preparation.—Horn shavings (2 lbs.) are boiled with H_2SO_4 (5 lbs.) and water (13 lbs.) for 24 hours with inverted condenser. The product is mixed with lime, filtered, and evaporated to a smaller bulk (12 lbs.). Oxalic acid is then added to acid reaction, and the liquid filtered and evaporated till a crystalline film forms on the surface. Leucine mixed with tyrosine is deposited in groups of yellowish laminæ. On recrystallisation from water tyrosine is deposited first, and the mother-liquor is then decolourised by animal charcoal and evaporated. The leucine is recrystallised from alcohol (Schwanert, *A.* 102, 221; *cf.* Hinterberger, *A.* 71, 72: Waage, *A.* 118, 295). Leucine may be detected and isolated by means of its sparingly soluble copper salt $(C_6H_{12}NO_2)_2Cu$, although the precipitation of this salt is hindered by free acids and by some organic bodies (Hoffmeister, *Sitz. W.* 75, 469).

Properties.—Soft nacreous scales (from alcohol) resembling cholesterin. It may be sublimed (Mulder). Decomposed on fusion, giving amylamine, CO_2, and NH_3. Lævorotatory (Lewkovitch, *B.* 17, 1439; *cf.* Mauthner, *H.* 7, 223). Sl. sol. water and alcohol, insol. ether. Its solubility in water is increased by the presence of acetic acid or an alkaline acetate. When heated with baryta-water at 160° it becomes inactive. The inactive leucine is changed to an active variety, lævorotatory when dissolved in aqueous HCl, by the action of *Penicillium glaucum* (Schulze a. Bosshard, *B.* 18, 388).

Reactions.—1. An alkaline solution exposed to the action of *ozone* yields CO_2, butyric acid, and NH_3 (Gorup-Besanez, *A.* 125, 210).—2. *Chlorine* passed into water in which leucine is suspended forms CO_2 and valeronitrile, as well as chloro-valeronitrile (Schwanert). Chlorine passed into an alkaline solution of leucine forms oxy-hexoic acid.—3. *Nitrous acid* converts it into α-oxy-hexoic (leucic) acid.—4. Distillation with MnO_2 and dilute H_2SO_4 yields CO_2 and valeronitrile.—5. Distillation with water and PbO_2 yields butyric aldehyde and NH_3 (Liebig, *A.* 70, 313).—6. Aqueous $KMnO_4$ yields NH_3, oxalic acid, and valeric acid (Neubauer, *A.* 106, 59).—7. *Potash-fusion* gives NH_3, hydrogen, and potassium valerate (Liebig, *A.* 57, 127).—8. When heated with fuming HIAq at 140° it gives hexoic acid and ammonia (Hüfner).—9. With KOH (2 mols.) and MeI (3 mols.) it forms potassium di-methyl-amido-hexoate methylo-iodide $C_5H_{10}(NMe_3I)CO_2K$, which, when heated with moist Ag_2O, yields methylamine, a salt $C_6H_9O_2K$, and potassium leuconate $C_6H_{11}O_3K$ (Körner a. Menozzi, *G.* 13, 353).—10. Leucine gives off more nitrogen when its solution is decomposed by NaBrO in presence of NH_3, than when the NH_3 is absent (E. Schulze, *J. pr.* [2] 31, 236).

Salts.—HA'HCl: crystals, v. sol. water (Laurent a. Gerhardt, *A. Ch.* [3] 24, 321; *A.* 68, 365).—$(HA')_2HCl$: laminæ (Schwanert).—$(HA')_2H_2PtCl_6$: yellow crystalline pp.—$HA'HNO_3$: colourless needles, v. e. sol. water.—CuA'_2: pale blue scales. S. ·033 in the cold, ·07 at 100° (Hoffmeister).—HgA'_2 aq: laminæ. Mercuric nitrate gives a white flocculent pp. in a solution of leucine (R. Hoffmann, *A.* 87, 183).—PbA'_2 aq: ppd. by adding NH_3Aq to an aqueous solution of leucine and lead acetate (Strecker, *A.* 72, 89).

Benzoyl derivative $C_5H_{12}BzNO_2$ *i.e.* $C_5H_{10}(NHBz).CO_2H$. From leucine and BzCl at 100° (Destrem, *Bl.* [2] 30, 481). Granules, sol. alcohol and ether. In the preparation of leucine anhydride there is also formed the anhydride $(C_5H_{10}(NHBz).CO)_2O$, which is an amorphous body [85°] insol. water and ether, v. e. sol. alcohol. Decomposed by boiling water into benzoic acid and the anhydride of leucine.

Phthaloxyl derivative $C_5H_{10}(CO_2H).NH.CO.C_6H_4.CO_2H$. [132°]. From leucine, alcoholic KOH, and phthalyl chloride (Reese, *B.* 21, 277).—K_2A'': concentric groups of small slender needles.

Anhydride $(C_5H_{12}NO)_2O$. When the product of the action of BzCl on leucine at 100° is treated with alcohol leucine anhydride remains undissolved, while its di-benzoyl derivative (*v. supra*) passes into solution (Destrem, *C. R.* 86, 481). Leucine anhydride is a white amorphous body, insol. alcohol, but becoming gelatinous when boiled therewith. It is not easily converted into leucine by boiling water.

LEUCINDIN SULPHONIC ACID *v.* Indin.

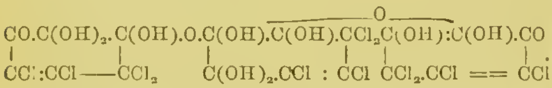
LEUCINIMIDE $C_6H_{11}NO$. Obtained in small quantity, together with leucine and tyrosine, by boiling proteïds with dilute H_2SO_4 (Limpricht a. Hesse, *A.* 116, 201; Erlenmeyer, *A.* 119, 17; Thudichum, *C. J.* 23, 409). Formed also when proteïds are treated with bromine-water (Hlasiwetz a. Habermann, *A.* 159, 328), and, together with benzoyl-leucine, by heating leucine with HOBz at 200° (Destrem, *Bl.* [2] 30, 481). Mi-

nute white trimetric needles; insol. cold, sl. sol. boiling water, sol. alcohol, m. sol. ether. May be sublimed. Not affected by boiling aqueous acids or alkalis.

Iso-leucinimide $C_6H_{11}NO$. Formed by heating α-amido-isohexoic acid in a current of HCl at 225° (Köhler, *A.* 134, 369). Minute white needles (from alcohol), may be sublimed. Insol. water, sol. alcohol. Not affected by boiling KOHAq or by acids.

LEUCO-BROMO-QUINONE PHENOLIMIDE *v.* BROMO-DI-OXY-DI-PHENYL-AMINE.

LEUCOGALLOL $C_{18}H_6Cl_{12}O_6$ 2aq. [104°]. Formed by passing chlorine into a cold mixture of pyrogallol (10 g.) and glacial acetic acid (20 g.), then adding conc. HClAq (5 c.c.), and continuing the passage of chlorine. The pp. is washed with benzene, dissolved in ether, and ppd. with benzene (Stenhouse a. Groves, *C. J.* 28, 1, 704). Crystalline crusts composed of small needles. Gives off HCl and water on fusion, and forms tri-chloro-pyrogallol and a body resembling quinone (Webster, *C. J. Proc.* 3, 130). V. sol. water and alcohol, m. sol. ether, insol. CS_2 and ligroïn, sl. sol. boiling benzene. Leucogallol is converted by zinc-dust and dilute H_2SO_4 to tri-chloro-pyrogallol $C_6Cl_3(OH)_3$ (Hantzsch a. Schniter, *B.* 20, 2033). It reacts with hydroxylamine and with phenyl-hydrazine. Its constitution may possibly be:



LEUCOLINE C_9H_7N. This base, occurring in coal tar, has been shown by Hofmann (*A.* 47, 76; 53, 427), Hoogeweiff a. van Dorp (*R. T. C.* 1, 1, 107), and others to be identical with quinoline.

LEUCOLINIC ACID $C_9H_9NO_3$. [162°]. Obtained from coal-tar quinoline (leucoline) (10 g.) by dissolving as neutral sulphate and treating with $KMnO_4$ (25 g.) in boiling water, adding the latter solution slowly. Cold solution of $KMnO_4$ (40 g.) gives only pyridine carboxylic acids (J. Dewar, *Pr.* 26, 65; 30, 168).

Properties. — Needles. Often syrupy. It then becomes crystalline by boiling with water for some days. Sl. sol. cold water, sol. alcohol. The lead salt is insoluble. The silver salt forms slender needles.

Reactions.—1. The crystalline acid forms with *glycerine* a substance resembling indole.—2. A solution of the potassium salt at 200° gives aniline.—3. *Potash fusion* gives salicylic acid, CO_2, NH_3, and hydrogen.—4. When heated with *soda-lime* to a low red heat it forms aniline, NH_3, and a small quantity of methyl-pyridine.

LEUCOMAÏNES. Bases occurring in living animals (Gautier, *Bl.* [2] 48, 16; *cf. J. Ph.* [5] 13, 351, 401; *Bl.* [2] 43, 158). Λεύκωμα = white of egg. Obtained by extracting fresh beef (30 kilos) with tepid water (60 kilos) to which ·25 g. oxalic acid and 1 c.c. oxygenated water is added per litre. At the end of 24 hours the whole is heated to boiling, filtered, and evaporated at 50° *in vacuo*. The residue is extracted with 99 p.c. alcohol, filtered, evaporated *in vacuo*, redissolved in alcohol, filtered, and the alcoholic solution ppd. with ether. The precipitate may be separated by a series of crystallisations from ether, alcohol, and water, and by precipitation with $HgCl_2$ into the six following bases.

Xantho-creatinine $C_5H_{10}N_4O$. Small sulphur-yellow micaceous laminæ, with greasy surface. Slightly bitter in taste. Gives off an odour like acetamide when heated. Smells in the cold like a dissecting room. When strongly heated it gives off an odour of roast beef, and carbonises, with evolution of NH_3 and methylamine. Neutral to litmus. Its hydrochloride and platinochloride are crystallisable and soluble. Its solution like creatinine is ppd. by $ZnCl_2$; this pp. crystallises from hot water on cooling in groups of needles. $AgNO_3$ gives a flocculent pp., crystallising from hot water in needles. Mercuric chloride gives a yellowish-white pp., sol. alcohol. It is not ppd. by iodine in KIAq. Sodium phosphomolybdate gives a pp. after a time. Treatment with HgO forms a substance melting at 174°.

Chruso-creatinine $C_5H_8N_4O$. Crystals (from water). Feebly alkaline. Its hydrochloride crystallises in needles, is soluble and not deliquescent. The aurochloride is slightly soluble and forms crystalline grains. The platinochloride is soluble. Chrusocreatinine gives no pp. with zinc acetate or mercuric nitrate, but it ppts. alumina from alum. $ZnCl_2$ gives a crystalline powder. $HgCl_2$ gives a pp. I in KIAq gives a pp. Sodium phosphomolybdate gives an abundant yellow pp.

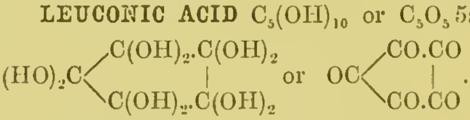
Amphicreatine $C_9H_{19}N_7O_4$. Feeble base, forming bright-yellow crystals. Its hydrochloride is crystalline and non-deliquescent. Its platinochloride is soluble and forms lozenge-shaped tables. It ppts. sodium phosphomolybdate, but not $HgCl_2$.

Pseudocreatine $C_4H_5N_3O$. Flesh-coloured powder composed of minute crystalline grains. Forms a very soluble hydrochloride, resembling that of hypoxanthine, crystallising in whetstone-like shapes. Its aqueous solution is ppd. by $HgCl_2$. $AgNO_3$ gives a gelatinous pp. Ppd. by ammoniacal but not by neutral lead acetate. When evaporated with HNO_3 like xanthine it leaves a residue which is turned orange-red by potash.

A base $C_{11}H_{24}N_{10}O_5$ crystallising in colourless rectangular tables, with crystalline hydrochloride and platinochloride.

A base $C_{12}H_{25}N_{11}O_5$ resembling both the preceding and xanthocreatinine.

LEUCONIC ACID $C_5(OH)_{10}$ or C_5O_5 5aq *i.e*



. *Oxy-croconic acid. Deca-oxy-pentamethylene.* Prepared by adding finely powdered pure croconic acid (1 pt.) to cooled HNO_3 of S.G. 1·36 (6–8 pts.); the mixture solidifies to a magma of colourless needles, which are washed with ether-alcohol and finally with ether (Nietzki a. Benkiser, *B.* 19, 301; *cf.* Will, *A.* 118, 117; Lerch, *A.* 124, 20). Gum-like mass. V. c. sol. water, sl. sol. alcohol, insol. ether. Sweet taste. It is readily reduced to croconic acid. By dissolving in alkalis it is entirely altered. Treated with tri-amido-benzene it forms a violet colouring matter, turned brown by alkalis (Witt, *C. J.* 49, 402).—$KC_5H_7O_9$:

amorphous, sl. sol. water.—$Ba_3(C_5H_3O_9)_2$: flocculent pp.—$Pb_3(C_5H_3O_9)_2$: pp.—$Ag_3C_5H_3O_9$ (W.).

Penta-oxim $C_5(NOH)_5$. Yellow crystalline solid. Formed by the action of hydroxylamine upon croconic or leuconic acid. Decomposes suddenly at 172°.—$C_5H_3N_5O_5K_2$: very explosive. The penta-oxim may be reduced by $SnCl_2$ to

$$CH(NH_2)\begin{cases} C(NH_2):C(NH_2) \\ \quad | \\ C(NH_2):C(NH_2) \end{cases}$$

which forms crystalline salts.

Tetra-acetyl derivative of the penta-oxim $C_5(NOH)(NOAc)_4$ aq (from benzene). From the penta-oxim and Ac_2O at 45° (Nietzki a. Rosemann, *B.* 22, 916). Plates (from Ac_2O) or needles containing chloroform (from chloroform). Sl. sol. hot benzene. Decomposed at 100°.

Tetra-oxim $C_5H_4N_4O_5$ *i. e.*

$$CO\begin{cases} C(NOH).C(NOH) \\ \quad | \\ C(NOH).C(NOH) \end{cases}$$

When potassium croconate (30 g.) is gradually added to a cooled mixture of HNO_3 (45 g. of S.G. 1·39) and water (40 g.), and the product is diluted with water (500 c.c.) and heated with hydroxylamine hydrochloride (180 g.) for some hours at 45° and finally at 100° there is formed a pp. of mixed oxims. This is dissolved in aqueous Na_2CO_3 and CO_2 is passed in, whereupon the penta-oxim is ppd. while the tetra-oxim can be ppd. from the filtrate by HCl. Yellow pp. Explodes at 160°. Its sodium derivative is v. sol. water, but is ppd. on adding alcohol or NaCl, apparently in the form of $Na_2C_5H_2N_4O_5$.

Carbonyl-di-toluquinoxaline $C_{19}H_{12}N_4O$ *i.e.*

$$C_7H_6\begin{cases} N.C \diagup CO \diagdown C.N \\ \; | \; \| \qquad\qquad \| \; | \\ N.C \text{———} C.N \end{cases}C_7H_6.$$

Leuconic-acid-di-tolylene-o-diamide. [above 300°]. Formed by adding a salt of tolylene-*o*-diamine to a cold aqueous solution of leuconic acid. Golden-yellow needles. V. sol. warm chloroform, sl. sol. hot alcohol and acetic acid, insol. water. Weak base.

Phenyl hydrazide $(C_7H_6N_2)_2C_4{:}C{:}N_2HPh$: Red needles (from acetic acid); v. sol. chloroform, sl. sol. alcohol. Weak base. The hydrochloride forms a dark-green pp. (Nietzki a. Benkiser, *B.* 19, 776).

LEUCOTIN *v.* COTO BARK.

LEUCOTURIC ACID $C_6H_6N_4O_6$. *Oxalantin.* Formed when a solution of alloxanic acid is rapidly boiled down to a syrup; cold water is then added which leaves the leucoturic acid undissolved (Schlieper, *A.* 56, 1). Formed also by reducing parabanic acid with zinc and HClAq in the cold (Limpricht, *A.* 111, 134). White crystalline powder, insol. cold, m. sol. hot, water. Decomposes alkaline carbonates on boiling. Decomposed by heating with KOH, giving off NH_3, and forming oxaluric acid. Its ammoniacal solution is ppd. by $AgNO_3$, and on boiling reduction takes place. Boiling conc. HNO_3 does not attack it.

LEVONIC ACID $C_{11}H_{12}O_8$ 3aq. An acid said by Wiederhold (*C. C.* 1884, 971) to be obtained by boiling lævulose with baryta-water. Yellowish-brown powder, v. sol. alcohol and water. Decomposed by heat.

LICARENE $C_{10}H_{16}$. (168°–172°). S.G. $\frac{18}{}$ ·835. An inactive terpene obtained by the action of $ZnCl_2$ or P_2O_5 on the essential oil of *Licari Kanali* (Morin, *A. Ch.* [5] 25, 427). Conc. HClAq forms $C_{10}H_{16}2HCl$, a colourless liquid, S.G. $\frac{15}{}$ 1·069, inactive to light, and decomposed on distillation into licarene and hydrochloric acid. The essential oil $C_{10}H_{18}O$ might be looked upon as licarene hydrate and exhibits the following properties:—(198°) at 755 mm. S.G. $\frac{15}{}$ ·868. $[\alpha]_D = -19$ at 15°. It is sol. alcohol, ether, and glycerin.

LICHENINE $C_6H_{10}O_5$. Occurs in Iceland moss.

Preparation.—*Cetraria islandica* or other similar lichen is heated for several hours with a 2 p.c. solution of K_2CO_3. The aqueous solution is ppd. by alcohol (Honig a. Schubert, *M.* 8, 460; *cf.* Knop a. Schnedermann, *A.* 55, 164; Maschke, *J. pr.* 61, 7; Davidson, *N. Ed. P. J.* 28, 260; Errera, *Bn.* 1, 882; Bauer, *J. pr.* [2] 34, 49; Klason, *B.* 19, 2541).

Properties.—Gelatinous pp., v. sl. sol. cold water. Boiling water forms an opalescent solution; reppd. on cooling or on adding alcohol. Gives no blue colour with I and H_2SO_4. Dissolves in HCl, from which solution it is ppd. in snow-white flocks by alcohol. Weak hot acids convert it after some time into a dextro-rotatory sugar. $[\alpha]_j = +55°$. Glucose is also formed. Two carbohydrates, resembling soluble starch in their properties, are present in the aqueous solution.

LICHENO-STEARIC ACID $C_{14}H_{24}O_3$. [c. 120°]. An acid occurring in Iceland moss (Schnedermann a. Knop, *A.* 55, 149), and probably also in the fly-agaric or toadstool (Bolley, *A.* 86, 50). Obtained by boiling Iceland moss for 15 minutes with dilute alcohol and some K_2CO_3, filtering, adding HClAq and 4 volumes of water. The pp. is boiled with alcohol of 45 p.c., whence a mixture of licheno-stearic and cetraric acids separates on cooling. The licheno-stearic acid is extracted from the mass by petroleum, and recrystallised from alcohol. Mass of radiating needles which soon change to delicate pearly laminæ. Has a rancid taste. Insol. water, v. sol. alcohol, ether, and oils. Is not attacked by AcCl. On oxidation it yields CO_2 and decoic acid (Hilger a. Buchner, *B.* 23, 461). The ammonium salt forms a jelly containing extremely slender needles.—BaA'_2: greyish-white pp. which cakes together in boiling water.—PbA'_2: flocculent pp. fusing under water.—AgA'.

LIEBERMANN'S REACTION. A blue or green colour obtained by warming phenol with H_2SO_4 containing nitrous acid. It may be used as a test for phenol or for nitrous acid. Various derivatives of phenol may be used instead of phenol, while nitroso- and oximido-compounds usually react like nitrous acid.

LIGHT. For an account of the applications of optical methods of inquiry to chemical problems, *v.* PHYSICAL METHODS, section OPTICAL.

LIGNIFICATION *v.* LIGNONE.

LIGNO-CERIC ACID $C_{24}H_{48}O_2$ or $C_{23}H_{47}.CO_2H$. [81°]. Occurs in the paraffin obtained from beech-wood tar (Hell, *B.* 13, 1709). Occurs also in the product of the saponification of earth-nut oil (Kreiling, *B.* 21, 880). Colourless felted needles or plates (from alcohol).

Salts.—A'Na: white powder.—A'K: white

powder, sol. alcohol.—A′Ag: white pp. [c. 155°]. —A'_2Cu: green powder, sol. hot benzene.—A'_2Pb: white powder, [117°] v. sol. hot benzene.

Methyl ether A′Me. [58°]. White glistening plates. Sol. CS_2, $CHCl_3$, C_6H_6, ether, and ligroïn; sl. sol. alcohol. Distils undecomposed at a high temperature.

Ethyl ether A′Et. [55°]; (310° at 20 mm.; 360° at 760° mm.). Glistening plates.

Chloride $C_{23}H_{47}.COCl$. [48°–50°]. Plates. Sol. ether.

LIGNONE (*Lignin, Lignose: Lignification*). Lignification, or the process of wood formation, is one of the principal of the modifications of the cell-wall, by which it and the tissues containing it are differentiated for fulfilling their several functions. The history of a lignified cell, or rather of the substance of the cell-wall, is usually stated to consist of (1) the elaboration of the primary cell-wall from materials in protoplasm, and formed at its limiting film as an envelope of pure cellulose; (2) the induration of this cell-wall, *i.e.* lignification, by the infiltration of substances, which when deposited are known as 'lignin,' or more vaguely as 'incrustive' substance. Lignification is recognised by the morphological changes with which it is associated, as well as by the very characteristic reactions of the product (Goodale, *Phys. Botany*, 1885). These products, although presenting a wide range of differences, corresponding with variations in structural and other characteristics of the tissues which they compose, fall naturally, and as regards their chief constituent, into a homogeneous chemical group, designated by the term lignocellulose, of which the typical features are represented in the substance of the jute fibre (vol. i. p. 719).

It is the purpose of this article to give a brief account of more recent researches into the constitution of this typical lignocellulose, and to show the bearings of the results arrived at upon the chemistry of the woods, the most numerous and important section of the group. The advantages of the jute fibre over the latter as a subject of study are that it is a simple tissue, whereas the woods are complex aggregates, that as an isolated fibred it is much more easy of penetration by reagents, and that as a product of only a few months' growth it has not undergone such secondary changes in composition as necessarily take place in the substance of a perennial stem or true wood. Such characteristics mark out the jute fibre substance as a natural basis for the general solution of the chemical problem of lignification.

Evidence has already been given (vol. i. *loc. cit.*) for regarding this product as chemically homogeneous, which view is further developed in the investigations referred to (*C. J.* 1889. 199). In all reactions in which hydroxyl groups only are brought into play—hydrolysis and etherification—it behaves as an integral compound (lignocellulose), of which the formula $C_{12}H_{18}O_9$ is an approximate empirical expression. The limit of 'nitration' is the tetranitrate, indicating a number of OH groups in the original less by two than in the molecule of cellulose, similarly represented, *i.e.* as $C_{12}H_{20}O_{10}$. The product is of a bright gold colour, with a silky lustre. In further contradistinction to cellulose, the OH groups of the lignocellulose react with acetic anhydride at its boiling-point. Its reaction with chlorine has been studied quantitatively; 1 grm. of the purified fibre-substance takes up 54–55 c.c. Cl (calc. at 0° and 760 mm.), or approximately 16 p.c. by weight, the quantity of Cl as HCl formed being equal to that entering the molecule. The chlorinated product $n(C_{19}H_{17}Cl_4O_9)$,[1] a simple substitution-derivative of the non-cellulose constituent (which we may regard as $n(C_{19}H_{21}Cl_4O_9)$), contains mairogallol in combination with a body not yet completely studied, but yielding furfural on hydrolysis. In addition to the molecular groupings thus indicated, the presence of methyl groups is proved by the formation of methyl chloride on heating this compound, and of acetic acid on destructive distillation of the fibre substance, as also by dissolving it in sulphuric acid, diluting and distilling. These results afford a general view of the constitution of the 'lignin' substance, as it has been termed hitherto. We may regard it as containing closed C_6 chains, further characterised by the presence of ketone- or quinone-oxygen, and united to the furfural-yielding body, which is probably related to 'wood-gum' ('Holzgummi'). Tollens has, in fact, isolated xylose from the jute-fibre (*B.* 22, 1046), though in very small quantity, and we would note here the increase in the proportion of the parent substance, wood-gum, with the more advanced lignification of perennial stems, as additional evidence for this view. It is difficult to localise the methyl groups; but they would appear to be independent of the above, and may be regarded as existing in an acetic residue in combination. For a substance of marked ketonic and aldehydic characteristics, the terms lig*nin* and lig*nose* are obviously unsuited, and should give place, according to present views, to lig*none*, by which, therefore, we shall designate the non-cellulose component of the lignocelluloses generally.

The lignone of plant cells generally in the earlier stage of growth, *i.e.* lignification, appears to be not merely similar to but identical with that of jute. Proof of this has been afforded by the particular investigation of such widely differing structures as the stony concretions of pears—Erdmann's glycodrupose—the fibrovascular bundles of *Musa Paradisiaca* (Monocot.), and the bast fibres of the Sida species (*C. J.* 1882, 108; 1883, 19; 1889, 212).

But very few of the woods have been particularly investigated in regard to the constitution of the wood substance, and for the most part only in regard to the products of hydrolysis (*v.* vol. i. p. 719). Thus Erdmann concluded from his study of coniferous wood that its chief constituent—'glycolignose'—is a chemical individual $C_{30}H_{18}O_{21}$, a species of glucoside resolved by treatment with boiling acids into 'lignose' $C_{18}H_{23}O_{11}$ and a fermentable sugar (glucose). The presence of closed C_6 chains in the 'lignose' molecule was evidenced by its yielding protocatechuic acid on fusion with alkaline hy-

[1] A more direct conversion of the lignone into definitely aromatic products is that which takes place spontaneously when masses of jute are exposed to moisture and heat. From specimens of fibre 'rotted' under such conditions Cross and Bevan obtained an astringent substance $C_{28}H_{34}O_{16}$, which yielded phloroglucol and protocatechuic acid on fusion with potash (*C. S. J.* 1882, 93).

drates. It was also concluded that the wood of the widely different poplar species was similar if not identical in composition (*A. Suppl.* 5, 223).

The later researches of F. Bente (*D. P. J.* 217, 235), although modifying these views, chiefly in the variation in the results of hydrolysis, nevertheless in the main confirm them. The general conformity of the woods to the types above described as representative is shown:

(1) In the close similarity of their characteristic reactions. Of these we may mention (*a*) the colouration produced with solutions of the aromatic amines (golden-yellow), and of solutions of the phenols in hydrochloric acid, most characteristic of which is the reaction with phloroglucol (crimson); (*b*) the powerfully reducing action of the wood substance upon the oxides of copper, silver, gold, and mercury—showing the presence of aldehydic groups; (*c*) the reactions with the halogens yielding, in the case of chlorine, substitution products of definite quinone-chloride characteristics, attended by complete resolution into lignone (chloride) and cellulose: with bromine and iodine less definite compounds, but constant under constant conditions; (*d*) with nitric and sulphuric acids yellow-coloured explosive nitrates; (*e*) with acetic anhydride at its boiling-point and with benzoyl chloride in presence of alkalis, the corresponding ethereal derivatives; (*f*) with solutions of the caustic alkalis at 160°–190°, with bisulphites (of the alkaline earths) at 150°–170° and with sulphurous acid (7 p.c. solution) at 90°–105°, attended by complete resolution into lignone (soluble derivatives) and cellulose (insoluble).

(2) In their empirical composition, which shows a remarkable uniformity throughout the group. This is illustrated in the appended table of results of analyses and determinations of calorific equivalents (Gottlieb, *J. pr.* [2] 28, 385):—

Wood	Ash	Nitrogen	Carbon	Hydrogen	Calorific equivalents per 1 gram
Oak . .	0·37	—	50·16	6·03	4620
Ash . .	0·57	—	49·18	6·17	4711
Hornbeam .	0·50	—	48·99	6·20	4728
Beech . .	0·57	0·09	49·06	6·11	4777
Birch . .	0·29	0·10	48·88	6·06	4771
Fir . .	0·28	0·05	50·36	5·92	5035
Pine . .	0·37	0·04	50·31	6·20	5085

An investigation by N. Schuppe of the chemical composition of a number of woody tissues (*Pharm. J.* [3] 14, 52) led to the following conclusions: (*a*) that the woods are uniform in their characteristics, being composed of cellulose and 'lignin' in somewhat variable proportions; (*b*) the cellulose when isolated (Schultze's process) having the composition $C_6H_{10}O_5$; and (*c*) 'lignin,' being represented by the empirical formula $C_{19}H_{18}O_8$, which is closely similar to that obtained for the 'lignone' of jute. Further, G. W. Hawes has examined the woods of typical acrogens, *e.g.* lycopodium, equisetum, and aspidium, and finds that they do not differ essentially in composition from exogenous woods (*Am. S.* [3] 7, 585).

(3) In the products of their destructive distillation, which, when carried out under uniform conditions, gives results which are very similar for the several woods. A very elaborate series of such distillations was carried out by M. Senff (*B.* 18, 60), the results being given in percentages of the wood, under (1) total distillate, (2) tar, (3) crude vinegar, (4) anhydrous acid (acetic), (5) charcoal, (6) gases. The following numbers represent the limits of the percentages observed: (1) 40 50, (2) 3–8, (4) 2–6, (5) 20–30, (6) 17–35. The woods of all the more important species, *e.g.* Quercus, Populus, Betula, Fagus, and Pinus, were included in the research, and shown by the results to resemble one another very closely in composition. The products may be more particularly classified as regards the light which they throw upon the molecular grouping of the parent substance into: (*a*) members of the *fatty series*: alcohols, ketones, aldehydes, and acids generally of low molecular weights; (*b*) *furfural* and its homologues; (*c*) a group of *aromatic* bodies, constituting 'creosote,' which may be described as a mixture of guaiacol and creosol, containing besides, methyl-creosol and the dimethyl ethers of pyrogallol and its homologues in varying proportions (Schorlemmer, 'History of Creosote,' *S. C. I.* 4, 152). These divisions, it will be noted, correspond with the ascertained grouping of the complicated lignone molecule (*supra*), of which they afford additional confirmation. It is obvious that the process of destructive distillation must be attended with complications arising from secondary reactions, but the temperatures in the case of wood are sufficiently low to reduce these to a minimum: thus the yields of furfural are at a maximum when the temperature does not exceed 200° (Heill, *B.* 10, 936), and the acetic acid is increased considerably beyond the percentages given by Senff (*supra*), viz. from 2–6 to 5–10, by raising the temperature very gradually through 150°–300° (W. Rudnew, *D. P. J.* 264, 88 & 128), no doubt at the expense of the methylation of the aromatic derivatives. This subject, however, except in regard to the outlines which we have sketched, belongs rather to the general theory of destructive distillation.

The fundamental tissue of the woods we regard, therefore, in all cases as a lignocellulose, of which the lignone portion, while possessing the typical characteristics common to the group, is no doubt variously differentiated with the specialised characteristics of families, and indeed species and individuals.

In addition to the fundamental tissue the woods contain other constituents, which from their nature are seen to be more or less adventitious. They are, in fact, generally removable by the action of solvents (in the case of resins, gum-resins, balsams, &c.), or by simple hydrolysis. In this group we may mention such definitely aromatic derivatives as coniferin and vanillin (M. Singer, *M.* 3, 395), the tinctorial constituents of the dye woods; also the very characteristic and important constituent of most exogenous woods known as 'wood-gum' (Holzgummi), first described by Thomsen (*J. pr.* [2] 19, 146), who found quantities varying from 8 p.c. to 20 p.c. of the woods examined. This body yields on hydrolysis the C_5 sugar, xylose (Tollens, *Unters. a. d. Agr. Chem. Lab. Göttingen An-*

nalen, 254, 325), which by further resolution yields furfural. Whether the wood gum is a product of resolution of the lignone molecule has not yet been disclosed, but it would appear to be probable. A similar remark applies to the aromatic derivatives above mentioned.

In conclusion we must briefly notice a recent contribution to the subject of the 'constitution of lignin' (Lange, *Ztschr. Physiol. Chem.* 14, 217). This consists in a study of the soluble products of resolution of certain woods—beech, oak, and fir—by heating with strong solutions of the alkaline hydrates at 185°. In addition to formic and acetic acids, traces of higher fatty acids, oxalic acid and small quantities of pyrocatechol and protocatechuic acids, there were obtained certain amorphous bodies of brown colour, which the author terms lignic acids. These were resolved by treatment with alcohol into (*a*) soluble, (*b*) insoluble in this menstruum. The empirical composition of these derivatives is subjoined:

		(*a*)		(*b*)	
Lignic acids from	Beech	C. 61·3	H. 5·4	C. 59·0	H. 5·4
	Oak	C. 60·9	H. 5·4	——	
	Fir	C. 61·5	H. 5·0	C. 60·4	H. 5·0

The yield of these bodies is from 12-15 p.c. of the weight of the wood. The insoluble residues from the original alkaline digestion are described as 'celluloses,' but the description is doubtful. These results have an empirical value, but throw little light on the constitution of the wood substauce. They afford additional evidence, however, of the general similarity of woods of various origin.

Digested with alkalis at higher temperatures (200°-250°) than those employed in the researches detailed above, the lignocelluloses are resolved for the most part into oxalic aud carbonic acids. With potassium hydrate—which appears to give the maximum yield—the following proportions of oxalic acid have been obtained, the yield being calculated on the dry woods: pine, 94·7 p.c.; poplar, 93·2 p.c.; oak, 83·4 p.c. (W. Thorn, *D. P. J.* 210, 24). It is evident that the oxalic acid is derived from both lignone and cellulose, which are therefore probably similarly constituted as regards the arrangement of the C. atoms.

The action of the alkalis, however, at the point at which they resolve the lignocellulose is too severe to afford any trustworthy evidence, from the study of the products, as to the constitution of the original substance. The problem can only be solved by first studying those reactions which yield definite substitution or ethereal derivatives; these are chiefly chlorination, conversion into nitrates, acetates, and benzoates, and the reaction with bisulphites (solutions) at high temperatures.

In this article we do not attempt a special description of the woods or their constituents; our endeavour is rather to generalise what is known concerning the wood substance proper, that which resists mechanical solvents altogether, and hydrolytic agents up to a certain degree of intensity. C. F. C.

LIGROÏN. The mixture of homologues of methane obtained by collecting the portion of petroleum that boils below 100°.

LIGULIN. A crimson colouring matter in ripe privet berries (Nicklès, *J. Ph.* [3] 35, 328), sol. water and alcohol, insol. ether. Does not contain nitrogen. Coloured green by alkalis.

LIGUSTRIN. A yellow hygroscopic bitter mass extracted from leaves of the privet (*Ligustrum vulgare*), insol. ether and alcohol, sol. water and dilute alcohol. Conc. H_2SO_4 gives an indigo-blue solution (Polex, *Ar. Ph.* [2] 17, 75).

LIGUSTRON. [c. 100°]. (260°-280°). Occurs in privet bark (Reinsch, *J.* 1847, 787). Needles; v. sol. water, alcohol, and ether. Tastes bitter. Reduces ammoniacal $AgNO_3$.

LIME. Oxide of calcium, CaO; *v.* vol. i. p. 666.

LIME, CHLORIDE OF. A name sometimes given to *bleaching powder*; *v.* BLEACHING POWDER, vol. ii. p. 17.

LIME LEAF OIL. The fragrant oil obtained by distilling the leaves of *Citrus Limetta* with steam contains a citrene (c. 176°), inactive to light, and with refractive index for red rays 1·4611 at 30°, terpinol, methyl ennyl ketoue, and a colophene (F. Watts, *C. J.* 49, 316).

LIMES, OTTO OF. Obtained by rasping and squeezing from the unripe peel of the fruit of *Citrus limetta.* Contains a terpene (176°) and a soft resin, not volatile at 250°. On standing the resin deposits $C_{24}H_{23}O_5$ [102°] (Wright a. Piesse, *C. J.* 32, 548).

LIMETTIC ACID $C_{11}H_8O_6$. Obtained by the action of H_2SO_4 and $K_2Cr_2O_7$ on the oil of lime (from *Citrus Limetta*) and on oil of rosemary (Vohl, *N. Ber. Arch.* 74, 16). White crystalline body; may be sublimed. Has no taste or smell. Sl. sol. water, v. sol. alcohol.—Ag_2A'': powder, sl. sol. water, blackening on exposure to light.

LIMETTIN $C_6H_{14}O_6$. [122°]. A neutral body occurring in oil of limes (Tilden, *C. J. Proc.* 6, 30). Tufts of pale-yellow needles (from alcohol). Not acted upon by AcCl or by pheuylhydrazine. Bromine forms colourless scales of $C_{16}H_{11}Br_3O_6$. Boiling conc. NaOHAq forms NaOAc and crystalline $C_{14}H_{11}(OH)O_4$.

LIMONENE. A terpene occurring in oil of lemon and in many other essential oils; *v.* TERPENES.

LIMONIN $C_{22}H_{26}O_7$. [275°]. (Paterno a. Oglialoro, *G.* 9, 64); [245°] (Hoffmann, *Ar. Ph.* [3] 14, 839). A bitter substance contained in the pips of oranges and lemons (Bernays, *Buchner's Rep.* [3] 21, 306; *A.* 40, 317; Schmidt, *A.* 51, 338). The pips are exhausted with boiling water, alcohol is added, and the mixture is boiled with inverted condenser. After filtering, and distilling off the alcohol, limonin is left, together with a fatty substance which may be removed by CS_2. 1500 g. of pips yield 80 g. of limonin (P. a. G.). Laminæ; sl. sol. water, ether, and NH_3Aq, v. sol. alcohol, HOAc, KOHAq, and baryta-water. The barium salt is not decomposed by CO_2. Conc. H_2SO_4 forms a red liquid, from which the limonin is ppd. by water.

LINALOES OIL. The essence of linaloes, obtained from the wood of *Licari kanali*, the white cedar of Cayenne, is a slightly coloured liquid with an odour like rose and lemon. After distillation over $CaCl_2$ it consists of $C_{10}H_{18}O$ (198°) S.G. $\frac{15}{}$ ·868. $[\alpha]_D = -19$ at 15°. It is sol. alcohol, ether, and glycerin. When distilled with $ZnCl_2$ it yields a terpene, *v.* LICARENE. By prolonged treatment with saturated HClAq and

exposure to light it yields $C_{10}H_{16}2HCl$, an optically inactive liquid with a camphor-like odour, and S.G. $\frac{16}{}$ 1·069. When distilled with lime it yields licarene $C_{10}H_{16}$, (c. 170°), S.G. $\frac{14}{}$ ·835 (Morin, *C. R.* 92, 998; 94, 733).

LININ. C. 62·9 p.c. H. 4·7 p.c. A crystallisable substance obtained by digesting *Linum catharticum* with milk of lime, filtering, ppg. with HCl, and extracting with ether (Pagenstecher, *A.* 40, 322; C. Schröder, *N. Rep. Pharm.* 10, 11). Silky crystals, v. sl. sol. water, v. e. sol. alcohol and ether, m. sol. chloroform and HOAc. The alcoholic solution is intensely bitter.

LINOLEÏC ACID $C_{18}H_{32}O_2$. *Linolic acid.* S.G. $\frac{14}{}$ ·92. Occurs as glyceryl ether in linseed oil, hemp oil, poppy oil, olive oil, nut oil, cotton-seed oil, earth-nut oil, almond oil, oil of sesame, palm oil, cacao butter, and probably in most fixed vegetable oils (Pelouze a. Boudet, *A. Ch.* [2] 59, 43; Laurent, *A. Ch.* [2] 65, 150, 298; Liebig, *A.* 33, 113; Sacc, *A.* 51, 214; Schüler, *A.* 101, 252; Oudemans, *J.* 1858, 304; Hazura a. Grüssner, *M.* 9, 944; 10, 242; Benedikt a. Hazura, *M.* 10, 353). It does not occur in animal oils, so that when the acids obtained by saponifying animal oils are oxidised by $KMnO_4$ no sativic acid will be formed, but di-oxy-stearic acid will be among the products, this being derived from oleïc acid (B. a. H.).

Preparation.—Crude linseed oil or hemp oil is evaporated with aqueous NaOH, the sodium soap is decomposed by H_2SO_4, and the crude acid dissolved in alcohol, neutralised with NH_3, and ppd. by $BaCl_2$. The barium salt is dissolved in ether, HCl is added, the ether decanted from ppd. $BaCl_2$, evaporated, and the liberated acid dried *in vacuo* over H_2SO_4 (Schüler; Bauer a. Hazura, *M.* 7, 216). The acid so obtained is a mixture of oleïc, linoleïc, linolenic, and iso-linolenic acid (Hazura). By treatment with bromine at 0° and reduction of the product $C_{18}H_{32}Br_4O_2$ with zinc and HCl pure linoleïc acid is got.

Properties.—Faintly-yellow limpid oil. Does not solidify at −18°. Insol. water, v. sol. ether, m. sol. alcohol. When distilled under 90 mm. pressure one-third passes over at 290°, and the distillate contains sebacic acid $C_{10}H_{18}O_5$ [130°] and an oily mixture (Hazura a. Grüssner, *M.* 9, 206; *cf.* Norton a. Richardson, *B.* 20, 2735).

Reactions.—1. *Potash*-fusion gives myristic, acetic, and formic acids, with traces of azelaïc acid.—2. $KMnO_4$, *hydrogen peroxide*, and MnO_2 with H_2SO_4, oxidise it to azelaïc acid.—3. $KMnO_4$ in presence of KOHAq converts it into sativic acid, some azelaïc acid also being formed. But alkaline $KMnO_4$ oxidises crude linoleïc acid from linseed oil (100 g.) into sativic acid $C_{18}H_{32}(OH)_4O_2$ [173°] (6·5 g.), linusic acid $C_{18}H_{30}(OH)_6O_2$ [204°] (4·5 g.), isolinusic acid [175°] (15·8 g.), and di-oxy-stearic acid $C_{18}H_{34}(OH)_2O_2$ [137°] (1·2 g.) (Hazura, *M.* 9, 180; *cf.* Dieff a. Reformatsky, *B.* 20, 1211). It appears therefore that crude linoleïc acid consists of linoleïc acid $C_{18}H_{32}O_2$ (which gives sativic acid on oxidation), linolenic acid $C_{18}H_{30}O_2$ (which gives linusic acid), isolinolenic acid (which gives isolinusic), and oleïc acid (which gives di-oxy-stearic acid). The formation of sativic acid in this manner may be made use of as a test for linoleïc acid.—4. *Bromine* at ordinary temperatures forms with crude linoleïc acid solid $C_{18}H_{30}Br_6O_2$ [177°]. Bromine at 0° forms a tetrabromide $C_{18}H_{32}Br_4O_2$ [115°] (Hazura, *M.* 8, 147; Hazura a. Friedrich, *M.* 8, 155, 265). Of these two compounds the former is formed from linolenic, the latter from linoleic acid. Pure linoleïc acid gives only $C_{18}H_{32}Br_4O_2$ [115°].—5. Fuming HIAq and amorphous phosphorus converts it into stearic acid (Peters, *M.* 7, 552).

S a l t s.—The salts are not crystalline. With the exception of the salts of the alkalis they are insol. water. They are sol. ether. With the exception of the Pb, Mn, Na, and NH_4 salts they are insol. alcohol.—BaA'_2 (Peters).

Linolenic acid $C_{18}H_{30}O_2$. Obtained by treating the compound $C_{18}H_{30}Br_6O_2$ [177°] (*v. supra*) dissolved in alcohol with zinc and HCl (Hazura, *M.* 8, 267). Yields on oxidation by alkaline $KMnO_4$ no solid acid except linusic (hexa-oxy-stearic) acid [201°]. Bromine forms only $C_{18}H_{30}Br_6O_2$ [177°]. Linolenic acid 'dries' rapidly when exposed to air, through oxidation. Its salts behave in like manner. The more glyceryl linolenate there is in an oil the more rapidly does it dry. Glyceryl linolenate and isolinolenate also possess drying properties, but glyceryl oleate does not. The product produced by exposing the acids to air is an anhydride, insol. ether, but furnishing soluble acids when heated with alkalis.

Isolinolenic acid $C_{18}H_{30}O_2$. An acid assumed to exist in crude linoleïc acid on account of the formation of isolinusic acid on its oxidation. When crude linoleïc acid is oxidised by $KMnO_4$ in alkaline solution, and the product ppd. by H_2SO_4, there is obtained a mixture of fatty acids whence cold ether extracts di-oxy-stearic acid, sativic acid remaining undissolved. The filtrate from the ppd. acids is neutralised with NaOH, evaporated, again ppd. with H_2SO_4, the pp. extracted with ether, and the residue crystallised from alcohol and then from water, whereby it may be separated into linusic and isolinusic acids.

LINSEED OIL. The oil expressed from the seeds of flax (*Linum usitatissimum*). Like other drying oils when exposed to the air it dries up to a transparent resinous mass. Linseed oil is composed of the glyceryl ethers of oleïc, linoleïc, linolenic, and isolinolenic acids. *v.* LINOLEÏC ACID. Linseed oil dissolves some oxide of lead when heated therewith, being decolourised and rendered more easily drying (boiled oil).

LINUSIC ACID *v.* HEXA-OXY-STEARIC ACID.

Isolinusic acid *v.* HEXA-OXY-STEARIC ACID.

LIQUIDAMBAR. A balsam obtained from a large tree, *Liquidambar styracifolia*, growing in Florida and Mexico. It resembles balsam of Peru, containing cinnamyl cinnamate, styrene, and cinnamic acid (Harrison, *Ar. Ph.* [3] 6, 541; Maisch, *Ar. Ph.* [3] 6, 545).

LIQUIDS, *diffusion*, *dispersion*, *osmose*, *refraction*, *transpiration*, *of*; *v.* PHYSICAL METHODS.

LITHIUM. Li. At. w. 7·01. Mol. w. probably 7·01 (*v.* p. 149). [180°] (Bunsen, *J.* 8, 324). S.G. ·578 to ·589 (Bunsen, *l.c.*). S.H. 27° to 100° = ·9408 (Regnault, *A. Ch.* [3] 63, 11). E.C. at 20° (Hg at 0° = 1) 10·69 (Matthiessen, *P. M.* [4] 12, 199; 13, 81). Characteristic lines in emission spectrum are Liα in the red 6705·2, and a

weaker line in the orange 6102, and a weak line in the blue 4602·7 (Thalén, 1868; *v.* also L. de Boisbaudran, *Spectres Lumineux*, p. 55; Schönn, *W.* 10, 143; Liveing a. Dewar, *T.* 1883. 187). S.V.S. 11·9.

Occurrence.—Salts of Li are very widely distributed, but occur only in small quantities. Several phosphates of Fe and Al contain Li phosphate, especially *triphyline*, which contains c. 7 p.c. Li_2O; many silicates of Al and Fe contain small quantities of Li silicate, especially *lepidolite*, which sometimes contains from 3 to 5 p.c. Li_2O. Tourmalines, borates, &c., often contain traces of lithia. Very many mineral springs contain lithia; according to Kirchoff a. Bunsen lithia is present in almost all mineral waters (*P.* 113, 357). Truchot found lithia in the soil of Limargue in the Auvergne; nearly all the plants growing on this soil take up lithia (*C. R.* 78, 1022). Dieulafait has found traces of Li in sea-water from all parts of the globe, in the water of marshes, in mineral springs, in primary rocks, in gypsum of different formations (*A. Ch.* [5] 17, 377). Lithia is found in many plants, and in all sorts of tobacco; but not in raw sugar, cocoa, coffee, or tea (Focke, *Der Naturforscher*, 1872. 307; Grandeau, *A. Ch.* [3] 67, 216). Lithia has also been found in the milk and blood of cows (Bunsen a. Kirchoff), in different parts of the human organism (Bence Jones, *P. M.* [4] 29, 394), and in normal urine (Schiaparelli a. Peroni, *G.* 10, 390).

While investigating various silicates in 1817, Arfvedson (*S.* 22, 93; 34, 214) found a new alkaline base with a molecular weight smaller than that of soda or potash. Berzelius gave the name *lithia* to the new base (λιθειος) supposing that, unlike soda and potash, it was to be found only in minerals. The new alkali was decomposed by electrolysis in 1818 by Davy, also in 1820 by Brandes (*S.* 8, 120); but the metal was first prepared approximately pure and in considerable quantity by Bunsen and Matthiessen in 1855 by electrolysing fused LiCl (*A.* 94, 107).

Preparation.—The metal is obtained by electrolysing molten LiCl. Bunsen a. Matthiessen (*A.* 94, 107) passed the current from 4-6 Bunsen-cells through LiCl kept molten in a thick-walled porcelain crucible, using a cylindrical rod of retort graphite as positive electrode, and an iron wire the thickness of an ordinary knitting needle as negative electrode. The metal separated on the iron wire in small pellets, which were quickly removed by an iron spoon and placed under petroleum. Some of the metal was always oxidised, occasionally with ignition. To obviate this, Hiller (*Neues Handwörterbuch der Chemie*, 3, 534) passed the negative electrode (iron wire) through the stem of a tobacco-pipe, which he connected with an apparatus supplying pure dry H; he allowed H to pass through the pipe until air was completely expelled, then plunged the bowl open end downwards, with the end of the wire inside, into the molten LiCl, stopped the H, and sent the current through the LiCl; when sufficient Li had collected inside the bowl, the pipe was broken and the metal collected under petroleum. To prevent any action between the Li and the silica in the pipe, the inside of the bowl is covered with a thin layer of graphite; this is done by mixing powdered graphite with dilute LiClAq so as to form a thick paste, spreading this inside the bowl, and drying first in air and then at a moderate red heat. It is advantageous to mix the LiCl before fusion with some NH_4Cl.

There are many methods for preparing LiCl from Li-containing minerals; the methods vary according to the composition of the mineral dealt with, all seek to prepare a solution containing only the alkalis, from which Li may be separated by taking advantage of the comparatively small solubility in water of Li_2CO_3. LiCl is obtained by dissolving Li_2CO_3 in HClAq, evaporating, and drying the crystals which separate. Lepidolite is the usual starting-point; different specimens contain from less than 1 to c. 5 p.c. Li_2O. The mineral is very finely powdered and triturated with water; the finest powder is dried and heated to redness with twice its weight of lime; the cold mass, in which the SiO_2 is combined with lime, is treated with HClAq; CaO is ppd. from the solution by H_2SO_4Aq and evaporation; the filtrate is evaporated to dryness, and the solid is heated until H_2SO_4 is all removed; the residue is dissolved in water, the solution is digested with $CaCO_3$, to remove Al_2O_3, and Ca is removed by ppn. with $(NH_4)_2C_2O_4$; the filtrate is evaporated to dryness, and the residue is strongly heated; the Li_2SO_4 thus obtained is dissolved in water, and the liquid is ppd. by Ba acetate; after filtration the Li acetate is strongly heated and so transformed into Li_2CO_3 (Arfvedson, *S.* 22, 93; 34, 214).

The method recommended by v. Hauer (*J. pr.* 68, 310) consists in strongly heating for 2 hours a mixture of equal parts of very finely powdered lepidolite and gypsum, lixiviating the mass with water, filtering, evaporating until $CaSO_4$ and K_2SO_4 crystallise out, adding to the mother-liquor a mixture of NH_3Aq, NH_4HSAq, and $(NH_4)_2C_2O_4Aq$, whereby all bases are ppd. except the alkalis; after filtering, Li_2CO_3 is ppd. from the warm solution by $(NH_4)_2CO_3$.

The process adopted in Schering's manufactory at Berlin is described by Filsinger (*D. P. J.* 219, 183; 222, 321, 385). Finely ground and sifted lepidolite is mixed with conc. H_2SO_4 in a warm brick trough to the consistence of a thin paste, which is heated with slight stirring till it forms into lumps; the lumps are calcined in a reverberatory furnace, and, while warm, are lixiviated with water; the liquid is mixed with enough K_2SO_4 to convert all Al_2O_3 into alum, which separates on boiling, the residual Al_2O_3 being removed by milk of lime; the salts in the filtrate are converted into chlorides by ppn. with $BaCl_2Aq$, and the liquid is evaporated to dryness; digestion with absolute alcohol dissolves the chlorides of Li and Ca; after distilling off alcohol, Ca is ppd. by $(NH_4)_2C_2O_4Aq$, the liquid is filtered, and a little NH_4HSAq is added to ppt. any Fe, &c., still present; the filtrate is boiled to remove NH_4HS and evaporated to dryness in a silver dish; pure LiCl is thus obtained. The LiCl may be converted into Li_2CO_3 by dissolving in water, adding NH_3Aq and $(NH_4)_2CO_3$, and washing the pp. with alcohol of 60 p.c.

Schrötter's method is said to be one of the best (*J. pr.* 93, 275). Lepidolite is melted, at full red heat, with frequent stirring; the molten mass is ladled out by an iron spoon into water;

when cold the solid is powdered and triturated with water; HClAq S.G. 1·2 is added little by little to the pasty mass; care must be taken that sufficient water is present to prevent the whole mass from solidifying; after standing for 24 hours, with frequent stirring, the semi-liquid substance is heated nearly to boiling, and a little more HClAq S.G. 1·2 is added; the total quantity of HCl used should be c. 2 parts to 1 part lepidolite; after a few hours most of the SiO_2 has separated; a little of the filtered liquid should be so acid that no permanent pp. is formed on addition of a few drops of Na_2CO_3Aq; a little HNO_3Aq is now added to completely oxidise $FeCl_2$ to $FeCl_3$; the liquid is filtered from ppd. SiO_2 (which separates as a powder), and Fe_2O_3, Al_2O_3, CaO, MgO, &c., are ppd. by careful addition of Na_2CO_3Aq to the boiling liquid. The alkaline filtrate is nearly free from all salts except chlorides of the alkalis; it is evaporated until the small quantities of $MgCO_3$, $MnCO_3$, &c., still present separate out, and Li_2CO_3 is ppd. from the filtrate by addition of Na_2CO_3 and evaporation.

Commercial Li_2CO_3 generally contains small quantities of salts of Mg, Ca, K, Na, &c.; it may be purified by one of the foregoing methods. For the other methods of preparing Li_2CO_3 from lepidolite, &c., *v.* Hugo Müller, *J. pr.* 58, 148; Fuchs, *J. pr.* 5, 319; Troost, *A. Ch.* [3] 51, 103; Mallet, *A.* 101, 389; Lunglmayr, *D. P. J.* 171, 293; Allen, *J. pr.* 87, 480; Reichardt, *D. P. J.* 172, 447; L. Smith, *A.* 159, 82; Stolba, *D. P. J.* 198, 225; L. de Boisbaudran, *Bl.* [2] 17, 551. A detailed criticism of various methods will be found in *D. P. J.* 219, 183; 222, 271, 385.

Properties.—A silver-white metal; very soft, but harder than K or Na; when freshly cut, the surface appears yellowish; when melted and at once pressed between glass plates, it forms a silver-like mirror. Li makes a grey streak on paper. It may be drawn into wire, but shows very little tenacity. Li is the lightest known solid; S.G. c. ·59; it swims on rock oil. Melts at 180°. Is not acted on by dry O at its M.P.; heated in air to c. 200° it burns with a very brilliant white flame. May be vapourised in H at full red heat. Li decomposes cold water without itself melting; it combines rapidly with Cl, Br, I, S, O; it burns when heated in dry CO_2. Li reacts with most acids to form salts; conc. HNO_3Aq oxidises it with great rapidity, the metal usually melts, and is sometimes ignited. Li dissolves in liquid NH_3, and on evaporation of the NH_3 it is left unchanged (Seeley, *C. N.* 23, 169).

The atomic weight of Li has been determined: (1) By converting LiCl into AgCl (Arfvedson, *S.* 22, 93; Mallet, *Am. S.* [2] 22, 349; Troost, *A. Ch.* [3] 51, 108; Stas, *Nouv. R.* 268); (2) by determining O in Li_2O (Berzelius, *P.* 17, 379); (3) by ppg. Li_2SO_4 by $BaCl_2$ (Berzelius, *P.* 17, 379; Hermann, *P.* 15, 482; Hagen, *P.* 48, 361; Diehl, *A.* 121, 97); (4) by determining CO_2 in Li_2CO_3 (Hermann, *P.* 15, 480; Troost, *A. Ch.* [3] 51, 108; Diehl, *A.* 121, 95); (5) by converting Li_2CO_3 into Li_2SO_4 (Troost, *A. Ch.* [3] 51, 108); (6) by converting LiCl into $LiNO_3$ (Stas, *Nouv. R.* 274); (7) by determining S.H. of Li (Regnault, *A. Ch.* [3] 63, 11).

Ramsay (*C. J.* 55, 521) has endeavoured to determine the mol. w. of Li by measuring the lowering of vapour pressure of Hg produced by dissolving Li in Hg: the results make it probable that the mol. w. of Li is the same as the at. w. This result is based on the assumption that Van't Hoff's law holds good, viz., that equal volumes of dilute solutions contain equal numbers of molecules of the dissolved substances; it also presupposes that the molecular weight of liquid Hg is the same as the atomic weight.

As the V.D. of no Li compound has yet been determined, the valency of the atom Li in gaseous molecules is not certainly known, but from the close analogy between Li and the other alkali metals there can be little doubt that the atom of Li is monovalent in gaseous molecules.

Li is a strongly positive metal; it belongs to the group of alkali metals, none of which shows any tendency to enter into the negative radicle of salts. Li shows closer resemblances to the alkaline earths than are exhibited by any other metal of the alkalis; LiOH, Li_2CO_3, and Li_3PO_4 are much less soluble in water than the corresponding compounds of Na, K, Rb, and Cs; Li does not form an alum. The position and analogies of Li are discussed in the article ALKALIS, METALS OF THE, vol. i. p. 114.

Reactions and Combinations.—1. Li decomposes cold *water* rapidly without itself melting. Thomsen (*Th.* 3, 227) gives the thermal data $[Li, H^2O, Aq] = 48,970$ (to form LiOHAq + H).—2. Very rapidly oxidised by *conc. nitric acid.*—3. Slowly acted on by *conc. sulphuric acid*; rapidly dissolved by dilute H_2SO_4Aq, also by *dilute hydrochloric acid* (Matthiessen, *A.* 94, 10). 4. Burns when heated in dry *carbon dioxide* or *sulphuretted hydrogen.*—5. At temperatures lower than its melting-point Li acts on *silica*, *alkaline silicates*, *iron*, *gold*, *silver*, and *platinum.*—6. Combines readily with *sulphur*, *phosphorus*, and the *halogens*.

Detection.—Li compounds give a red colour to a non-luminous flame. Examination by the spectroscope will detect ·000009 mgrms. Li present as LiCl (Bunsen). To detect Li in silicates, the powdered mineral is treated with HFAq, the liquid is poured off, and the residue is evaporated with addition of a little H_2SO_4; the residue is extracted with absolute alcohol, and the liquid is evaporated to dryness; the residue is again treated with absolute alcohol, and this solution is again evaporated, and the residue ($\frac{1}{30}$ mgm. is sufficient) is examined in the spectroscope; if the mineral is non-siliceous, the treatment with HFAq may be omitted. Li is estimated in the form of Li_2SO_4.

Lithium, antimonate of. $LiSbO_3$. By adding LiCl to $KSbO_3$Aq (*cf.* ANTIMONATES, vol. i. p. 285).

Lithium, borate of. $Li_2B_4O_7$, and hydrates with $5H_2O$, $6H_2O$, and $10H_2O$; by adding Li_2CO_3 to boric acid solution (Arfvedson, *A. Ch.* [2] 10, 82; Filsinger, *Ar. Ph.* [3] 8, 198; *cf.* BORATES, vol. i. p. 529).

Lithium, borofluoride of. By double decomposition between $Ba(BF_4)_2$Aq and Li_2SO_4Aq and evaporation at 40°, large deliquescent prisms are obtained, sl. sol. water; these crystals are probably $LiBF_4$, but they have not been accurately examined (Berzelius).

Lithium, bromide of. LiBr. H.F. [Li,Br,Aq] = 91,310 (*Th.* 3, 227); [LiBr,Aq] = 11,350 (Bodisko, *J. R.* 1889. [1] 7). S.G. 3·102 at 17° (Clarke, *Am. S.* [3] 13, 293). A white crystalline, very deliquescent, mass. Obtained by dissolving Li_2CO_3 in HBrAq and evaporating (Troost, *A. Ch.* [3] 51, 103); or by ppg. excess of $CaBr_2Aq$ by K_2CO_3, after 24 hours adding enough Li_2CO_3 to ppt. all the Ca, filtering, and evaporating (Klein, *A.* 128, 239). S. 143 at 0°, 196 at 34°, 222 at 59°, 244 at 82°, 270 at 103° (Kremers, *P.* 103, 65).

Lithium, chloride of. LiCl. S.G. 2·074 at 3·9° (Schröder, *P.* 106, 226), 1·998 at 0°, 1·515 at M.P. (Quincke, *A.* 138, 141); S.G. fused 1·575 (Wernicke, *P.* 138, 141). H.F. [Li,Cl] = 93,810; [Li,Cl,Aq] = 102,250 (*Th.* 3, 227). S.H. ·282 (Regnault).

Preparation.—1. By dissolving Li_2CO_3 in HClAq and evaporating.—2. By decomposing Li_2SO_4Aq by $BaCl_2Aq$, filtering from $BaSO_4$, and evaporating.

Properties.—Crystallises from aqueous solution in regular octahedra; very deliquescent, more so than $CaCl_2$; tastes like NaCl; melts at dark-red heat to a clear liquid, which gives off some Cl and becomes alkaline when heated for a long time in the air; the same change occurs to a slight extent when LiClAq is evaporated. E. sol. alcohol, also in a mixture of ether and alcohol in which KCl and NaCl are nearly insoluble. Volatilised at white heat. S. 63·7 at 0°, 80·7 at 20°, 104·2 at 65°, 115 at 80°, 129 at 96°, 139 at 140°, 145 at 160°. Gerlach (*Fr.* 8, 279) gives the following:—

S.G. LiClAq	P.c. LiCl	S.G. LiClAq	P.c. LiCl
1·006	1	1·148	25
1·030	5	1·182	30
1·058	10	1·219	35
1·086	15	1·256	40
1·117	20		

B.P. of saturated LiClAq = 171° (Kremers, *P.* 103, 65).

Reactions.—1. *Heated in air* for some time is partially decomposed with evolution of Cl; residue is alkaline (Schulze, *J. pr.* [2] 21, 407). Evaporation of LiClAq is accompanied by slight decomposition.—2. Completely decomposed by *heating in steam*, with evolution of HCl; decomposition is rapid in presence of silica, but is prevented by admixture of NH_4Cl (Kunheim, *J.* 1861. 149).

Combinations.—1. With *water* to form two hydrates. (1) $LiCl.2H_2O$; obtained as quadratic crystals by evaporating LiClAq under 10°. Dried between paper, the crystals become opaque and powdery; when warmed, melts in water of crystallisation, then solidifies, and then the dry LiCl melts again at red heat; (2) by evaporating a solution of LiCl in aqueous alcohol, Rammelsberg obtained the monohydrate $LiCl.H_2O$ (*P.* 66, 79).—2. With *alcohol* to form $LiCl.2C_2H_6O$, and with *methylic alcohol* to form $2LiCl.3CH_4O$; obtained by evaporating solution of LiCl in the respective alcohols (Simon, *J. pr.* [2] 20, 371).—3. With *platinic chloride*, to form $Li_2PtCl_6.6H_2O$; orange-red salt, sol. in water, alcohol, and ether-alcohol.

Lithium, chromate and dichromate of; *v.* vol. ii. pp. 155, 157.

Lithium, fluoride of. LiF. Small crystalline tablets; by dissolving excess of Li_2CO_3 in HFAq, filtering, and evaporating. Slightly sol. in water; melts at red heat (Berzelius, *A.* 1, 17). S.G. 2·295 at 21·5° (Clarke, *Am. S.* [3] 13, 292). By solution of LiF in HFAq and evaporation, crystals of LiF.HF are obtained; when heated LiF and HF are formed. Flückiger (*A.* 87, 261) describes the double salt $2LiF,SbF_3$. LiF combines with SiF_4 to form the *silicofluoride* Li_2SiF_6 (*v.* LITHIUM, SILICOFLUORIDE OF, p. 151).

Lithium, haloid compounds of. Lithium combines directly with the halogens; the haloid compounds, LiX, are generally prepared by dissolving Li_2CO_3 in the respective acids and evaporating. As the V.D. of none of the compounds has been determined, their molecular weights are not known with certainty; but from the close similarities between compounds of Li, K, Na, and Cs there can be little doubt that the formula LiX (X = F, Cl, Br, I) expresses the composition of the molecules of the haloid compounds of Li.

Lithium, hydrosulphide of. ?LiSH. Obtained by reducing Li_2SO_4 by C, and passing H_2S into a solution of the product. Only known in solution (Berzelius, *P.* 6, 439). Thomsen gives H.F. [Li, S, H, Aq] = 66,120 (*Th.* 3, 227).

Lithium, hydroxide of. LiOH. Obtained by boiling Li_2CO_3 with CaOAq in a silver dish (Pt cannot be used as it is acted on by LiOH), filtering, evaporating, and heating to 100°; better by ppg. Li_2SO_4Aq by an equivalent quantity of BaOAq, filtering, evaporating, and heating to 100°. Also obtained by dissolving Li_2O (*q. v.*) in H_2O and evaporating. Thomsen (*Th.* 3, 227) gives H.F. [Li, O, H, Aq] = 117,440; and heats of neutralisation [2LiOHAq, H^2SO^4Aq] = 31,290; [2LiOHAq, H^2Cl^2Aq] = 27,700. Beketoff (*Bl.* 41, 312) gives [Li^2O, Aq] = 13,000 (to form LiOHAq).

A white crystalline mass which melts when heated, without decomposition; sol. in water, but less so than KOH or NaOH; insol. in ether-alcohol. Gmelin obtained small crystals of LiOH by evaporating a solution *in vacuo*; according to Muretow (*B.* 5, 331) the crystals are a *hydrate of lithium hydroxide*, $LiOH.H_2O$ (*cf.* Dittmar, *S. C. I.* 7, 730).

Lithium, iodide of. LiI. Obtained by saturating HIAq, containing a little H_3PO_4, with Li_2CO_3, warming the ppd. Li_3PO_4 with BaI_2 and a trace of H_2SO_4, filtering, adding enough Li_2CO_3 to decompose excess of BaI_2 present, filtering again, evaporating, crystallising, and drying by pressure between filter paper (Liebig, *A.* 121, 222). Liebig (*l.c.*) also recommends to neutralise half of an HI solution containing a little H_3PO_4 by BaO or CaO, to add the other half of the acid, neutralise by Li_2CO_3, filter from Ba or Ca phosphate and evaporate. The crystals are generally yellowish from a little separated I; this is removed by quickly pressing between filter paper. LiI forms small, colourless, deliquescent crystals. S.G. 3·485 at 23° (Clarke, *Am. S.* [3] 13, 293). H.F. [Li, I, Aq] = 76,100 (*Th.* 3, 227). S. 151 at 0°, 164 at 19°, 179 at 40°, 200 at 59°, 263 at 75°, 435 at 80°, 476 at 99°, 588 at 120° (Kremers, *P.* 103, 65). By evaporating a solution of Li_2CO_3 in HIAq over H_2SO_4, Ram-

melsberg obtained the *hydrate* $LiI.3H_2O$ (*P.* 66, 79).

Lithium, oxide of. Li_2O. Obtained by burning small quantities of Li, in a small iron vessel, in dry O at 200°, cooling in O, and heating in the air to decompose Li peroxide (Troost, *A. Ch.* [3] 51, 103). Also prepared by heating Li_2CO_3 with C in a Pt crucible; and by heating $LiNO_3$ to redness in a Ag dish, best mixed with Cu turnings (H. Müller, *J. pr.* 58, 148).

A white crystalline solid; S.G. 2·102 at 15° (Brauner a. Watts, *P. M.* [5] 11, 60). Not decomposed by heating with C or Fe. Does not act on Pt at high temperatures; corrosion of the Pt vessel in the preparation of Li_2O indicates the presence of Rb_2O or Cs_2O. Reacts with Cl, S, and P. Heated in O, Li_2O is superficially changed to peroxide. Thomsen gives $[Li_2O,Aq] = 166,520$ (*Th.* 3, 227); and Beketoff (*Bl.* 41, 312) gives $[Li_2O,Aq] = 13,000$; hence $[Li_2,O] = 153,520$.

Lithium peroxide is said to be formed by heating Li_2O, or Li_2CO_3, for some time in air or O, but to be decomposed at a little above the temperature of formation.

Lithium, phosphide of. According to Troost (*A. Ch.* [3] 51, 103) Li and P combine, when heated together, to form a brown substance which is decomposed by water with evolution of inflammable P hydride.

Lithium, silicofluoride of. $Li_2SiF_6 2H_2O$. Transparent monoclinic crystals; obtained by adding H_2SiF_6Aq to Li acetate or carbonate, evaporating, treating the residue with water, filtering, and crystallising (Stolba, *J. pr.* 91, 456). S. 52·6 at ordinary temperature; sol. alcohol, insol. ether. S.G. 2·33. Dehydrated at 100°; melts at a higher temperature with evolution of SiF_4.

Lithium, salts of. *Compounds produced by replacing H of acids by Li.* The Li salts belong to one series Li_2X where $X = 2Cl, 2NO_3, SO_4, CO_3, \frac{2}{3}PO_4$, &c.; they are generally obtained by dissolving Li_2CO_3 in the different acids; some are prepared by double decomposition from LiCl or Li_2SO_4. Most of the salts of Li are sol. in water, but Li_3PO_4 and Li_2CO_3 are considerably less sol. than the corresponding salts of the other alkali metals; LiOH is also less soluble than the other alkalis (*cf.* ALKALIS, METALS OF THE, vol. i. p. 114). Few, if any, basic salts of Li are known. The chief Li salts are the following (*v.* CARBONATES, NITRATES, SULPHATES, &c.): *Antimonate, arsenate, borates, bromate, carbonate, chlorate, chromates, dithionate, hypochlorite, hypophosphite, iodate, nitrate* and *-ite, perchlorate, periodate, phosphates, selenate* and *-ites, silicates, sulphates* and *-ite, tellurate* and *-ite, thio-arsenate.*

Lithium, sulphide of. Li_2S. Li and S combine when heated together; the solution in water is yellow from presence of polysulphides. Li_2S is obtained by reducing Li_2SO_4 by an equivalent quantity of C at full red heat; excess of C makes the product pyrophoric (Berzelius, *P.* 6, 439). Naudin a. Montholon (*C. R.* 83, 58) say that Li_2S may be prepared by the long-continued passage of H_2S through Li_2CO_3 suspended in water. Li_2S is easily sol. water and alcohol. $[Li_2, S, Aq] = 115,260$ (*Th.* 3, 227).

Lithium polysulphides are said to be obtained by melting LiOH with S (Vauquelin, *A. Ch.* 7, 284); they closely resemble the polysulphides of the other alkali metals.

Lithium, sulphydrate of; *v.* LITHIUM, HYDROSULPHIDE OF, p. 150. M. M. P. M.

LITHO-BILIC ACID $C_{30}H_{54}O_6$. [199°] Occurs, together with lithofellic acid, in Oriental bezoar, and is prepared by decomposing the barium salt with hydrochloric acid and recrystallisation from alcohol. Long pale-yellow needles; insol. water, v. sol. alcohol, m. sol. ether. Its alcoholic solution is dextrorotatory. It resembles lithofellic and the biliary acids in its behaviour with Pettenkofer's reaction and its distillation products (Roster, *G.* 9, 462; Grattarola, *J.* 1880, 831).—$BaA'_2 6aq$. Ppd. by adding $BaCl_2$ to a warm aqueous solution of crude sodium lithofellate; usually a yellowish semi-transparent resin; was obtained on one occasion in minute monoclinic crystals.

LITHOFELLIC ACID $C_{20}H_{36}O_4$. [205°]. S. (alcohol) 3·4 at 20°; 15 at 78°. S. (ether) ·225 at 20° (Göbel). $[\alpha]_D = 13·8$ at 9·5° (independent of concentration). Forms the chief constituent of some kinds of Oriental bezoars (Göbel, *A.* 39, 237; Ettling, *A.* 39, 242; Wöhler, *A.* 41, 150; Heumann, *A.* 41, 303; Malaguti a. Sarzeau, *C. R.* 15, 518). The finely-powdered bezoars are extracted with boiling alcohol, and the solution evaporated. The crude acid then deposited is converted into sodium salt, and then into the Ba salt. On recrystallising, barium lithobilate remains undissolved, and the solution of barium lithofellate is then decomposed by HCl (Roster, *G.* 9, 364). Minute hexagonal crystals (containing aq) (Hoppe-Seyler, *Virchow's Arch.* 25, 528; Grattarola, *J.* 1880, 831). Insol. water. Dextrorotatory. Its salts are also dextrorotatory, somewhat bitter in taste. On distillation it gives off aromatic fumes.

Reactions.—1. When heated with sugar and H_2SO_4 it gives a crimson colour (Pettenkofer's reaction) (Strecker, *A.* 67, 53).—2. Boiling HClAq resinifies it.—3. Hot *nitric acid* gives a yellow acid, $C_{20}H_{28}(NO_2)_4O_3$, which may be crystallised from HOAc.

Salts.—The sodium salt forms a pale-yellow gummy mass, exceedingly sol. water and alcohol. $[\alpha]_D = +18·16$ at 14·5°.—$BaA'_2 10aq$: large prisms, sol. boiling water and alcohol. $[\alpha]_D = +19·7$ at 15°.—AgA': flocculent pp.

LITHOSPERMUM ERYTHRORHIZON (M. Kuhara, *C. J.* 35, 22). The Japanese prepare a dye called Shikon or Tokio purple from the root of this plant. The colouring matter may be extracted by exhausting successively with water and alcohol. Lead subacetate is added to the latter extract, and the purple pp. washed and decomposed by aqueous H_2S. The dye is extracted from the dried pp. by means of alcohol. It is resinous with green lustre. Its composition may be represented by $C_{20}H_{30}O_{10}$. Its alcoholic solution is purple, and shows an absorption spectrum similar to that of alkanet. Alkalis turn the solution blue; acids turn it red. Baryta gives a purple pp. $C_{20}H_{28}BaO_{10}$. The dye is readily oxidised to a brown scaly substance, $C_{20}H_{30}O_{15}$. Bromine forms a product of substitution, $C_{20}H_{25}Br_5O_{10}$. With PCl_5 it forms a black resinous body, $C_{20}H_{28}Cl_2O_{10}$.

LITHURIC ACID $C_{15}H_{19}NO_9$ (?). [205°]. Occurs as magnesium salt in some urinary

calculi of oxen (Roster, *A.* 165, 104). Slender, silky needles. M. sol. boiling water and alcohol.—MgA'_2: minute monoclinic prisms; m. sol. boiling water, v. sl. sol. cold water, insoluble in alcohol.

LITMUS. Obtained chiefly from various species of *Roccella*, *Variolaria*, and *Lecanora*, the same lichens that yield archil. The blue colouring matter appears to be developed by fermentation after the mass has been treated with alkaline carbonate (Gélis, *Rev. Scient.* 6, 50; *J. Ph.* 24, 277).

When 2 pts. of *Roccella tinctoria* and 1 pt. of K_2CO_3 are repeatedly moistened with a solution of ammonium carbonate, the mass acquires a fine blue colour in forty days. The mass is then mixed with chalk and gypsum.

According to Kane (*T.* 1840, 298), litmus contains azolitmin, spaniolitmin, erythroleïn, and erythrolitmin. Azolitmin is a reddish-brown amorphous powder, which dissolves in ammonia with blue colour, and forms blue and violet lakes. Spaniolitmin was not isolated by Kane, but appeared to be light red. According to Kane, erythroleïn is a red viscid mass, forming a purple solution in ammonia, while erythrolitmin forms deep-red crystalline grains, forming a purple solution in ammonia. The method employed by Kane to isolate these substances is as follows: Litmus is exhausted with boiling water, the residue is acidified by HCl, again washed, and then boiled with alcohol. The alcoholic solution is evaporated to dryness, and the residue extracted with ether, which leaves erythrolitmin undissolved. The ether leaves erythroleïn on evaporation. The reddish-brown powder left after boiling with alcohol is impure azolitmin.

De Luynes (*C. R.* 59, 49), by heating orceïn with aqueous NH_3 and Na_2CO_3 at 70°, obtained a blue substance, which he regarded as the blue colouring matter of litmus.

According to Wartha (*B.* 9, 217), cold alcohol extracts from litmus a red substance, which is not affected by acids, and the residue yields to water the blue colouring matter. If the aqueous extract be evaporated, and the residue treated with absolute alcohol and some HOAc, a scarlet dye, turned purple by NH_3, is extracted, while the residue is the pure litmus-blue, left as a brown powder.

A blue ethereal extract of litmus shows an absorption-band at D; a red ethereal extract shows an absorption-band extending to E (Vogel).

An aqueous solution of litmus, kept in a closed vessel, gradually becomes decolourised. This is due to the action of a micrococcus, which reduces the colouring matter to a leuco-derivative, which is readily re-oxidised by air (Dubois, *Bl.* [2] 49, 963; *cf.* Bellamy, *J. Ph.* [5] 18, 433).

According to Förster (*Fr.* 28, 428), litmus is best purified by exhausting with alcohol in the cold, digesting with water, filtering, and evaporating. The residue is dissolved in water, filtered, and ppd. by a mixture of alcohol and HOAc. The pp. is washed with alcohol, and the solution, ppn., and washing repeated as long as any reddish-violet substance is removed thereby. The pp. is then dried, dissolved in water, the solution filtered and ppd. by feebly ammoniacal alcohol. The pp. is finally washed with alcohol and dried.

LIVER OF SULPHUR. A name formerly applied to a mixture of the polysulphides of potassium, obtained by heating together K_2CO_3 and S in a closed vessel (*v.* POTASSIUM, SULPHIDES OF).

LIXIVIATION. The application of water to solid mixtures, for the purpose of extracting the soluble parts.

LOBARIC ACID $C_{17}H_{16}O_5$. A resinoid acid obtained by extracting the lichen *Lobaria adusta* with ether (Knop, *C. C.* 1872, 172). Warty masses, made up of thin plates. Insol. water and baryta-water. In aqueous or alcoholic NH_3 it forms colourless solutions, which turn rose-red on exposure to air. KOHAq forms a yellow solution, turning brown on evaporation.

LOBELINE. An alkaloid existing in *Lobelia inflata* (Bastick a. Procter, *Ph.* 10, 270, 456). Obtained by extracting the leaves with dilute acetic acid, and ppg. with magnesia. Thick, oily mass, decomposed by heat. V. sol. water, alcohol, and ether. Narcotic. Forms crystalline salts with HCl, HNO_3, H_2SO_4, and oxalic acid. Its solutions are ppd. by tannin.

Lobelia nicotianæfolia contains also a second alkaloid, dissolved by $CHCl_3$ from solutions made alkaline by NH_3. It resembles lobeline in physiological action, and, like it, exhibits no characteristic colour reactions (Dragendorff a. von Rosen, *C. C.* 1886, 873).

LOGANIN $C_{25}H_{34}O_{14}$. [215°]. A glucoside found by Dunstan and Short (*Ph.* [3] 14, 1025) in the pulp in which the seeds of *Strychnos nux vomica* are embedded. Extracted by alcohol-chloroform, and recrystallised from alcohol. Prisms. V. sol. water and alcohol, less sol. ether, $CHCl_3$, and benzene. The aqueous solution is not ppd. by reagents for alkaloids, nor by lead acetate or $AgNO_3$. Not coloured by $FeCl_3$, HNO_3, or H_2SO_4 and $K_2Cr_2O_7$. Conc. H_2SO_4 gives a red colour on warming, changing to purple. Loganin does not reduce Fehling's solution. Boiling dilute H_2SO_4 splits it up into glucose and l o g a n e t i n. Loganetin is sol. water and alcohol, less sol. ether and $CHCl_3$. It also gives a purple with H_2SO_4.

LOKAONIC ACID $C_{42}H_{48}O_{27}$ (K.) or $C_{36}H_{48}O_{21}$ (C. a. G.) *Lokaïn.* The colouring matter of Chinese green, obtained from the berries of the buckthorn (*Rhamnus utilis*), contains lokaonic acid (Kayser, *B.* 18, 3417; *cf.* Cloëz a. Guignet, *J.* 1872, 1068). Lokao, the commercial article, consists of calcium and aluminium lokaonates. It is decomposed by boiling with ammonium carbonate, and on adding alcohol to the filtrate ammonium lokaonate is ppd. This is decomposed by oxalic acid. Lokaonic acid is a deep-blue or bluish-black mass, which exhibits metallic lustre when rubbed. It is insol. water, alcohol, ether, and chloroform. In aqueous alkalis it forms a blue solution, changed to red by mild reducing agents, such as H_2S. Boiling dilute H_2SO_4 splits it up into a sugar, lokaose, and lokanic acid.

S a l t s.—NH_4HA'' (at 100°): deep-blue pp., with bronze lustre when dry; sol. water, insol. alcohol.—$(NH_4)_2A''$: similar to the preceding. Begins to lose NH_3 at 40°.—K_2A'': dark-blue

powder.—BaA″ (at 100°): deep-blue powder, insol. water.—PbA″ (at 100): blue-black pp.

Lokanic acid $C_{36}H_{36}O_{21}$ (K.) or $C_{18}H_{16}O_{10}$ (C. a. G.). *Lokaëtin.* Obtained by boiling lokaonic acid with dilute H_2SO_4, dissolving the pp. in NH_3Aq, and ppg. with oxalic acid. Violet-black crystalline powder, which exhibits a bronze lustre when rubbed. Insol. water, alcohol, ether, and chloroform. Alkalis form a violet solution. At 120° it becomes $C_{36}H_{34}O_{20}$. Conc. H_2SO_4 dissolves it in the cold, and on adding water a reddish-brown powder, $C_{36}H_{26}O_{16}$, is ppd. This dissolves in NH_3Aq, and the solution gives, with $BaCl_2$, a reddish-brown pp., $BaC_{36}H_{24}O_{16}$. Lokanic acid is decomposed by boiling conc. KOHAq into phloroglucin and delokanic acid. Hot dilute nitric acid forms nitro-phloroglucin.

Salts.—NH_4HA'' (dried at 100°): bluish-black powder, sol. water, insol. alcohol. Dyes cotton, silk, and wool deep violet without mordant. Mixed with $Na_2S_2O_3$ it dyes cotton a permanent sky-blue (C. a. G.).—BaA″ (dried at 100°): blue-black powder, insol. water and alcohol.—PbA″: deep-blue powder, insol. water and alcohol.

Delokanic acid $C_{15}H_{9}O_{6}$. Formed as above. Brown powder, insol. water, sol. alcohol. Its solution in alkalis is cherry-red. It reduces Fehling's solution with difficulty in the cold.

Lokaose $C_6H_{12}O_6$. A sugar formed by hydrolysis of lokaonic acid. It reduces chloride of gold and Fehling's solution in the cold. It reduces half as much CuO as glucose.

LOPHINE *v.* vol. i. p. 474.

LOTURINE. [234°]. Occurs to the extent of ·24 p.c., together with ·02 p.c. of colloturine and ·06 p.c. of loturidine, in lotur bark from *Symplocos racemosa*, growing in India (Hesse, *B.* 11, 1542). The alkaloids are extracted from the bark by hot alcohol, and are converted into acetates. Loturine and colloturine are ppd. from the neutral solution by potassium sulphocyanide, leaving loturidine in solution. The crystalline pp. is decomposed by Na_2CO_3, and the alkaloids are extracted with ether and recrystallised from alcohol. The efflorescent crystals of loturine are separated mechanically from the non-efflorescent crystals of colloturine.

Properties.—Long prisms. May be sublimed. Insol. water, sol. alcohol, acetone, ether, and chloroform. Its acid solutions exhibit violet fluorescence. It gives no colour with $FeCl_3$, conc. H_2SO_4, HNO_3, or bleaching powder followed by ammonia. Its hydrochloride forms white prisms. The hydrochloride, nitrate, and chromate crystallise in needles. The platinochloride is a yellow pp.

Colloturine. Long prisms; may be sublimed. Its solutions in aqueous HCl and H_2SO_4 fluoresce violet. Its aurochloride is a yellow amorphous pp.

Loturidine. Extracted from the filtrate from the ppd. sulphocyanides of loturine and colloturine by adding NH_3 and shaking with ether. Yellowish-brown amorphous mass. Forms amorphous salts. Its solutions in dilute mineral acids fluoresce violet.

LOXOPTERYGINE $C_{26}H_{34}N_2O_2$. [81°]. Occurs, together with another alkaloid and tannin, in red Quebracho bark from *Loxopterygium Lorentzii* (Hesse, *A.* 211, 274). Extracted by alcohol; the alcoholic solution being evaporated, the residue treated with aqueous NaOH and the alkaloids extracted with ether. The acetic acid solution of the alkaloids is mixed with potassium sulphocyanide, which ppts. one alkaloid and leaves the loxopterygine in solution, whence it is ppd. by ammonia. White amorphous mass, sl. sol. cold water, v. sol. alcohol, ether, chloroform, and benzene. Its solutions exhibit alkaline reaction. Tastes intensely bitter. Conc. H_2SO_4 and a little $K_2Cr_2O_7$ gives a violet colour.

LUPANINE $C_{15}H_{24}N_2O$. Occurs in the seeds of the blue lupine (*Lupinus angustifolius*), from which it is extracted by alcohol containing HCl (Hagen, *A.* 230, 370). Viscid yellow liquid with green fluorescence, characteristic smell, and very bitter taste. Sl. sol. water, but separates on warming; m. sol. cold alcohol, v. sol. ether and chloroform. Not volatile with steam. Strongly alkaline, fuming with HCl.

Salts.—B′HCl 2aq. [127°]. M. sol. water and alcohol, insol. ether. The base is set free from this salt by KOH but not by NH_3.—B HI $1\frac{3}{4}$aq: yellow crystals (from hot water), sol. CS_2, insol. alcohol and ether.—B′HCyS $\frac{1}{2}$aq: pale yellow crystals; v. sol. hot alcohol, sl. sol. water, insol. ether.—$B'H_2PtCl_6$ $3\frac{1}{2}$aq.—$B'HAuCl_4$: splendid yellow needles, sl. sol. ether, insol. water and alcohol.

Methylo-iodide B′MeI. [215°]. Crystals, sl. sol. water, insol. alcohol and ether. The methylo-hydroxide is formed by treatment with Ag_2O but not with KOH.

Methylo-chloride B′MeCl 2aq. [128°]. Extremely deliquescent crystals, insol. ether.—$B'MeHPtCl_6$aq: red crystals, insol. ether, sl. sol. alcohol. — $B'MeAuCl_4\frac{1}{2}AuCl_3$: lemon-yellow needles.

LUPETIDINE *v.* Di-methyl-pyridine hexahydride.

LUPINIDINE *v.* Lupinine.

LUPININ $C_{29}H_{32}O_{16}$. *Lupiniin.* A glucoside in the buds of the yellow lupine (*Lupinus luteus*). Extracted by 50 p.c. alcohol (Schulze a. Barbieri, *B.* 11, 2200). Slender yellowish-white needles (containing 7aq). Sl. sol. water and alcohol. Alkalis form a deep yellow solution. Its ammoniacal solution gives a lemon-yellow pp. with lead acetate. Boiling with water or dilute acids splits it up into glucose and lupigenin.

Lupigenin $C_{17}H_{12}O_6$. Formed as above. Minute yellow needles, insol. water, sl. sol. alcohol. Forms a deep-yellow solution in aqueous NH_3.—NH_4A'aq: lemon-yellow powder.

LUPININE $C_{21}H_{40}N_2O_2$. [68°]. (256°). An alkaloid in the seeds of the yellow lupine (*Lupinus luteus*), and extracted by alcohol containing HCl. The extract is evaporated to a syrup, treated with KOH, and shaken with light petroleum. The petroleum is shaken with aqueous HCl, the solution treated with KOH, and the alkaloid extracted by ether, from which it is recrystallised (Baumert, *L. V.* 27, 15; *cf.* Beyer, *L. V.* 14, 161; *v. also* lupinidine, *infra*).

Properties.—Trimetric crystals; may be distilled in a current of hydrogen. Tastes bitter. V. sol. cold water and alcohol, less sol. hot water; v. sol. benzene, chloroform, and CS_2. Strong base; liberating NH_3 from its salts and fuming with HCl. In its solutions tannin gives a flocculent pp.; phospho-molybdic and phos-

photungstic acids give yellow pps.; iodine gives a dirty brownish-red pp.

Reactions.—1. HI gives $C_{21}H_{50}N_2O_2I_2$.—2. With fuming HCl at 200° it forms anhydro-lupinine $C_{21}H_{38}N_2O$ and finally di-anhydro-lupinine $C_{21}H_{36}N_2$ (Baumert, *A.* 214, 366).—3. P_2O_5 heated with the hydrochloride at 180° forms oxylupinine, which with platinic chloride forms $C_{21}H_{40}N_2O_3H_2PtCl_6$, crystallising in yellow plates. If the mother-liquor be heated with P_2O_5 to a higher temperature anhydro-lupinine is formed (Baumert, *A.* 214, 360).—4. *Sodium* dissolves in fused lupinine, but the product is decomposed by water into NaOH and lupinine (Baumert, *B.* 15, 631).

Salts.—$B''H_2Cl_2$: large trimetric crystals.—$B''2HNO_3$: crystals, v. e. sol. water and alcohol. — $B''H_2SO_4$: deliquescent prisms. — $B''(HAuCl_4)_2$: needles, v. sl. sol. water. — $B''H_2PtCl_6$ 6aq: crystals, sol. water.

Acetyl derivative $C_{21}H_{38}Ac_2N_2O_2$. Obtained by heating lupinine with AcCl or with Ac_2O and NaOAc (Baumert, *A.* 224, 313). Oil.—$B''H_2PtCl_6$: orange trimetric plates.

Methylo-iodide $B''Me_2I_2$: white hexagonal plates; sl. sol. alcohol (Baumert, *B.* 14, 1221).

Methylo-chloride $B''Me_2Cl_2$: pearly plates.—$B''Me_2PtCl_6aq$: orange-red needles.—$B''Me_2Au_2Cl_8$: yellow pp.

Ethylo-iodide $B''Et_2I_2$: hexagonal plates (Baumert, *B.* 14, 1321). Decomposed by Ag_2O, but not by KOH. From it may be obtained $B''Et_2PtCl_6aq$ and $B''(EtAuCl_4)_2$. [70°].

Anhydro-lupinine $C_{21}H_{38}N_2O$. Formed by heating lupinine with fuming HCl at 150°-200° (Liebscher, *B.* 14, 1880). Liquid which cannot be distilled. Oxidised by air. Smells like conine. Forms crystalline salts.—$B''H_2PtCl_6$: red tables, v. sol. water.

Di-anhydro-lupinine $C_{21}H_{36}N_2$. (220°). From lupinine and conc. HClAq at 200° (Liebscher a. Baumert, *A.* 214, 371). Oil. Readily oxidised by air.—$B''H_2PtCl_6$: dark-red crystals; v. sol. warm water.

Lupinidine $C_8H_{15}N$.

Preparation.—Lupine seeds are extracted with dilute alcohol acidified with H_2SO_4, and, after as much fat as possible has been removed, the sulphate solution is evaporated to a syrup and the residue triturated with absolute alcohol, when it solidifies to a mass of crystalline plates. This mass is again triturated with absolute alcohol, when a white crystalline meal of acid lupinidine sulphate separates. The mother-liquors are treated again in the same manner, until the residue, on trituration with alcohol, either remains liquid or at least redissolves on washing with absolute alcohol; in this case it consists for the most part of lupinine sulphate. The mother-liquors containing the lupinine sulphate are freed from alcohol, dissolved in water, and ppd. by $BaCl_2$. The filtrate now contains chiefly lupinine chloride, from which any lupinidine salt present can be ppd. as platino-chloride (G. Baumert, *A.* 225, 365). Lupinidine is obtained by decomposing the acid sulphate by one of the stronger bases, shaking with ether, and distilling in a current of hydrogen. The fact that this alkaloid distils over in a stream of hydrogen, between the wide limits of 250°-320°, is explicable on the assumption that the lupinidine got from the seeds of the yellow lupine is a mixture of crystallisable hydrate (see below) and a liquid anhydride. The formula $C_8H_{15}N$ is calculated from analyses of its salts.

Properties.—Thick yellow oil of intensely bitter taste and disagreeable hemlock-like smell; but this smell is probably due to a decomposition product. Strong base. Very easily oxidisable by the air when in contact with acids or with KOHAq, but not with NH_3Aq. Gives no acetyl derivative or ethylo-iodide (Baumert, *A.* 225, 365). Lupidine is a feeble poison, acting on frogs like curare (Kobert, *A.* 227, 219).

Salts.—B'HCl: yellow deliquescent crystals.—B'HI ½aq: rather large crystals resembling alum, v. sol. hot water, m. sol. alcohol.—B'_2HI(?) Formed by heating lupinidine with EtI. Thus lupinidine resembles berberine in giving a hydroiodide when heated with EtI (Baumert, *A.* 227, 207).—$B'H_2SO_4$: minute crystals, v. e. sol. water, v. sl. sol. alcohol.—$B'_2H_2PtCl_6$ 2aq: trimetric crystals, $a{:}b{:}c = \cdot885{:}1{:}1\cdot171$ (Luedecke, *Z. K.* 12, 297), sl. sol. water, m. sol. HClAq, v. sol. dilute alcohol (Baumert, *A.* 225, 365).

Hydrate $C_8H_{15}Naq$? The liquid and crystalline portions of the lupine alkaloid are to be considered as modifications of the same base (the hydrate being crystalline), since both yield the same double salt with $PtCl_4$. The existence of a hydrate, stable only in the cold, may also explain why cold aqueous solutions of lupinidine, lupinine, and coniine become milky on heating. A further proof of the correctness of this view is that the yellow oil only (probably the pure anhydride $C_8H_{15}N$) was got on treating the lupinidine with P_2O_5 (Baumert).

Lupinine. A crystalline alkaloid, called by this name, was obtained by Bettelli (*G.* 11, 240) by extracting white lupine (*Lupinus albus*) with alcohol. It forms white needles, v. sol. water. An alcoholic extract of the plant has been used with some success in cases of intermittent malarial fever. Solutions of the alkaloid give white pps. with tannin, $HgCl_2$, and $AgNO_3$, in the last case reduction soon takes place. Platinic and gold chlorides and picric acid give canary-yellow pps. HIAq containing iodine gives a red amorphous pp. It does not reduce Fehling's solution. Boiling KOH gives off ammonia.

Lupinine. A liquid alkaloid, also called lupinine, was obtained by Campani (*G.* 11, 237) from the white lupine. It boiled between 210° and 218° and was poisonous.

The young shoots of the yellow lupine contain an alkaloid called ARGININE (*q. v.*). The danger to sheep from eating lupines appears to be due to another substance 'icterogen,' perhaps produced by a parasite growing on the lupines (Baumert, *Ar. Ph.* [3] 24, 49; Kobert a. Liebscher, *J.* 1886, 1696; Kühn, *ibid.*).

LUPULIN. The yellow granular aromatic powder situate at the base of the cones of the hop and forming from 8 to 18 p.c. of the cones. It contains hop oil, a resin, a nitrogenous substance, a gummy substance, and a bitter principle. Lermer (*D. P. J.* 179, 54) extracted the bitter principle by ether, shook the ether with aqueous KOH, ppd. by $CuSO_4$, decomposed the copper compound with H_2S, and recrystallised from ether. He describes

the 'lupulin' so obtained as large white prisms, insol. water, v. sol. alcohol, ether, and chloroform. The alcoholic solution, diluted with water, had a bitter taste and acid reaction. Lermer also obtained a compound [110°] which likewise formed a copper salt. Lupulic acid, as described by Bungener, appears to be Lermer's lupulin. Issleib (*Ar. Ph.* [3] 16, 345) found a 'pseudo-glucoside' $C_{29}H_{46}O_{10}$ which he extracted by cold water. The extract was treated with animal charcoal, the charcoal dried and exhausted with 90 p.c. alcohol, and the yellow solution partially evaporated. A brown resin $C_{10}H_{21}O_3$ is deposited while a bitter uncrystallisable substance remains in solution. From the aqueous solution of this bitter substance ether extracts only the bitter principle (which amounts to ·004 of the hops) and leaves in the water $C_{10}H_{18}O_6$, a tasteless product of the oxidation of oil of hops $C_{10}H_{18}O$. The bitter principle, according to Issleib, forms a yellow solution in alkalis, and is split up by boiling dilute H_2SO_4 into lupuliretin $C_9H_{16}O_4$ and lupulic acid $C_{40}H_{82}O_{19}$. This lupulic acid forms a crystalline barium salt $BaC_{18}H_{80}O_{19}$ 5aq. According to Bissell (*Ph.* [3] 8, 508) lupulin does not contain all the active principle of the hop. The bitter principle may usually, but not always, be ppd. from an infusion of hops by lead acetate (Allen, *An.* 13, 43). According to Hayduck (*C. C.* 1887, 694), when hops are exhausted with ether, and after evaporating the ether, the residue is treated with alcohol, a white wax is left behind. The alcoholic solution gives a yellow pp. with lead acetate, and the filtrate contains two resins, one soluble, and the other insoluble, in light petroleum.

Lupulic acid $C_{50}H_{70}O_8$. [93°].

Preparation.—By extracting hop-flour with light petroleum spirit, distilling off the solvent, cooling, filtering off the black liquid from the crystals formed, and recrystallising the crude acid from alcohol and petroleum spirit.

Properties.—Colourless prismatic crystals, rapidly altered by exposure to the air. V. sol. alcohol, ether, benzene, $CHCl_3$, CS_2, and the ethereal oil of the hop, sol. petroleum spirit, insol. water. Easily reduces ammoniacal $AgNO_3$. Exposed to the air is transformed into a yellowish resin. This product of oxidation is sl. sol. water, to which it imparts an intense bitter taste, and this resin is the bitter principle of the hop.—CuA'. A crystalline powder (Bungener, *Bl.* [2] 45, 487).

LUPULINE *v.* Hopeïne.

LUTEÏC ACID $C_{20}H_{20}O_{12}$ (?). [274°]. S. ·009 in the cold; ·03 at 100°. S. (alcohol) 4·2 in the cold. S. (ether) ·37. A yellow colouring matter prepared from the flowers of *Euphorbia Cyparissias* (Höhn, *Ar. Ph.* [2] 140, 218). The fresh flowers are exhausted with alcohol of 60 p.c., the greater part of the alcohol distilled off, and the residual liquid filtered and ppd. with basic lead acetate. The pp. is suspended in water, decomposed by H_2S, and filtered. The filtrate is evaporated over H_2SO_4, and the yellowish crusts that separate are recrystallised from ether-alcohol, and then from hot water containing 4 p.c. of alcohol. Slender yellow needles. Has no smell and a bitter taste. Sublimes at 220°. Its solutions exhibit acid reaction. Luteïn somewhat resembles luteolin and, like the latter, gives protocatechuic acid by potash-fusion. It dissolves in caustic and carbonated alkalis forming yellow solutions. It reduces $AgNO_3$ mercurous nitrate, and Fehling's solution on heating. $FeCl_3$ gives a green colour, changing to reddish-brown on further addition of $FeCl_3$. Conc. H_2SO_4 dissolves luteïc acid, but water reppts. it unaltered. Boiling dilute H_2SO_4 does not attack it.

LUTEÏN. This name is given by Thudichum (*Pr.* 17, 253) to the yellow substance obtained by Piccoli and Lieben (*Z.* 1868, 645) from the ovary of the cow, and called by them 'hæmoluteïn' (*cf.* Holm, *Z.* 1867, 779). It occurs also in the human ovary. The same or a similar substance occurs in butter, yolk of egg, serum of blood, in some diseased swellings, in carrots, &c. It occurs also in the retina of the eyes of fowls (Capranica, *J. Th.* 1877, 317; Kühne, *J. Th.* 1877, 317). According to Maly (*C. C.* 1881, 485; *M.* 2, 359), the luteïn in yolk of egg of hens and shrimps is a mixture of vitello-luteïn and vitello-rubin. If the yolk is extracted with alcohol, and the extract treated with hot baryta-water, vitellorubin is ppd. while vitelloluteïn remains in solution. Or the yolk extract may be boiled with a little acid, and the ppd. albumen treated with petroleum which extracts vitelloluteïn, while CS_2 extracts vitellorubin from the residue. Vitellorubin contains no nitrogen. It is red, and forms a Mg compound sol. ether, chloroform, and CS_2 but ppd. by alcohol in red flakes. An alcoholic solution of vitellorubin shows a broad but weak absorption band including the line F. Vitelloluteïn forms a yellow alcoholic solution which exhibits two narrow absorption bands, one including F, the other between F and G. It contains no nitrogen.

LUTEOCHROMIUM SALTS; *v.* vol. ii. p. 160.

LUTEOCOBALTIC SALTS; *v.* vol. ii. p. 228.

LUTEOLIN $C_{20}H_{14}O_8$ (Moldenhauer, *A.* 100, 180) or $(C_{12}H_8O_5)_2$ 3aq (Schutzenberger a. Paraf, *A. Suppl.* 1, 256). [320°]. S. ·007 in the cold, ·02 at 100°. S. (alcohol) 2·7. S. (ether) ·16. The yellow colouring matter of weld (*Reseda luteola*) (Chevreul, *J. Chim. Méd.* 6, 157). Obtained by boiling weld with water (16 pts.) mixed with alcohol (1 pt.), filtering, evaporating, dissolving the yellow flakes in alcohol, and pouring into water. It is recrystallised from a mixture of water and glycerin (Rochleder, *J. pr.* 99, 433). Yellow, four-sided needles in radiate groups. May be sublimed. Partially decomposed on fusing. Has a slightly bitter, astringent taste. Reddens litmus slightly. Dissolves with deep yellow colour in caustic and carbonated alkalis. Conc. H_2SO_4 forms a yellow solution, whence water reppts. it. Potash-fusion gives CO_2, phloroglucin, and protocatechuic acid. Very dilute $FeCl_3$ gives a green pp., excess of $FeCl_3$ forms a brownish-red solution. Alcoholic lead acetate gives a pp. $C_{12}H_6PbO_5$ aq.

(β)-**LUTIDINE** C_7H_9N. *Ethyl-pyridine* (?). Mol. w. 107. (166°). S.G. $\frac{0}{0}$ ·956 (W.); ·959 (C.). V.D. 3·79 (calc. 3·70). S. 4 (W.). Obtained, together with homologues, by distilling cinchonine with KOH; a mixture of some ten bases is obtained and these are separated by fractional distillation (Greville Williams, *J.*

1855, 549; 1864, 437; *Pr.* 13, 305; Oechsner de Coninck, *C. R.* 92, 413; *Bl.* [2] 35, 296; *R. T. C.* 1, 132; *A. Ch.* [5] 27, 462, 488). The same base appears to be formed by distilling with zinc-dust the syrupy acid formed by oxidising cinchonine with chromic acid mixture (Weidel a. Hazura, *M.* 3, 780). This, or an isomeric ethyl-pyridine, is formed by distilling brucine with KOH (O. de Coninck, *Bl.* [2] 42, 100). Liquid; sl. sol. water, sol. alcohol and ether. The aqueous solution does not become turbid on warming, the base being more soluble in hot than in cold water. It appears to form an unstable hydrate $C_7H_9NH_2O$. Smells somewhat like nicotine. Physiologically it is a violent poison and stops tetanus produced by strychnine (Greville Williams a. Waters, *Pr.* 32, 162). By chromic acid mixture or by $KMnO_4$ it is oxidised to pyridine carboxylic (nicotinic) acid [231°]. When heated with sodium it appears to form di-(β)-lutidine $C_{14}H_{18}N_2$ (Greville Williams, *Pr.* 33, 159). Chlorine passed into (β)-lutidine containing dissolved iodine appears to form tri-chloro-(β)-lutidine. Chloroacetic acid gives $C_7H_9NClCH_2.CO_2H$ (163°) forming $(C_9H_{12}NO_2Cl)_2PtCl_4 2aq$ (Pictet, *J.* 1882, 1079).

Salts.—B'HCl. Very deliquescent crystals. —B'HBr.—$B'_2H_2PtCl_6$: orange-red leaflets. Its ppn. is not retarded by presence of excess of HCl (difference from bone oil lutidine). Hot water decomposes it forming B'_2PtCl_4 crystallising in pale-yellow leaflets.—B'_2PtCl_2. From platinous chloride (1 pt.) and lutidine (1 pt.): combination takes place with rise in temperature (of 70°), the product being a hard brittle mass (Williams).—$B'HAuCl_4$. Yellow pp. On boiling with water it forms yellow $B'_2HAu_2Cl_7$ and ultimately B'_2AuCl_3: a red crystalline powder. —$B'_2H_2PdCl_4$: garnet-red prisms, obtained by mixing solutions of the hydrochloride and of palladium chloride (W.). Decomposed at 100°, giving off HCl and leaving B'_2PdCl_2, sl. sol. water. —$B'_2H_2Cl_2Ur_2O_2Cl_2$. Formed from uranyl chloride and (β)-lutidine hydrochloride. Yellow. —$B'_2H_2SO_4(UrO)_2(SO_4)_3$. From uranyl sulphate and (β)-lutidine sulphate. Small yellow needles. —Picrate $B'C_6H_2(NO_2)_3OH$. Yellow needles (Williams, *Pr.* 33, 159).

Combinations.— $B'_2CuSO_4 4aq$. When (β)-lutidine is added to a solution of cupric sulphate a copious pale-green pp. is formed, which dissolves in excess, forming a rich-blue liquid, which deposits blue prisms of $B'_2CuSO_4 4aq$.— B'_3AgNO_3. Formed by ppg. silver nitrate solution with (β)-lutidine and recrystallising from alcohol.

Di-(β)-lutidine. When sodium is warmed with (β)-lutidine dissolved in toluene a product is obtained from which it is possible to get a platinochloride containing a percentage of platinum corresponding to the formula $C_{14}H_{18}N_2HPtCl_5$ (Williams, *C. N.* 44, 308).

Tetra-(β)-lutidine. When sodium is warmed with (β)-lutidine a violent action takes place, and from the product a platinochloride may be obtained containing a percentage of platinum corresponding to the formula $C_{28}H_{36}N_4HPtCl_5$ (Williams).

Hydride of (β)-lutidine $C_7H_{15}N$. Greville Williams found that sodium-amalgam had no action on (β)-lutidine. According to Oechsner de Coninck (*Bl.* [2] 42, 121), however, a hexahydride (155°–160°) may be formed by the action of sodium on an alcoholic solution of the base (*cf.* Wyschnegradsky, *B.* 13, 2401). It combines with MeI and the product, when distilled with KOH, yields $C_8H_{17}N$ (160°). It also combines with EtI, and the product treated with potash yields a tertiary base boiling at 175°.

Lutidine C_7H_9N. (173°). Obtained by distilling strychnine with zinc-dust (Scichloni a. Magnanini, *G.* 12, 445). Yellow liquid, insol. water, sol. alcohol and ether. Smells like pyridine. Gives with sodium phosphomolybdate a dark yellow pp., sol. ammonia. Potassio-mercuric iodide gives a yellow amorphous pp. Mercuric chloride gives a white pp. Iodine in KIAq gives a crimson pp., insol. dilute HClAq.

Coal tar lutidines *v.* Di-methyl-pyridine.

Isomerides *v.* Ethyl-pyridine and Di-methyl-pyridine.

LUTIDINE CARBOXYLIC ACIDS *v.* Di-methyl-pyridine carboxylic acid.

LUTIDINIC ACID *v.* Pyridine-di-carboxylic acid.

LUTIDONE *v.* Oxy-di-methyl-pyridine.

LUTIDO-STYRIL *v.* Oxy-di-methyl-pyridine.

LUTIDYL-QUINOLINE *v.* Di-methyl-pyridyl-quinoline.

LYCACONITINE *v.* Aconite alkaloids.

LYCINE. The base from *Lycium barbarum* to which this name was applied has been shown to be identical with betaïne.

LYCOPODINE $C_{32}H_{52}N_2O_3$. [115°]. Occurs in *Lycopodium complanatum* (club moss), from which it is obtained by extracting the root with alcohol, evaporating the extract, dissolving the residue in water, adding lead subacetate, removing excess of lead by H_2S, adding NaOH, and shaking with ether. When the ether is evaporated the alkaloid is left, and may be purified by dissolving in HClAq and ppg. with conc. NaOHAq (Bödeker, *A.* 208, 363). Monoclinic prisms, v. sol. most menstrua. Tastes bitter.— $B''H_2Cl_2$ aq: glassy hexagonal crystals (Söffing, *J.* 1884, 463).—$B''(HAuCl_4)_2$ aq: small glistening yellow needles.

LYCOPODIUM BITTER. The alcoholic and aqueous extracts of *Lycopodium chamæcyparissus* are evaporated, and the residues mixed and extracted with water. The solution is treated with lead acetate and subacetate, filtered, freed from lead by H_2S and evaporated. The residue is then washed with alcohol and dissolved in water. From this solution lead subacetate ppts. the bitter principle, and the pp. is then suspended in water and decomposed by H_2S. The filtrate is concentrated, freed from sugar by careful fermentation with yeast, dried, and extracted with absolute alcohol, which leaves the bitter principle on evaporation (Kamp, *A.* 100, 300). Slender needles (from water). V. e. sol. water, alcohol, and ether. Extremely bitter. Neutral to litmus. Contains no nitrogen. Colours tincture of iodine orange-red. Does not reduce Fehling's solution, but after boiling with dilute H_2SO_4 it does so.

LYCOPODIUM OIL. The oil from the fresh spores of club moss contains phytosterin $C_{26}H_{44}O$, together with glyceryl ethers of lycopodic

$C_{18}H_{30}O_4$, oleïe, arachic, stearic, and palmitic acids (Bukowski, *Chem. Zeit.* 1889, 174; *cf.* Langer, *Ar. Ph.* [3] 27, 625).

LYCORESIN $C_9H_{16}O$. [170°]. Extracted from *Lycopodium chamæcyparissus* by alcohol, and remaining in the mother-liquor after lycostearone has separated (Kamp, *A.* 100, 300). Minute crystals; almost insol. boiling water, v. sol. alcohol and ether, v. sl. sol. cold alkalis.

LYCOSTEARONE $C_{15}H_{30}O_2$. [75°–100°]. An amorphous tasteless substance, which may be extracted by alcohol from *Lycopodium chamæcyparissus* (Kamp, *A.* 100, 300). Insol. cold water, sol. hot water forming a jelly on cooling. Sl. sol. cold alcohol and ether, v. sol. alkalis.

LYDINE. A violet dye obtained by pouring a solution of aniline (100 g.) in fuming HClAq (100 g.) diluted with water (120 c.c.) into a solution of K_3FeCy_6 (90 g.) in water (850 c.c.), and heating the mixture to boiling. The product is dissolved in dilute oxalic acid and ppd. by alkalis. Violet powder, sol. alcohol, sl. sol. ether and benzene, insol. water. Poisonous (Guyot, *C. R.* 69, 829). Possibly identical with mauvine.

M

MACLEYIN $C_{20}H_{19}NO_5$ (?). [201°]. S. ($CHCl_3$) 7. S. (ether) ·1. An alkaloid in *Macleya cordata* the Japanese *Tachiobaku* (Eijkman, *R. T. C.* 3, 182; *Ph.* [3] 13, 87). Extracted from the root by alcohol and dilute H_2SO_4, and separated from sanguinarin by ether in which it is very slightly soluble. Prisms. Almost insol. water and alkalis, v. sl. sol. hot alcohol. Its salts have a bitter taste. Its ehemical properties resemble those of protopine. Conc. H_2SO_4 gives a faint yellow changing through violet to green. Fumes of nitric acid give an ultramarine colour. H_2SO_4 and a little $K_2Cr_2O_7$ give a blue eolour.

Salts. — B'HCl. Prisms. S. ·7. — $B'_2H_2PtCl_6$2aq: yellowish-white pp.—$B'_2H_2Cr_2O_7$: orange prisms.—Hydroiodide: crystalline spheres. — Normal sulphate: colourless needles. Thiocyanate: needles.—Acetate: needles.—Acid oxalate: erystals.—Aeid tartrate: needles.—Benzoate: [166°]: long needles.

MACLURIN $C_{13}H_{10}O_6$ (H. a. P.); $C_{15}H_{12}O_8$ (L.). *Morintannic acid.* [200°] (Wagner). S. ·52 at 14°. Oceurs, together with morin (*q. v.*), in old fustic, the wood of *Morus tinctoria*, from which it is obtained by extracting with water. The evaporated extract deposits morin, and from the filtrate maclurin may be ppd. by HCl (Hlasiwetz a. Pfaunder, *A.* 127, 352; *J. pr.* 94, 65; Löwe, *Fr.* 14, 117; Benedikt, *A.* 185, 114). Almost pure maclurin is also found in patches in the wood (Wagner, *J.* 1850, 529).

Properties.—Yellow, erystalline powder (eontaining aq), v. sol. aleohol and ether, sl. sol. water. Above 270° it gives CO_2 and pyrocatechin. Its aqueous solution is ppd. by alkaloids, gelatin, and albumen. $FeSO_4$ gives a greenish-black pp. Its alkaline solution turns brown in air. It dyes mordanted cotton pale brownish-yellow. Boiling conc. KOHAq gives phloroglucin and protocatechuic acid: $C_{13}H_{10}O_6 + H_2O = C_6H_6O_3 + C_7H_6O_4$. Dilute H_2SO_4 at 120° does the same. Bromine gives tri-bromo-maclurin $C_{13}H_7Br_3O_6$ aq: minute needles. Conc. H_2SO_4 at 190° gives brown $C_{26}H_{14}O_{15}$ (Hlasiwetz, *A.* 143, 308). Reduction with zinc and H_2SO_4 gives phloroglucin and machronin. When its solution is heated with sodium-amalgam and the product acidified, ether extracts phloroglucin and amorphous $C_{14}H_{12}O_5$, which is sol. water and aleohol, is ppd. by lead acetate, gives a grass-green eolour with $FeCl_3$, and reduces $AgNO_3$ and Fehling's solution.

Salts.—$PbC_{13}H_8O_6$ aq: yellow erystals.—$C_{15}H_{12}O_7$3PbO (L.).

Acetyl derivative $C_{13}H_9AcO_6$ 1½aq: viscid oil.

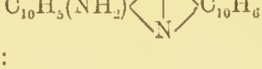
Machronin $C_{14}H_{10}O_5$3aq (?). Formed by the action of zinc and dilute H_2SO_4 on maclurin, and separated from phloroglucin by ppn. with lead acetate. The pp. is decomposed by H_2S. Colourless spangles composed of tufts of minute needles (from dilute alcohol). V. sl. sol. water and alcohol, m. sol. ether. Turns dark blue when exposed to air or when heated. The hot aqueous solution turns violet-blue in air, and then yields an indigo-blue pp. with HCl. $FeCl_3$ gives, in a very dilute alcoholic solution, a violet-red colour, changing to blue. Alkaline solutions also turn blue on exposure to air. $AgNO_3$ gives a violet colour with reduction of silver. Reduces hot Fehling's solution. Conc. H_2SO_4 gives an orange solution, turning emerald green on warming or diluting.

Rufimoric acid $C_{16}H_{14}O_9$ (?). Obtained by boiling maclurin with dilute HCl (Wagner, *J.* 1851, 420). Dark-red mass; v. sol. alcohol, m. sol. water, v. sl. sol. ether. Forms a erimson solution in alkalis.

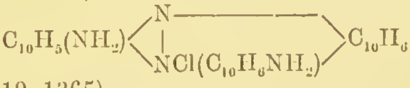
MACROCARPINE *v.* THALICTRINE.

MADDER *v.* OXY-ANTHRAQUINONES.

MAGDALA RED $C_{30}H_{21}N_4Cl$. Formed by heating naphthalene-azo-(α)-naphthylamine with (α)-naphthylamine hydrochloride (Hofmann, *B.* 2, 374, 412). Appears to be a compound of amido-naphthazine



allied to saffranine, viz.:



(Julius, *B.* 19, 1365).

MAGNESIA. *Magnesium oxide* MgO (*q. v.*).

MAGNESIA ALBA. A basic carbonate of Mg, varying somewhat in composition; *v.* CARBONATES. vol. i. p. 699.

MAGNESIA USTA. A name given in pharmaceutical nomenclature to MgO prepared by calcining *magnesia alba.*

MAGNESIUM. At. w. 24. Mol. w. probably same as at. w. (*v. infra*). [c. 450°] (Deville a. Caron, *A.* 101, 359); [c. 500°] (Ditte, *C. R.* 73, 108); [between 700 and 800°] (V. Meyer, *B.* 20, 497). Scarcely volatilises in CO at red to white heat (V. M. *l.c.*). S.G. 1·69 to 1·71 at 17° (Kopp);

1·77 at 0° (Wurtz, *Am. Ch.* 1876 (March)). S.H. 20° to 51° ·245 (Kopp, *T.* 155, [1] 71). C.E. at 40° ·00002694 (Fizeau, *C. R.* 68, 1125). T.C. (Ag = 100) 34·3 (Lorenz, *W.* 13, 422). E.C. (Hg at 0° = 1) 22·84 at 0°, 16·34 at 100° (Lorenz, *W.* 13, 422, 582). S.V.S. c. 14·1. Characteristic lines in emission-spectrum 5527·4, 5183, 5172, 5166·7 (Thalén, Upsala, 1868; *v.* also Liveing a. Dewar, *Pr.* 44, 241).

Occurrence.—The metal does not occur native, but compounds of Mg are very widely distributed, and are found in some places in large quantities; they usually accompany Ca compounds. *Magnesite* $MgCO_3$, *dolomite* a mixture of the isomorphous carbonates of Mg and Ca, *kieserite* $MgSO_4.H_2O$, *carnallite* $MgCl_2.KCl.6H_2O$, various silicates *e.g. asbestos* $(MgCa)SiO_3$, *spinelle* $MgAl_2O_4$, &c., occur as minerals. Borate, phosphate, sulphate, chloride, nitrate, and hydroxide, of Mg are found in mineral waters, and some of them in sea water; Mg compounds, chiefly phosphate and carbonate and compounds of organic acids, are found in plants and animals.

Magnesia alba (a basic carbonate of Mg) was introduced as a medicine in the beginning of the 18th century; the name is said to have been given merely in contradistinction to *magnesia nigra*, a term applied to the mineral pyrolusite because of its colour and supposed magnetic properties. Magnesia was long supposed to be the same, or nearly the same, as lime. Hoffmann, Bergmann, Marggraff, and especially Black (1755) established the characteristic properties of magnesia. Black showed *magnesia alba* to be a compound of *fixed air* (CO_2) with an earthy base, to this base he gave the name magnesia. In 1800 Davy obtained a small quantity of a metal by reducing magnesia at white heat by vapour of K; in 1830 Bussy obtained the metal in greater quantity and purity, by heating together $MgCl_2$ and K.

Formation.—1. By heating together $MgCl_2$ and K in a Pt crucible, and washing out KCl by water (Bussy; Buff, *P.* 18, 140; Liebig, *P.* 19, 137).—2. By electrolysing fused $MgCl_2$ (Bunsen, *A.* 82, 137), or a mixture of $MgCl_2$ and KCl with a little NH_4Cl (Matthiessen, *C. J.* 8, 107).—3. By reducing a molten mixture of $MgCl_2$, CaF_2, KCl, and NaCl, by Na (Deville a. Caron, *C. C.* 1863. 993).—4. By reducing $MgF_2.NaF$ by Na (Tissier, *C. R.* 56, 848).—5. By electrolysing a mixture of $MgSO_4$ and $(NH_4)_2SO_4$ dissolved in water (Gerhard, *English Patents*, No. 16,691; 1884).—6. Puettner patented a method for reducing $MgCO_3$ by heating with Fe_2O_3 and C (*German Patents*, No. 31,319). 7. Lauterborn reduces a double Mg-Na cyanide by Zn (*German Patents*, No. 39,915).

Preparation.—1. The upper part of a porcelain crucible is divided vertically into two halves by a thin porcelain plate; the crucible is closed by a porcelain cover, through which pass the carbon electrodes of a battery of 8-10 Bunsen-cells, one electrode on each side of the dividing vertical plate; indentations are cut in the negative electrode; the crucible is heated to redness, then filled with fused $MgCl_2$, and the current is passed through the molten mass. The Mg lodges in the cavities of the negative electrode, and is thus prevented from floating to the surface; the dividing plate serves to prevent contact between the Cl, evolved at the positive electrode, and the Mg (Bunsen, *A.* 82, 137).—2. A mixture of $MgCl_2$ and KCl, prepared by evaporating a mixture of the salts, in the ratio $4MgCl_2$:3KCl, to dryness, is mixed with a little NH_4Cl, and is electrolysed when fused in the apparatus described in 1; as Mg is heavier than the molten mixture of salts it is not necessary to form serrations in the negative electrode (Matthiessen, *C. J.* 8, 107).—3. A mixture of 6 pts. dry $MgCl_2$, 1 pt. of a mixture of 7 pts. NaCl and 9 pts. KCl, 1 pt. powdered CaF_2, and 1 pt. Na carefully freed from oil, is heated to bright redness in a covered earthen crucible. The Mg, which separates in globules, is heated nearly to whiteness in a boat of compact charcoal, placed in an inclined tube of the same material through which is passed a stream of dry H; the Mg condenses on the upper part of the tube; it is then melted into large globules with a flux of $MgCl_2$, NaCl, and CaF_2. To free the Mg from C, Si, and N, it may be distilled in a current of H at a high temperature (Deville a. Caron, *A.* 83, 137; for an apparatus in which the distillation may be conveniently conducted *v.* Sonstadt, *J. pr.* 90, 307). In a later trial D. a. C. used 7 pts. $MgCl_2$, 4·8 pts. CaF_2, and 2·3 pts. Na (*C. C.* 1863. 993).—4. Wöhler (*A.* 101, 362) reduces a fused mixture of $MgCl_2.NaCl$ with excess of NaCl by Na; the mixture is obtained by adding excess of NaCl to $MgCl_2Aq$ and evaporating to dryness. The amount of $MgCl_2$ in the mixture must be known in order that the quantity of Na to be used may be calculated; for every 1 pt. $MgCl_2$ about $\frac{1}{2}$ pt. Na should be used.

Properties.—A silver-white, very lustrous, moderately hard, metal; malleable; not very tenacious; may be filed and polished; S.G. c. 1·75. Mg occludes c. $\frac{2}{3}$ its volume of H; by heating *in vacuo* the H is suddenly evolved. Obtained in lustrous, white, crystals; hexagonal, $a:c = 1:1·639$, isomorphous with Zn (Des Cloizeaux, *C. R.* 90, 1101). Unchanged in dry air; superficially oxidised in ordinary air. Heated in air, burns to MgO giving out a brilliant white light, very rich in actinic rays. Burns when heated in steam, also in CO_2, and in SO_2. Combines directly with the halogens, S, P, As, N. Hot water is slowly decomposed by Mg. Dissolves readily in dilute acids.

Mg is a distinctly metallic element; it forms one series of salts MgX_2 where X = Cl, NO_3, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c.; a few basic salts, and many double salts, are known. In its chemical relations, Mg is analogous to the alkaline earth metals Ca, Sr, and Ba, and also to the metals Be, Zn, Cd, and Hg. MgO and MgO_2H_2 are alkaline; MgO_2H_2 is formed by the reaction of H_2O and MgO, and is dehydrated to MgO by heat. As the V.D. of no binary compound of Mg with H or one of the halogens has been determined, the valency of the atom of Mg in gaseous molecules is not known with certainty; but from the close similarities between Mg, Zn, and Cd, there is little doubt that the atom of Mg is divalent in gaseous molecules (*v.* MAGNESIUM GROUP OF ELEMENTS, p. 163; *cf.* ALKALINE EARTHS, METALS OF THE, vol. i. p. 112).

The atomic weight of Mg has been determined (1) by determining SO_4 in $MgSO_4 7H_2O$

(Gay-Lussac, *A. Ch.* [2] 13, 308; Scheerer, *P.* 69, 535); (2) by converting MgO into $MgSO_4$ (Berzelius, *P.* 8, 188; Svanberg a. Nordenfeldt, *J. pr.* 45, 474; Jacquelain, *A. Ch.* [3] 32, 202; Marignac, *A. Ch.* [6] 1, 289); (3) by converting $MgC_2O_4.2H_2O$ into MgO (S. a. N. *l.c.*); (4) by converting $MgCO_3$ into MgO (Marchand a. Scheerer, *J. pr.* 50, 385); (5) by determining Cl in $MgCl_2$ by ppn. with Ag (Dumas, *A. Ch.* [3] 55, 189); (6) by determining S.H. of Mg.

Molecular weight of magnesium.—Ramsay (*C. J.* 55, 521) has determined the lowering of vapour-pressure of Hg produced by dissolving Mg in Hg; the results make it probable that the molecular weight of Mg is the same as the atomic weight. This conclusion assumes the accuracy of Van't Hoff's law, that equal volumes of dilute solutions contain equal numbers of molecules of the dissolved substances, and it also supposes the molecular weight of liquid Hg to be the same as the atomic weight of Hg.

Reactions.—1. Slowly oxidised in *moist air.*—2. Decomposes warm *water* slowly; heated in steam burns to MgO.—3. Heated in *air or oxygen* to above its M.P. burns to MgO, with brilliant white light, rich in actinic rays.—4. Heated in *chlorine*, *bromine*, or *iodine* forms $MgCl_2$, $MgBr_2$, or MgI_2.—5. Heated in *sulphur* forms MgS.—6. Heated in *nitrogen* forms Mg_3N_2, with *phosphorus* forms Mg_3P_2, and with *arsenic* forms Mg_3As_2.—7. Decomposes *carbon monoxide* and *dioxide*, also *sulphur dioxide*, when heated in these gases, forming MgO.—8. Reduces *ferric chloride* and *sulphate solutions* to $FeCl_2$ and $FeSO_4$ (Pfeiffer, *J. pr.* 61, 441).—9. Reduces *nitric acid* to HNO_2 (Jenzsch, *N. T. für Mineralogie*, 1853. 535).—10. Reduces *carbonates of the alkali metals* except Cs, also *oxides of copper, silver, and gold*, when heated with them in solid form (Winkler, *B.* 23, 44); also reduces oxides of Ca, Sr, Ba, Zn, Cd, and Hg (W. *B.* 23, 120).—11. Dissolves in *dilute acids* with formation of salts MgX_2, X = Cl, $\frac{1}{2}SO_4$, &c., and evolution of H, or N oxides from HNO_3. Conc. hot H_2SO_4 forms $MgSO_4$ and SO_2.—12. Dissolves in *hydrogen peroxide* solution with formation of MgO_2H_2. From solutions of *salts of copper, iron, manganese*, and *cobalt* Mg ppts. the metals, with evolution of H; from some metallic salts Mg ppts. hydrated oxides, *e.g.* AlO_3H_3 from solutions of Al salts; from *solutions of salts of arsenic or antimony*, Mg evolves AsH_3 or SbH_3.—13. Mg forms *alloys* with most of the metals (*v. Magnesium, alloys of*).

Detection and estimation.—Solutions of Mg salts are not ppd. by HClAq, H_2SO_4Aq, H_2S, or NH_4HS. Fixed alkalis and their carbonates ppt. MgO_2H_2 or $MgCO_3$, insoluble in excess, but soluble in NH_4 salts, especially in NH_4ClAq; hence Mg salts are not ppd. by NH_3Aq in presence of NH_4Cl. Na_2HPO_4Aq, added to Mg salt solutions, in presence of NH_3Aq, ppts. $MgNH_4PO_4$.

Mg is usually estimated by ppn. as $MgNH_4PO_4$ by addition of NH_3Aq and Na_2HPO_4Aq; when strongly heated, the pp. is changed to $Mg_2P_2O_7$. For details, and methods of separation of Mg from other metals, *Manuals of Analysis* must be consulted.

Magnesium, alloys of. Mg forms alloys with most of the metals. By reason of the easy oxidation of Mg, the preparation of alloys of this metal is somewhat difficult. They may be prepared by melting the metals in H; also by melting the other metal and rapidly immersing the Mg in it. According to Parkinson (*J. pr.* 101, 375), Mg forms alloys with the alkali metals, Al, Sb, Bi, Cd, Cu, Au, Pb, Hg, Pt, Ag, Tl, Sn, Zn; also with Cu and Ni together, but not with Co, Fe, or Ni alone. The alloys of Mg are generally very brittle.

Magnesium, aluminate of; $MgAl_2O_4$; *v.* ALUMINATES, vol. i. p. 141.

Magnesium, antimonate of; $Mg(SbO_3)_2.12H_2O$; *v.* ANTIMONATES, vol. i. pp. 285, 286.

Magnesium, arsenates of; *v.* ARSENATES, vol. i. p. 308.

Magnesium, arsenide of. Mg_3As_2. Brown mass. Formed by heating a mixture of As and Mg turnings in H (Parkinson, *J. pr.* 101, 375; *cf.* ARSENIC, *Combinations* No. 9, vol. i. p. 303).

Magnesium, arsenites of; *v.* ARSENITES, vol. i. p. 306.

Magnesium, borates of; *v.* BORATES, vol. i. pp. 529, 530.

Magnesium, boride of. According to Phipson (*C. N.* 9, 219), a greenish-black mass, which is probably a boride of Mg, is produced by heating Mg with boric acid.

Magnesium, borofluoride of. $Mg(BF_4)_2$ (Berzelius, *P.* 2, 113), *v.* BOROFLUORIDES, vol. i. p. 526.

Magnesium, bromide of. $MgBr_2$. Mol. w. unknown, as V.D. has not been determined. Occurs in small quantity in sea-water, and in some mineral springs; also in the Stassfurt salt deposits. Obtained by passing Br vapour over melted Mg. The reaction is very violent (Lerch, *J. pr.* [2] 28, 338). A white, very deliquescent, fusible, wax-like, crystalline mass. By concentrating a solution of MgO in HBrAq, white deliquescent crystals of the *hydrated bromide*, $MgBr_2.6H_2O$, are obtained (Rammelsberg, *P.* 55, 239); the same hydrate is formed, along with an insoluble oxybromide, by the reaction between Mg and Br under water (Lerch, *l.c.*). Evaporation of $MgBr_2Aq$ to dryness, or heating the crystals of $MgBr_2.6H_2O$, is attended with evolution of HBr and formation of an oxybromide. Heated in a stream of O, $MgBr_2$ is entirely decomposed to MgO (Schulze, *J. pr.* [2] 21, 407). Kremers (*P.* 108, 118) and Gerlach (*Fr.* 8, 285) give the following data for S.G., and percentage composition, of $MgBr_2Aq$:—

P.ct. $MgBr_2$	S.G. of solution	P.ct. $MgBr_2$	S.G. of solution
5	1·043	30	1·310
10	1·087	35	1·377
15	1·137	40	1·451
20	1·191	45	1·535
25	1·247	50	1·625

The *double compounds* $MgBr_2.KBr.6H_2O$ and $MgBr_2.NH_4Br.6H_2O$ are obtained by evaporating mixed solutions of the constituent salts (Lerch, *J. pr.* [2] 28, 338).

Magnesium, chloride of. $MgCl_2$. Mol. w. unknown, as V.D. has not been determined.

Occurrence.—In sea-water and in several mineral springs, also in the salt deposits of Stassfurt.

Formation.—1. The mother-liquor, after re-

moving KCl from the Stassfurt salts, is evaporated to S.G. 1·375 and allowed to crystallise. The crystals of $MgCl_2.6H_2O$ are heated to melting, whereby they are partially dehydrated, but at the same time some oxychloride is formed. By exposing the crystals to a temperature of c. 100° under greatly reduced pressure almost pure $MgCl_2$ is obtained.—2. $MgCl_2$ is obtained as a by-product in Weldon's process for making Cl, and in Solway's soda-ammonia process when MgO is used to decompose NH_4Cl.—3. By heating MgO with NH_4Cl, adding some NH_4Cl from time to time.

Preparation.—1. Powdered MgO, or *magnesia alba*, is dissolved in HClAq, NH_4Cl is added in quantity sufficient to prevent ppn. of MgO_2H_2 on addition of NH_3Aq, the solution is made slightly alkaline by NH_3Aq, any silica which separates is filtered off, the liquid is neutralised by HClAq, and evaporated to dryness. The double salt $NH_4Cl.MgCl_2.xH_2O$ is thus obtained; it is heated to melting (c. 460°) in a Hessian crucible, in the bottom of which is placed a smaller Pt dish (Bunsen, *A.* 82, 137), until NH_4Cl is entirely removed; the $MgCl_2$ collects in the Pt dish at the bottom of the Hessian crucible (*cf.* Döbereiner, *S.* 28, 90).—2. By heating $MgCl_2.6H_2O$ in a current of HCl (Hempel, *B.* 21, 897).

The *hydrated chloride* $MgCl_2.6H_2O$ is obtained by evaporating the solution of MgO in HClAq to the crystallising point.

Properties.—A white, deliquescent, solid, consisting of a mass of small pearly crystals; S.G. 2·177 (Playfair a. Joule, *C. S. Mem.* 2, 401). Can be distilled in H at red heat. Dissolves readily in water with production of much heat; $[MgCl^2,Aq] = 35,920$ (*Th.* 3, 243). Thomsen (*l.c.*) gives the thermal data $[Mg,Cl^2] = 151,010$; $[Mg, Cl^2,Aq] = 186,930$. Sol. in alcohol, also in amylic alcohol. Gerlach (*J.* 1859. 43) gives the following table:—

P.ct. $MgCl_2$.	S.G. $MgCl_2Aq$.	P.ct. $MgCl_2$.	S.G. $MgCl_2Aq$.
1	1·0084	19	1·1686
2	1·0169	20	1·1780
3	1·0253	21	1·1879
4	1·0338	22	1·1977
5	1·0422	23	1·2076
6	1·0510	24	1·2175
7	1·0597	25	1·2274
8	1·0684	26	1·2378
9	1·0772	27	1·2482
10	1·0859	28	1·2586
11	1·0949	29	1·2690
12	1·1040	30	1·2794
13	1·1130	31	1·2903
14	1·1220	32	1·3012
15	1·1311	33	1·3121
16	1·1404	34	1·3230
17	1·1498	35	1·3340
18	1·1592		

The hydrate $MgCl_2.6H_2O$ crystallises in monoclinic forms; S.G. 1·558 (Filhol, *A. Ch.* [3] 21, 415). S. 167 cold water, 367 hot water (Casaseca, *C. R.* 37, 350). S. 20 in alcohol ·9 S.G., 50 in alcohol ·817 S.G.

Reactions. — 1. When the crystals of $MgCl_2.6H_2O$ are *heated in air*, water is given off and at the same time partial decomposition occurs with evolution of HCl and formation of oxychlorides.—2. $MgCl_2$ is partly decomposed by much *water* to MgO and HCl.

Combinations.—1. With *magnesia* to form oxychlorides (*v. Magnesium, oxychlorides of*, p. 162).—2. With *potassium chloride* to form $MgCl_2.KCl.6H_2O$; occurs native as *carnallite*, crystallising in rhombic forms according to Marignac (*C. R.* 155, 650), in hexagonal forms according to Rammelsberg (*Hand. der Krystall. Chemie*, 204). The double salt is prepared by mixing solutions of the constituents in the proper ratio, evaporating, and crystallising.—3. With *ammonium chloride*, and *calcium chloride*, to form $MgCl_2.NH_4Cl.6H_2O$ (*v.* Pfaff a. Hantz, *A.* 66, 250), and $MgCl_2.CaCl_2.12H_2O$, respectively. — 4. With *sodium chloride* to form $MgCl_2.NaCl.H_2O$ (Poggiale, *C. R.* 20, 1180).—5. With *ferric chloride*, and *chromic chloride*, to form $2MgCl_2.Fe_2Cl_6.2H_2O$, and $2MgCl_2.Cr_2Cl_6.2H_2O$, respectively (Neumann, *A.* 244, 328).—6. With *phosphorus oxychloride* to form $MgCl_2.POCl_3$ ($9MgCl_2.10POCl_3$ according to Cronander, *B.* 4, 753); a deliquescent solid, decomposed by hot water (Casselmann, *A.* 98, 223). 7. With *iodine trichloride* to form deliquescent, easily decomposed, crystals of $MgCl_2.2ICl_3.5H_2O$; obtained by dissolving $Mg(IO_3)_2$ in conc. HClAq, leading HCl into the liquid to saturation, and surrounding by a freezing mixture (Filhol, *J. Ph.* 25, 442).—8. With *ammonia* to form $MgCl_2.4NH_3$; a white sublimate by heating $MgCl_2$ in NH_3 (Clark, *A.* 78, 369).

Magnesium, chromate of; *v.* CHROMATES, vol. ii. p. 155.

Magnesium, fluoride of. MgF_2. Mol. w. unknown as V.D. has not been determined. Occurs native as *sellaïte*. Formed by dissolving *magnesia alba* in HFAq, evaporating to dryness, and heating the residue; also by ppg. a Mg salt in solution by a soluble fluoride. Obtained in crystals, either by melting the salt, prepared as described, with NaCl or KCl (Cossa, *Z. K.* [2] 1, 207), or by melting together 5 parts $MgCl_2$, 4 parts NaF, and 4 parts NaCl (Röder). Four-sided, very hard, white needles. S.G. 2·856 at 12° (Cossa, *B.* 10, 295). Guntz (*A. Ch.* [6] 3, 5) gives the thermal data: $[MgO^2H^2, 2HF] = 28,400$. Forms a *double compound* with NaF, viz. $MgF_2.NaF$. Obtained by adding MgO_2H_2 to NaFAq and evaporating; the decomposition according to Tissier (*J. pr.* 90, 50) is

$$3NaF + MgO_2H_2 = 2NaOH + MgF_2.NaF.$$

Magnesium, haloid compounds of. Mg forms a single compound, MgX_2, with each of the halogens. None of these compounds has been gasified, hence the molecular weight of none is known with certainty; but the great similarities between Mg, Zn, and Cd, make it extremely probable that the formula MgX_2 expresses the composition of the molecules of the compounds in question. $MgCl_2$, $MgBr_2$, and MgI_2 crystallise with $6H_2O$; when these crystals are heated they are partly decomposed to MgO and HX(X = Cl, Br, or I).

Magnesium, hydrosulphide of. MgS_2H_2. A solution of this compound is obtained by passing H_2S through MgO suspended in water; the MgO dissolves and leaves a nearly colourless solution, which evolves H_2S when exposed to air or heated. The solution thus prepared contains c. 16 p.c. MgS_2H_2, and has S.G. 1·118 at 12°

(Divers a. Shimidzu, *C. J.* 45, 699). MgS_2H_2Aq is also formed by treating MgS with water. A solution of MgS_2H_2 is a convenient source of H_2S; a steady stream of the gas is obtained by heating to 60°–65° (D. a. S. *l.c.*). Thomsen gives the thermal data: $[Mg, S^2, H^2, Aq] = 114,880$ (*Th.* 3, 243).

Magnesium, hydroxide of. MgO_2H_2. Occurs native as *brucite*, forming white, pearly, crystalline tablets (hexagonal rhombohedra), S.G. 2·35 to 2·46. Prepared by ppg. a Mg salt by NaOHAq, washing, and drying at 100°; also by direct combination of water with MgO, and drying at 100°; S.G. 2·36 at 15° (Schulten, *C. R.* 101, 72). MgO which has been heated to whiteness does not combine with water (*v.* Deville, *C. R.* 61, 975; Knapp, *D. P. J.* 202, 513; Schwarz, *D. P. J.* 186, 25; Ditte, *C. R.* 73, 111, 191, 270). $[Mg,O^2,H^2] = 217,320$; $[Mg,O,H^2O] = 148,960$ (*Th.* 3, 243). Soluble c. 100,000 parts water; MgO_2H_2Aq is feebly alkaline to litmus; with acids MgO_2H_2 reacts as a strong base, forming salts MgX_2, $X = Cl, NO_3, \frac{1}{2}SO_4, \frac{1}{3}PO_4$, &c.; $[MgO^2H^2,H^2SO^4Aq] = 31,220$; $[MgO^2H^2,2HNO^3Aq] = 27,520$; $[MgO^2H^2,2HClAq] = 27,690$ (*Th.* 3, 243) (*cf. Magnesium, oxide of*).

Magnesium, iodide of. MgI_2. Mol. w. unknown as V.D. has not been determined. Obtained by throwing I, in small quantities at a time, on to molten Mg (Lerch, *J. pr.* [2] 28, 338); reaction is very violent. A white, waxy solid; very deliquescent. A hydrate, $MgI_2.8H_2O$ according to Lerch (*l.c.*), is formed by the reaction between I and Hg under water (L.), or by dissolving *magnesia alba* in HIAq and evaporating over H_2SO_4; very deliquescent. MgI_2 is decomposed by heating in air, giving off I, and forming MgO; heated in O it is entirely changed to MgO (Schulze, *J. pr.* [2] 21, 407). MgI_2 forms *double compounds* with KI and NH_4I (Lerch, *l.c.*). The following table is given by Kremers (*P.* 108, 118):—

P.c. MgI_2	S.G. MgI_2Aq at 19°	P.c. MgI_2	S.G. MgI_2Aq at 19°
5	1·043	35	1·395
10	1·088	40	1·474
15	1·139	45	1·568
20	1·194	50	1·668
25	1·254	55	1·780
30	1·320	60	1·915

Magnesium, nitride of. Mg_3N_2. Mol. w. unknown, as V.D. has not been determined. Obtained in small transparent crystals by Deville a. Caron in making Mg. Briegleib a. Geuther (*A.* 123, 236) prepared Mg_3N_2 by heating Mg turnings in a stream of dry pure N. Mg_3N_2 is also formed, according to Mallet (*C. N.* 38, 39), when Mg is heated in a small quantity of air. Prepared by heating Mg in N, Mg_3N_2 is an amorphous, greenish-yellow, powder; becomes brown on heating. Heated in air it is slowly oxidised to MgO; the oxidation is rapid when O is substituted for air. With water, forms MgO and NH_3. With dilute acids, forms Mg salts and NH_4 salts. Heated in HCl, $MgCl_2$ and NH_4Cl are formed. Heated in dry H_2S, MgS and $(NH_4)_2S$ are slowly formed. Heated to redness in CO or CO_2, MgO, C, and C_2N_2 are produced. PCl_5 vapour reacts to form $MgCl_2$ and P nitride.

Magnesium, oxide of. MgO. (*Magnesia.*) Mol. w. unknown, as compound has not been gasified. S.G. 3·642 at 12° (Cossa, *B.* 10, 1747); S.G. crystallised 3·636 (Ebelmen, *J.* 4, 15); for S.G. of MgO heated to temperature from 350° to bright redness *v.* Ditte, *C. R.* 73, 111, 191, 270.

A new medicine was introduced in Rome in the beginning of the eighteenth century; the name *magnesia alba* given to it is supposed to have been suggested as a distinction from *magnesia nigra*, a term then applied to *pyrolusite*, MnO_2. The preparation of the new medicine was kept secret. In 1709 Slevogt showed that *magnesia alba* could be obtained by ppg. the mother-liquor from the preparation of saltpetre by K_2CO_3. *Magnesia alba* was supposed to be the same as lime, but Hoffmann found that some of its reactions differed from those of this compound. In 1755 Black demonstrated *magnesia alba* to be a compound of CO_2 with a new earthy base, to which he gave the name magnesia.

Occurrence.—MgO occurs as *periclase*; crystallised in regular octahedra; S.G. 3·67; usually coloured green from presence of a little FeO.

Formation.—1. By adding NaOHAq or KOHAq to solution of a Mg salt, washing, and strongly heating the pp. of MgO_2H_2.—2. By calcining *magnesia alba*, a basic Mg carbonate obtained by ppg. a Mg salt by an alkaline carbonate (*v.* CARBONATES, vol. i. p. 699).—3. By burning Mg in O.—4. By decomposing $MgCl_2Aq$ by calcined dolomite; $MgCl_2Aq + CaO.MgO = 2MgO + CaCl_2Aq$.—5. In crystals same as *periclase*, by strongly heating powdered MgO in a slow stream of HCl gas (Deville, *A.* 120, 183); also by heating powdered MgO in a porcelain oven (H. Rose).

Preparation.—1. A boiling solution of pure $MgSO_4.7H_2O$ is ppd. by Na_2CO_3Aq; after boiling for a little the pp. is washed and dried, and the product $(4MgCO_3.MgO_2H_2.xH_2O)$ is calcined in a Pt vessel until every trace of CO_2 and H_2O is removed.—2. *Magnesia alba* is treated with enough dilute HNO_3Aq to dissolve nearly but not quite all; after standing for some time in the air with frequent stirring, to ppt. $Fe_2O_3.xH_2O$, the liquid is filtered; the filtrate is mixed with a little pure $MgSO_4$, alcohol is added, and, after digesting for some time with pure $CaSO_4$, the liquid is evaporated to crystallisation, and again filtered; finally the filtrate is evaporated to dryness, the $Mg(NO_3)_2$ thus obtained is calcined, the residue is very thoroughly washed, and again calcined (Wurtz). (For preparation of pure MgO from *magnesite* *v.* Caron, *C. R.* 66, 840.)

Properties.—A white powder, more or less flocculent according to the temperature and length of time it has been heated. MgO absorbs water and CO_2 from the air, slowly forming $MgCO_3.xMgO_2H_2.yH_2O$. It is slightly soluble in water; 1 part requires 55,368 cold or hot water for solution according to Fresenius, 100,000 to 200,000 according to Bineau. The solution of MgO is feebly alkaline to litmus. When very strongly heated MgO does not melt but gives out a very clear white light. Made into a paste with a little water, MgO sets to a hard, white mass (Deville, *C. R.* 61, 975); MgO which has been heated to whiteness does not set with water (*v.* Knapp, *D. P. J.* 202, 513; Schwarz, *D. P. J.* 186, 25). MgO reacts with acids as a strong base

forming salts MgX_2, X = Cl, NO_3, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c.

Reactions.—1. With *water* to form the hydroxide MgO_2H_2.—2. Heated with *ammonium chloride* NH_3 is evolved and $MgCl_2$ formed.—3. With *acids* MgO reacts as a strong base forming salts MgX_2, X = Cl, $\frac{1}{2}SO_4$, &c.—4. With *salts of heavy metals* MgO reacts similarly to CaO, BaO, and SrO, ppg. hydrated oxides.—5. With *carbon dioxide and water*, basic carbonates $MgCO_3.xMgO_2H_2.yH_2O$ are formed.—6. Suspended in water through which is passed a current of *hydrogen sulphide*, a solution of MgS_2H_2 is obtained (*v. Magnesium, hydrosulphide of*, p. 160).—7. Heated in carbon disulphide vapour, MgO.MgS is formed (Reichel, *J. pr.* [2] 12, 55).

Magnesium, oxychlorides of. When freshly heated MgO is moistened with $MgCl_2Aq$, S.G. 1·16 to 1·26, the whole sets to a firm, hard mass, which probably consists of a mixture of oxychlorides $xMgO.yMgCl_2$ (*v.* Sorel, *C. R.* 65, 102). By warming 30 parts MgO with 1500 parts $MgCl_2$ in solution, in an atmosphere free from CO_2, needle-shaped crystals slowly form; when washed free from $MgCl_2$, pressed, and dried over soda-lime, the crystals are $10MgO.MgCl_2.18H_2O$; dried at 110° they lose $4H_2O$ (Krause, *A.* 165, 38).

Magnesium, oxysulphide of. Mg_2OS(= MgO.MgS). An amorphous, reddish, solid; obtained, along with COS, by passing CS_2 vapour over heated MgO (Reichel, *J. pr.* [2] 12, 55).

Magnesium, phosphide of. Mg_3P_2. A hard, brittle, steel-grey solid; obtained by heating molten P with Mg in H (Parkinson, *C. J.* [2] 5, 127, 309), or in a sealed glass tube (Emmerling, *B.* 12, 152). Decomposed by water, evolving PH_3 and forming MgO; with acids gives Mg salts and PH_3.

Magnesium, salts of. *Compounds obtained by replacing H of acids by Mg.* The salts of Mg belong to one series, MgX_2, where X = Cl, NO_3, $\frac{1}{2}SO_4$, $\frac{1}{2}CO_3$, $\frac{1}{3}PO_4$, &c. A few basic salts, and many double salts, of Mg are known. $MgCO_3$, the basic carbonates and phosphates, and a few other salts are insoluble in water, but most of the Mg salts readily dissolve in water. The salts are usually prepared by dissolving MgO, MgO_2H_2, or $MgCO_3$, in the various acids, and evaporating, some are prepared by double decomposition from the soluble salts, generally from $MgSO_4$. As none of the salts of Mg has been gasified the formulæ given are not necessarily molecular, they are based on the results of analysis and considerations of the similarities between the salts of Mg, Zn, and Cd (*v.* MAGNESIUM GROUP OF ELEMENTS). The Mg salts are numerous, and as a class very definite and stable bodies; the following are the chief salts derived from oxyacids:—*bromate, carbonates, chlorate, dithionate, hypochlorite, hypophosphite, iodate, nitrate* and *-ite, perchlorate, iodates, phosphates* and *-ite, selenate* and *-ite, silicates, sulphate* and *-ite, tellurate* and *-ite, thiosulphate* (*v.* CARBONATES, NITRATES, SULPHATES, &c.).

Magnesium, selenide of. A flesh-coloured pp., probably a selenide of Mg, is obtained by adding K_2Se to solution of a Mg salt; the pp. is decomposed by heat, and by acids, with separation of Se (Berzelius).

Magnesium, silicides of. A compound of Mg and Si is prepared by placing a layer of fused and powdered NaCl in the bottom of a Hessian crucible, adding one-half of a mixture of $2\frac{1}{2}$ parts NaCl and 7 parts Na_2SiF_6, then $2\frac{1}{2}$ parts Mg, and then the other half of the mixture of NaCl and Na_2SiF_6, covering the whole with NaCl, and heating in a wind-furnace; when the reaction is completed the contents of the crucible are stirred with a porcelain rod, and allowed to cool. The regulus formed at the bottom of the crucible is a mixture of Mg and Mg silicide; by washing with NH_4ClAq the Mg is dissolved out (Geuther, *J. pr.* 95, 424). As thus prepared the silicide has the composition Mg_5Si_3. It forms metal-like, lustrous crystals. Reacts with HClAq to form $MgCl_2$, SiH_4, H_2SiO_3, and H. This substance may be a compound, or a mixture, of Mg_2Si and MgSi ($Mg_5Si_3 = 2Mg_2Si + MgSi$). A silicide Mg_2Si is obtained by pulverising, in a warm mortar, 40 parts fused $MgCl_2$, 35 parts Na_2SiF_6, 10 parts NaCl, adding 20 parts Na in small pieces, and projecting the mixture into a hot Hessian crucible. After fusion and cooling, the greyish-black mass in the crucible is found to contain metal-like tablets and globules; these consist of Si and Mg_2Si; by treating with HClAq Si remains and SiH_4 is evolved (Wöhler, *A.* 107, 113; *cf.* Martius, *A.* 107, 112).

Magnesium, silicofluoride of. $MgSiF_6$; said to be obtained as a gum-like, very soluble substance, by dissolving MgO in H_2SiF_6Aq (Berzelius).

Magnesium, sulphydrate of, *v. Magnesium, hydrosulphide of*, p. 160.

Magnesium, sulphides of. MgS has been isolated; polysulphides, probably MgS_3, MgS_4, and MgS_5, seem to exist in the solution obtained by warming MgS with S and H_2O.

MAGNESIUM MONOSULPHIDE, MgS. Produced by passing H laden with S vapour over red-hot Mg (Reichel, *J. pr.* [2] 12, 55; *cf.* Parkinson, *C. J.* [2] 5, 125, 309). According to Fremy, MgS is formed, along with CO_2, when MgO is strongly heated in dry H_2S; but Reichel (*l.c.*) says that the products of this reaction are MgO.MgS and COS. MgS is also said to be formed, along with $(NH_4)_2S$, by heating Mg_3N_2 in dry H_2S (Brieglieb a. Geuther, *A.* 123, 236). Fremy (*A. Ch.* [5] 38, 324) gives [Mg,S] = 39,800. MgS is formed, but only in very small quantity, by strongly heating $MgSO_4$ with C. Alkaline sulphides do not ppt. MgS, but MgO_2H_2, from solutions of Mg salts.

MgS, formed by heating Mg and S, is described as a yellowish-grey amorphous, or as a reddish-brown crystalline, mass; analysis always gives rather more S than required by MgS. With water, MgS is decomposed to MgO_2H_2 and MgS_2H_2Aq, the latter being afterwards converted into MgO_2H_2 and H_2S.

MAGNESIUM POLYSULPHIDES. By warming, not boiling, MgS and S with water, a dark yellow solution is obtained, containing Mg and S in a ratio varying from Mg:3S to Mg:5S (Reichel, *J. pr.* [2] 12, 55). The solution decomposes in air, giving off H_2S and ppg. MgO_2H_2 and S.

Magnesium, sulphocyanide of; $Mg(SCN)_2.4H_2O$; *v.* vol. ii. p. 350.

M. M. P. M.

MAGNESIUM ETHIDE $Mg(C_2H_5)_2$. Magnesium filings act rapidly on ethyl iodide, gas

containing ethylene being given off. If the product be heated in a sealed tube at 125° the contents solidify to a white mass which on distillation leaves a residue of MgI_2 and a distillate which may be separated by fractional rectification into EtI and $MgEt_2$ (Cahours, *A.* 114, 227, 354; Hallwachs a. Schafarik, *A.* 109, 215). Colourless liquid with strong alliaceous odour, boiling at a higher temperature than EtI. Takes fire in air. Violently decomposes water.

MAGNESIUM GROUP OF ELEMENTS—*Beryllium*, *Magnesium*, *Zinc*, *Cadmium*, *Mercury*. Of these five metals, only Zn and Hg are found native, and these in small quantities. Be occurs chiefly as silicate in combination with Al silicate, not widely distributed; Mg salts, especially $MgCO_3$ and $MgSO_4$, are found in large quantities; the chief ores of Zn are $ZnCO_3$ and ZnS, they occur fairly widely distributed and in considerable quantities; small quantities of CdS and $CdCO_3$ accompany many Zn ores; the chief ore of Hg is HgS, which is found only in a few localities. Be is classed with the rare elements; approximately pure Be was not prepared until 1885. Mg was obtained by Davy, in small quantity and impure, in 1800; in 1830 Bussy prepared the metal in a state of approximate purity. Although brass has been made for very many centuries, yet it was not till the middle of the eighteenth century that the art of preparing metallic Zn was known in Europe. Cd was discovered and prepared in 1817 by Stromeyer. Hg has been known certainly from the beginning of the Christian era.

Be and Mg are prepared by reducing the chlorides MCl_2 by Na or K; ZnO and CdO are reduced by heating with C; Hg is prepared from HgS by heating with CaO, whereby CaS and $CaSO_4$ are formed and Hg is vapourised, or by heating with scrap iron, when FeS, SO_2, and Hg are produced.

The following table presents some of the prominent physical and chemical properties of the magnesium metals:—

	Beryllium	Magnesium	Zinc	Cadmium	Mercury
Atomic weights	9·08	24	64·9	111·7	199·8
	One or more compounds of each element, except Mg, have been gasified. Specific heats have been directly determined. Molecular weights of Zn, Cd, and Hg, and probably also of Mg, are the same as the atomic weights.				
Melting-points (approx.)	—	700°–800°	430°	320°	−39°
Sp. gr. (approx.)	1·85	1·7	7·2	8·7	13·5
Sp. heats (approx.)	·62	·245	·094	·056	·033
$\frac{At.\ w.}{Sp.\ gr.}$ (approx.)	4·92	14·1	9	12·8	14·8
Occurrence and preparation	Double silicate of Be and Al, and a compound of BeO and Al_2O_3, occur in a few rocks in small quantities. Prepared by reduction of molten $BeCl_2$ by Na; *not* by electrolysis of $BeCl_2$.	$MgCO_3$, $MgSO_4$, $MgCl_2$, and Mg silicates occur in large quantities and widely distributed. Prepared by reducing molten $MgCl_2$ by Na; also by electrolysis of $MgCl_2$.	ZnO, ZnS, and $ZnCO_3$ are fairly widely distributed; Zn found native in small quantities. Prepared by reducing ZnO by C at moderately high temperature.	Compounds frequently found accompanying Zn ores. Prepared by reducing CdO by C.	Hg found native in small quantities. Chief ore is HgS; found in a few localities in fair quantity. Prepared by heating HgS in air, or with Fe, or CaO, and condensing Hg.
Physical properties	Steel-coloured, hard, hexagonal crystals; lustrous.	Silver-white, very lustrous; moderately hard; malleable; not very tenacious. Crystallises in hexagonal forms, isomorphous with Zn. Melts at temp. much higher than M.P. of Cd or Zn; has not been gasified at white heat.	White, with tinge of blue; crystallises in hexagonal forms; soft; brittle at ordinary temperatures, malleable at 100°–150°, brittle again at 200°. Flexibility varies with temp. Melts at c. 430°; can readily be distilled.	White, with slight tinge of blue; crystallises easily in regular forms; soft, but harder than Zn; very malleable, ductile, and flexible. Vapour is yellow. Melts at moderate temperature, c. 320°; distils at lower temp. than Zn.	Liquid metal at temps. above −39°; white, showing faint tinge of blue when compared with Ag; very lustrous. Crystallises in regular octahedra. Boils at c.350°. Volatilises even at very low temperatures.

TABLE—*cont.*

	Beryllium	Magnesium	Zinc	Cadmium	Mercury
Chemical properties	Scarcely changed by heating in air or O; burns in O-H flame to BeO. Scarcely acted on by S at red heat. Burns in Cl to $BeCl_2$. Dissolves slowly in acids to form salts. Only one series of salts known, BeX_2, where X = Cl, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c. Dissolves slowly in alkali solutions, evolving H. Distinctly positive metal; does not show allotropy; BeO has no acidic properties. Atom of Be is divalent in gaseous molecules.	Unchanged in dry air; heated in air, or O, burns to MgO. Decomposes hot water slowly; burns when heated in steam, forming MgO. Decomposes CO_2 at red heat. Combines directly with halogens S, P, As, and N. Dissolves in acids to form salts. Only one series of salts is known, MgX_2, X = Cl, $\frac{1}{2}SO_4$, &c. MgO_2H_2 is a strong base; compounds of Mg do not show any acidic properties. Valency of atom of Mg not certainly known, as no binary haloid compounds have been gasified. Mol. w. probably same as at. w.	Unchanged in air; heated strongly in air, or O, burns to ZnO. Decomposes steam at red heat. Combines directly with halogens, but not with S. Slowly soluble in alkali solution, with evolution of H. Dissolves in acids to form salts. One series of salts known, ZnX_2, X = Cl, &c. ZnO_2H_2 dissolves in alkalis, but is ppd. again on evaporation over H_2SO_4 *in vacuo*. There are indications of existence of a hydride of Zn. Atom of Zn is divalent in gaseous molecules. Mol. w. same as at. w.	Slowly oxidised on surface in air; heated in air or O, burns to CdO. Cd vapour and steam heated together form H and CdO. Combines directly with halogens, also with S and P. Dissolves in acids to form salts. Only one series of salts known, CdX_2, X = Cl, &c. CdO_2H_2 is not soluble in alkalis. No compound of Cd shows any acidic properties. Atom of Cd is divalent in gaseous molecules. Mol. w. same as at. w.	Unchanged in air; heated nearly to B.P. is slowly oxidised to HgO. Does not decompose water or steam. Combines directly with halogens and S. Dissolves in acids to form salts. Two series of salts are known, HgX and HgX_2, X = Cl, &c.; salts of both series are numerous and stable. HgO dissolves in molten KOH to form $K_2O.2HgO$; HgS dissolves in Na or K sulphide solution to form compounds $xNa_2S.yHgS$. Hg forms very many ammonio-compounds. Atom of Hg is mono- and di-valent in gaseous molecules. Mol. w. same as at. w.

General formulæ and character of compounds. Oxides:—MO; also in case of Hg, Hg_2O. Hydroxides:—MO_2H_2. Sulphides:—MS; also in case of Hg, Hg_2S. Haloid compounds:—MX_2; also in case of Hg, HgX. Salts:—MX_2; also in case of Hg, MX; X = NO_3, ClO_3, $\frac{1}{2}CO_3$, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c.

The *oxides* MO are basic; they react with acids to form salts MX_2, X = NO_3, $\frac{1}{2}SO_4$, &c. MgO reacts with water to form MgO_2H_2; the other hydroxides MO_2H_2 are formed by ppg. solutions of salts by alkalis. HgO shows feebly marked acidic properties; it dissolves in molten KOH, and the compound $2HgO.K_2O$ is obtained on cooling. ZnO_2H_2 is sol. KOHAq, but is reppd. on evaporation *in vacuo* over H_2SO_4. Mercurous oxide Hg_2O is the only representative of the class M_2O; it is very easily resolved into Hg and HgO; it reacts with dilute acids, in the cold, as a basic oxide, forming salts HgX. Hg_2O in some respects resembles Cu_2O and Ag_2O, and exhibits the relations of Hg to the copper group (*v.* Copper group of elements, vol. ii. p. 250).

The *hydroxides* MO_2H_2 are all decomposed by heat to MO and H_2O; HgO_2H_2 if it exists is extremely easily separated into its oxide and H_2O; the only hydroxide obtained by direct reaction between MO and H_2O is MgO_2H_2. The hydroxides are basic; MgO_2H_2 is slightly alkaline.

The *sulphides* MS are basic. The existence of BeS is extremely doubtful; MgS is readily decomposed by water, giving MgS_2H_2Aq, and finally MgO_2H_2 and H_2S; ZnS, CdS, and HgS are more stable than MgS; HgS shows slightly acidic properties, it dissolves in K_2SAq or Na_2SAq to form compounds $xK_2S.yHgS$. Mercurous sulphide Hg_2S is very easily decomposed to HgS and Hg.

The *haloid compounds* MX_2 may be obtained by the direct union of the elements; the mercurous compounds HgX are also obtained in this way. MX_2 and HgX are also prepared by dissolving the corresponding oxides in HXAq and evaporating; but $MgCl_2$ cannot be thus obtained, as evaporation towards dryness of $MgCl_2Aq$ results in formation of HCl and MgO mixed with oxychlorides $xMgO.yMgCl_2$. The compounds

$BeCl_2$, $BeBr_2$, $ZnCl_2$, $CdBr_2$, $HgCl_2$, HgI_2, and probably HgCl, have been vapourised without decomposition. The haloid compounds form many double compounds. They all combine with NH_3; various ammonio-derivatives of HgX_2 and HgX are known. Numerous *oxyhaloid compounds*, $xMO.yMX_2$, are known.

The *salts* MX_2 are numerous and well marked; they are obtained by dissolving the corresponding oxides or carbonates in acids, and evaporating. Mercurous salts HgX are prepared by digesting excess of Hg with the various acids in the cold. Many basic salts of Be, Zn, and Hg have been prepared; most of the salts of Mg are normal.

The five metals Be, Mg, Zn, Cd and Hg belong to Group II., as the elements are arranged in accordance with the periodic law. The following table shows their positions in the Group:—

Even Series.

2	4	6	8
Be = 9	Ca = 40	Sr = 87	Ba = 137

Odd Series.

3	5	7	9	11
Mg = 24	Zn = 65	Cd = 112	—	Hg = 200

The properties of Be, the first member of the group, suggest those both of the even and odd series members. Physically it approaches Mg, Zn, and Cd more than Ca, Sr, and Ba; in the conditions under which it is oxidised, the basic but non-alkaline character of its hydroxide, the existence of many basic salts, &c., Be shows closer resemblances to Zn, Cd, and Hg than to Ca, Sr, and Ba. The solubility of BeO_2H_2 in KOHAq also suggests the solubility of ZnO_2H_2 in KOHAq, and of HgO in molten KOH; the hydroxides of Ca, Sr, Ba, and Mg are quite insoluble in alkalis. Mg is closely related in many respects to the metals of the alkaline earths, Ca, Sr, and Ba; but its much greater stability in air, its non-decomposition of cold water, the easy resolution of its hydroxide into MgO and H_2O by heat, &c., exhibit the analogies between Mg and Zn, Cd, Hg. Sulphides of Ca, Sr, and Ba are readily formed, but MgS is only produced by heating Mg to redness in H laden with S vapour; the difficulty of forming MgS recalls the non-isolation of any compound of Be and S. Alkali carbonate solutions ppt. MCO_3 from solutions of salts of Ca, Sr, and Ba; but the pps. obtained from Mg salts are basic carbonates $xMgCO_3.yMgO_2H_2$. The sulphates of Ca, Sr, and Ba are reduced to MS by heating with C, but $MgSO_4$ is scarcely, if at all, reduced in this way. Hg is distinguished from the other members of the magnesium family by its physical properties, the formation of two series of salts, the formation of a large number of ammonio-derivatives of both series of Hg salts, and in other ways.

In the composition of their salts, and sometimes in the isomorphism of salts, the metals of the Mg family resemble those of the Fe family, viz. Mn, Fe, Ni, Co (*v.* IRON GROUP OF ELEMENTS, p. 65). For a further treatment of the elements of Group II. *v.* CLASSIFICATION, vol. ii. pp. 204-207; *cf.* also ALKALINE EARTHS, METALS OF THE, vol. i. p. 112.

M. M. P. M.

MAGNETIC ROTATORY POWERS *of liquid compounds*; *v.* PHYSICAL METHODS, section *Optical methods.*

MAIROGALLOL $C_{18}H_7Cl_{11}O_{10}$ (?) [190°]. (From μαίρω, I glitter). Obtained, together with leucogallol, by passing chlorine through pyrogallol (15 g.) dissolved in 60 p.c. acetic acid (45 g.) until the liquid is brown, and allowing the liquid to stand (Groves, *A.* 179, 237; Stenhouse a. Groves, *C. J.* 28, 706; Webster, *C. J.* 45, 208). Trimetric prisms, insol. water, v. sol. hot alcohol, extremely sol. ether, insol. CS_2 and petroleum ether. Decomposed by boiling with water yielding CO, oxalic acid, and tri-chloro-pyrogallol. Reduced by zinc and H_2SO_4 to tri-chloro-pyrogallol (Webster, *C. J. Proc.* 3, 130; Hantzsch a. Schniter, *B.* 20, 2033). Boiling with dilute H_2SO_4 gives a condensation product, and also a substance that is ppd. from aqueous solution by gelatin. Aqueous $NaHSO_3$ and zinc-dust reduce it to tri-chloro-pyrogallol and an amorphous substance which yields furfuraldehyde when distilled with dilute H_2SO_4. Mairogallol gives a crimson colour with solution of sodium sulphite (Cross a. Bevan, *C. J.* 43, 18). Mairogallol when gradually heated gives a sublimate of tri-chloro-quinone and tetra-chloro-quinone. These reactions indicate that mairogallol is derived by condensation from $CO\left<\begin{matrix}C(OH)_2.C(OH)_2\\CCl{=\!=}CCl\end{matrix}\right>CCl_2$ (Webster).

MALACHITE GREEN *v.* TETRA-METHYL-DI-AMIDO-TRI-PHENYL-CARBINOL.

MALAMIC ACID *v.* MALIC ACID.

MALEÏC ACID $C_4H_4O_4$ *i.e.* $CO_2H.CH:CH.CO_2H$. Mol. w. 116 (confirmed by Raoult's method, Paternò, *B.* 21, 2158). [130°]. R_∞ 38·6 (in a 6·9 p.c. aqueous solution; Kanonnikoff, *J. pr.* [2] 31, 347; *cf.* Knop, *A.* 248, 175). H.C. v. 331,702 (Louguinine, *C.R.* 106, 1290). H.C. v. 326,900 (Stohmann, Kleber a. Langbein, *J. pr.* [2] 40, 217). H.C. p. 326,300 (S. K. a. L.). H.F. 187,700 (S. K. a. L.). *Heat of solution*: −4,438 (Gal a. Werner, *Bl.* [2] 47, 158). *Heat of neutralisation*: 26,648 (G. a. W.).

Formation.—1. Together with fumaric acid (*q. v.*) by the distillation of malic acid (Lassaigne, *A. Ch.* [2] 11, 93; Pelouze, *A. Ch.* [2] 56, 72; Liebig, *A.* 11, 276; Buchner, *A.* 49, 57; Kekulé, *A. Suppl.* 1, 129; 2, 85; Von Richter, *Z.* [2] 5, 453).—2. By heating silver succinate at 180° (Bourgoïn, *C. R.* 72, 52).—3. By saponification of the ether obtained from di-chloro-acetic ether by heating with reduced silver at 220°, or by the action of sodium upon its ethereal solution in the cold (Tanatar, *B.* 12, 1563).—4. By the action of KCN on α-di-bromo-propionic acid (Tanatar, *B.* 13, 159).—5. From (δ)-bromo-pyromucic acid and dilute HNO_3 (Hill a. Sanger, *A.* 232, 55).—6. By the action of baryta on tri-chloro-phenomalic acid $\left(\begin{matrix}CH.C(OH).CCl_3?\\ \| \qquad >O\\ CH.CO\end{matrix}\right)$.

Preparation.—Malic acid is rapidly distilled until the residue thickens, the flame being then withdrawn; the distillation then continues by itself until the residue is solid (fumaric acid). The distillate consists of maleïc acid and maleïc anhydride, and may be wholly converted into maleïc anhydride by AcCl. The maleïc anhydride may be purified by crystallisation from

HOAc and then converted by hot water into maleïc acid (Anschütz, *B.* 12, 2281; *cf.* Perkin, *B.* 14, 2547).

Properties.—Monoclinic prisms. V. sol. water and alcohol, m. sol. ether. Its aqueous solution reddens litmus strongly. Begins to boil at 160°, being then restored into maleïc anhydride and water, which partially re-unite in the receiver. An aqueous solution of maleïc acid is ppd. by baryta (difference from fumaric acid). Unlike fumaric acid, maleïc acid is not ppd. by adding mineral acids to solutions of its salts.

Reactions.—1. Reduced by water and *sodium amalgam* to succinic acid. *Zinc* added to an aqueous solution of maleïc acid yields zinc maleate and succinate.—2. Calcium maleate *fermented* in contact with cheese also changes to succinate (Dessaignes).—3. *Electrolysis* gives acetylene, succinic acid, and a small quantity of fumaric acid (Kekulé, *A.* 130, 1).—4. Combines readily with *bromine* in the cold, forming iso-di-bromo-succinic acid and some di-bromo-succinic acid derived from fumaric acid into which a portion of the maleïc acid is at the same time transformed (Kekulé; Petri, *A.* 195, 59). *Chlorine* gives a di-chloro-succinic acid (Petrieff, *Bl.* [2] 41, 309). Bromine in presence of water forms iso-di-bromo-succinic, bromo-fumaric, bromo-succinic, and fumaric acids (Wislicenus, *A.* 246, 53).—5. Dissolves easily in aqueous HBr, the solution even at 0° soon depositing fumaric acid and bromo-succinic acid in equimolecular proportions. The bromo-succinic acid may easily be extracted from the product by water (Fittig a. Dorn, *B.* 9, 1191).—6. Converted into fumaric acid by boiling conc. HIAq, HBrAq, dilute HNO_3, or HClAq (Kekulé, *A. Suppl.* 1, 134; 2, 93; Kekulé a. Strecker, *A.* 223, 186). When HIAq is used the ultimate product is succinic acid. Dry HCl does not convert maleïc acid into fumaric. Maleïc acid is converted into fumaric acid by heating its aqueous solution at 100°-130° (Semenoff, *Bl.* [2] 46, 816). An aqueous solution of sodium maleate is not affected by being heated for 10 hours in a sealed tube at 100° to 135°.—7. With *hypochlorous acid* it forms a compound which reduced by sodium amalgam yields inactive malic acid, oxymaleic acid (?), and a liquid which breaks up on heating into CO_2 and $C_6H_{10}O_5$ (Petrieff).—8. $KMnO_4$ oxidises it to inactive tartaric acid.—9. Alcoholic NH_3 at 150° slowly forms aspartic acid (Engel, *C. R.* 104, 1805).—10. The acids of the *maleic series* readily split off H_2O from their acid aniline salts, when the aqueous solution of the latter is left to stand for several days or boiled; a crystalline pp. being formed of the acid anilide $X''\!<\!\begin{smallmatrix}CONHPh\\CO_2H\end{smallmatrix}$ or of an isomeride thereof. Under the same conditions the acid aniline salts of the acids of the *fumaric series* are quite stable. This constitutes a ready method of determining to which of the two isomeric series a given acid belongs. The acid is half neutralised with aniline and either left to stand or heated to boiling, if a pp. is obtained insoluble in dilute HCl the acid belongs to the maleïc series (Michael, *B.* 19, 1372).

Salts.—K_2A'' (dried at 100°). Radiating crystals; v. sol. water, insol. alcohol.—$KHA''\frac{1}{2}aq$: small crystals; v. sol. water. The solution reddens litmus.—Na_2A'': needles. Ppd. as a granular crystalline powder by adding alcohol to its aqueous solution. Is not deliquescent.—$NaHA''3aq$. Triclinic crystals (Bodewig, *J.* 1881, 716). Sl. sol. cold water.—$KNaA''aq$: deliquescent crystalline powder (Büchner, *A.* 49, 60).—$BaA''2aq$: gelatinous pp., changing to scales. S. 11 at 20° (Regnault).—$BaA''aq$ (Anschütz).—$BaH_2A''_25aq$: indistinct crystals, which redden litmus; v. sol. water (Büchner).—$CaA''aq$ (dried at 100°): small needles, sol. water.—$CaH_2A''_25aq$: long prisms, v. sol. water, insol. alcohol.—$SrA''5aq$: silky needles.—$SrH_2A''_28aq$: rectangular prisms. — $MgA''3aq$. — $MgH_2A''_26aq$: hard crystals, v. sol. water, insol. alcohol.—$ZnA''2aq$: crystals, v. sol. water, insol. alcohol.—$NiA''aq$: apple-green crystals. — CuA'': light-blue crystals, sl. sol. boiling water, v. sol. NH_3Aq, forming a solution whence alcohol ppts. an azure-blue crystalline powder.—$PbA''3aq$: amorphous pp., changing to needles.—$Pb_2A''O$ (dried at 100°; Otto, *A.* 127, 178).—Ag_2A'': white pp., changing to lustrous needles.—$AgHA''$ (dried at 100°): needles.

Acid aniline salt $C_6H_5NH_3HA''\frac{1}{2}aq$: prisms, sol. water. On allowing the solution to stand for some days it forms phenyl-aspartic acid $C_6H_5NH.C_2H_3(CO_2H)_2$ [132°] (Anschütz a. Wirtz, *A.* 239, 140; *cf.* Michael, *B.* 19, 1373; *Am.* 9, 183, 197).—The neutral aniline maleate when boiled in aqueous solution deposits the phenylimide of phenyl-aspartic acid $C_6H_5NH.C_2H_3\!<\!\begin{smallmatrix}CO\\CO\end{smallmatrix}\!>\!NC_6H_5$, a body [212°] which was formerly described as the di-anilide of maleïc acid $C_2H_2(CONHPh)_2$.

Phenyl-imide $C_2H_2\!<\!\begin{smallmatrix}CO\\CO\end{smallmatrix}\!>\!NC_6H_5$. [91°]. (162° at 12 mm.). Formed by the dry distillation of acid aniline malate (Anschütz a. Wirtz, *Am.* 9, 238; *cf.* Michael a. Wing, *Am.* 7, 280). Long yellow needles; v. sol. benzene, $CHCl_3$ ether, and alcohol; sl. sol. CS_2 and ligroïn. Its solution in chloroform takes up bromine, forming the phenyl-imide of di-bromo-succinic acid [159°]. Baryta-water at 40° gives the acid anilide of fumaric acid.

Mono-methyl ether HMeA''. Probably exists in the solution of maleïc anhydride in MeOH. Such a solution becomes hot when mixed with NaOMe, probably forming NaMeA'', but the solution presently deposits a bulky white, partly crystalline, pp., which forms an alkaline aqueous solution, becoming neutral on boiling; the neutral solution contains the methyl derivative of sodium methyl malate

$C_2H_3(OMe)(CO_2Na)(CO_2Me)$

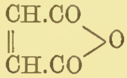
(Purdie, *C. J.* 47, 873).

Di-methyl ether Me_2A''. (205° i.V.). S.G. $\frac{14}{}$ 1·153. H.C. 669,570 (Ossipoff, *C. R.* 109, 312). From silver maleate and MeI, excess of iodine being avoided, as this would convert it into di-methyl fumarate (Anschütz, *B.* 12, 2282). Bromine effects the same change.

Mono-ethyl ether HEtA''. From the anhydride and boiling alcohol. Also from HAgA'' and EtI (Ossipoff, *J. R.* 20, 254). Not identical with the mono-ethyl ether of fumaric acid. Forms a salt NaEtA''. By treating HEtA'' with NaOEt and boiling the product with water $C_2H_3(OEt)(CO_2Et)(CO_2Na)$ is obtained, identical with that derived from fumaric acid (Purdie).

Di-ethyl ether Et_2A''. (225° i. V.). From Ag_2A'' and EtI (Anschütz, *B.* 11, 1644; 12, 2281). Vapour density corresponds to the formula (O.). Colourless liquid. Converted by iodine into the fumaric ether. Bromine gives di-bromo-succinic ether. Boiling with NaOMe forms a product whence boiling water produces $C_2H_3(OMe)(CO_2Et)_2$ (Purdie, *C. J.* 47, 868).

Di-isopropyl ether Pr_2A''. Vapour density corresponds to the formula.

Anhydride $C_4H_2O_3$ *i.e.*  [53°] (Anschütz); [57°] (Pelouze, *A. Ch.* [2] 56, 72); [60°] (Fittig, *A.* 188, 87). (202° i.V.). (A.) V.D. 48 (H = 1) (calc. 49) (Hübner a. Schreiber, *Z.* [2] 7, 712). H.C. 336,920 (Ossipoff, *C. R.* 109, 311). Appears to be the sole anhydride of both maleïc and fumaric acids.

Formation.—1. By rapidly distilling maleïc or fumaric acid, and frequently rectifying the product (Pelouze, *A.* 11, 263; Kekulé, *A. Suppl.* 2, 87). *In vacuo*, maleïc acid splits up into water and anhydride even at 100° (Reicher, *R. T. C.* 2, 312).—2. By heating fumaric acid with AcCl and HOAc at 100°.—3. From silver fumarate and fumaryl chloride (Perkin, *B.* 14, 2545).—4. By distilling chloro- or bromo- succinic anhydride (Anschütz a. Bennert, *B.* 15, 643).—5. By distilling malic anhydride.

Preparation.—1. Malic acid is treated with an excess of acetyl chloride, and the product (which probably chiefly consists of acetyl-malic anhydride) is distilled, when it splits up into acetic acid and maleïc-anhydride; the yield is 45 p.c. (Perkin, *C. J.* 39, 562; *B.* 14, 2547).—2. By dry distillation of malic acid and treatment of the residue and distillate with AcCl; the yield is 56 p.c. of the theoretical (Anschütz, *B.* 12, 2281).

Properties. — Trimetric crystals, $a:b:c$ = ·6408:1: ·4807 (Bodewig, *B.* 14, 2788). In contact with water it is converted into maleïc acid, which is conveniently prepared in this way. The abnormal rapidity of the etherification of maleïc acid by heating with alcohols appears to be due to an intermediate formation of anhydride (Reicher, *R. T. C.* 2, 308). Maleïc anhydride heated in a sealed tube at 260° gives a carbonaceous residue and gases (Semenoff, *Bl.* [2] 46, 816).

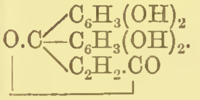
Reactions.—1. Unites with *bromine* at 100°, forming iso-di-bromo-succinic anhydride, which is resolved at 180° into HBr and bromo-maleïc anhydride.—2. PCl_5 gives the chloride of fumaric acid (Perkin, *B.* 14, 2548), but maleyl chloride (71° at 11 mm.) appears to be first formed (Anschütz a. Wirtz).—3. With a saturated solution of HCl in HOAc it forms at 100° chloro-succinic acid.—4. When heated with *phenyl-hydrazine* (1 mol.) at 150° it forms the phenyl-hydrazide $C_2H_2{:}C_2O_2{:}N_2HPh$, which crystallises in needles [259°], and turns brown at 180° (Hötte, *J. pr.* [2] 35, 295).—5. When heated with *phenols* it produces fluorescent compounds analogous to the phthaleïns, which may therefore be called '*maleïns*.' The resorcin-maleïn has a green fluorescence, (α)-naphthol-maleïn has a greenish-red fluorescence (Burckhardt, *B.* 18, 2864).

Constitution.—The constitution of fumaric and maleïc acids is discussed under FUMARIC ACID, vol. ii. p. 585. The anomalous formula $CO_2H.C.CH_2.CO_2H$ for maleïc acid, based on the formula $CO_2H.CBr_2.CH_2.CO_2H$, is rendered improbable by the observation that bromo-fumaric and not pyruvic acid is the product formed, together with CO_2, when barium iso-di-bromo-succinate is treated with moist Ag_2O in the dark (Demuth a. V. Meyer, *B.* 21, 264). Racemic acid is formed when silver iso-di-bromo-succinate is boiled with water. The representation of maleïc and fumaric acids by formulæ in space has been discussed by Wislicenus in his treatise *Ueber die raümliche Anordnung der Atome in organischen Moleculen.*

References.—AMIDO-, BROMO-, and CHLORO-MALEÏC ACIDS.

Allo-maleïc acid *v.* FUMARIC ACID.

MALEO-FLUORESCEÏN $C_{16}H_{12}O_6$ *i.e.*



Obtained by heating resorcin with maleïc anhydride (Lunge a. Burckhardt, *B.* 17, 1598). Small needles. Sol. alcohol, sl. sol. water. Dissolves in alkalis to a red solution, with a strong green fluorescence. With KOH, MeI, and MeOH it gives a dimethyl derivative, $C_{16}H_{10}Me_2O_6$, crystallising in red needles. AcCl in HOAc gives $C_{16}H_{10}Ac_2O_6$, crystallising from HOAc in yellowish needles, insol. water, $CHCl_3$, and benzene, sl. sol. alcohol (Burckhardt, *B.* 18, 2864).

MALEYL CHLORIDE *v. Chloride* of FUMARIC ACID.

MALIC ACID $C_4H_6O_5$ *i.e.* $CO_2H.CH_2.CH(OH).CO_2H$. Mol. w. 134. [100°]. S.G. $\frac{0}{0}$ 1·56 (Schröder, *B.* 12, 1611). S.G. of solutions (Schneider, *A.* 207, 262). *Heat of solution* −3148. *Heat of neutralisation* 24,919 (Gal a. Werner, *Bl.* [2] 46, 803). $[\alpha]_D = -3$ in dilute solutions; as the liquid becomes more concentrated it approaches +5·9.

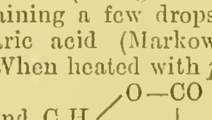
Occurrence.—Malic acid was discovered by Scheele in 1785, but its composition was first correctly determined by Liebig (*A.* 26, 166). It is very widely diffused in the vegetable kingdom, being contained in plants sometimes in the free state, sometimes in the form of potassium, calcium, or magnesium salt. It is found in abundance, together with citric acid, in unripe apples, in the fruits of the barberry, sloe, elder, and mountain ash, and in gooseberries, cherries, bilberries, strawberries, raspberries, and many other fruits. It is likewise found in the roots of marsh-mallow, angelica, aristolochia, bryony, liquorice, primrose, and madder; in carrots and potatoes; in the leaves and stems of aconite, belladonna, hemp, celandine, holy thistle, lettuce, tobacco, poppy, rue, sago, house-leek, tansy, thyme, valerian, and melilot; in the flowers of chamomile, elder, and mullein; in pine-apples and grapes; in the seeds of carraway, cumin, parsley, anise, flax, and pepper; in asafœtida, opoponax, and myrrh. It also occurs in the leaves of the common ash (Gintl, *Z.* [2] 5, 377), and in the fruit of the sumach (Reinsch, *Z.* 1866, 221). Yolk, the sweat of sheep, contains potassium malate to the extent of 2·5 p.c. of the solid residue (Buisine, *C. R.* 106, 1426).

Formation.—1. Malic acid, with the same

optical properties as those with which it exists in plants, may be formed from asparagine or active aspartic acid by treatment with nitrous acid (Piria, *A. Ch.* [3] 22, 160).—2. Malic acid, with a rotatory power equal and opposite to that contained in plants, may be obtained from ordinary tartaric acid by the action of phosphorus, iodine, and water (Dessaignes, *A.* 117, 134; Bremer, *Bl.* [2] 25, 6; *B.* 8, 861, 1594).

Preparation.—1. The juice of mountain-ash berries, not quite ripe, after being pressed, boiled up, and filtered, is partly neutralised with carbonate of potassium, leaving, however, a sufficient excess of acid to redden litmus pretty strongly; then precipitated by nitrate of lead; set aside for a few days, till the curdy precipitate is completely converted into small needles; these crystals freed from the admixed mucous or flocculent compound of lead oxide and colouring matter by careful elutriation with cold water, are, lastly, well washed with water. The needles of impure malate of lead are boiled with a slight excess of dilute sulphuric acid; the filtrate divided into two equal portions; one portion exactly neutralised with ammonia; the other portion then added, and the reddish liquid evaporated and cooled; it then yields nearly colourless crystals of acid malate of ammonia, which may be rendered quite colourless by recrystallisation. These crystals are then precipitated by acetate of lead, and the precipitate, after thorough washing, is decomposed by sulphydric or sulphuric acid (Liebig).—2. The juice is boiled for some time with milk of lime in quantity not quite sufficient for neutralisation, and the pp. poured into a boiling mixture of HNO_3 (1 pt.) and water (10 pts.). The acid calcium malate which crystallises out on cooling is recrystallised from water, dissolved in water, ppd. by lead acetate, and the lead malate decomposed by H_2S (Liebig, *A.* 38, 259). By similar processes malic acid may be obtained from house-leek, from cherries or barberries, from the berries of *Rhus coriaria*, from the stems of rhubarb, from apples, and from tobacco.

Properties.—The aqueous solution, concentrated to a syrup and left to evaporate in a warm place, yields groups of colourless shining needles or prisms of 4 or 6 faces. They melt at 83° (Pelouze) or 100° (Pasteur), and do not suffer any loss of weight at 120°. They deliquesce in the air, and are v. e. sol. water and alcohol. Dilute solutions of malic acid are lævorotatory, but the rotation changes so rapidly with concentration that concentrated solutions are dextrorotatory. These dextrorotatory solutions are rendered lævorotatory by the addition of H_2SO_4 or of HOAc. $[\alpha]_D = 5{\cdot}891 - {\cdot}0895q$ (where q = percentage of water in solution) (Schneider, *A.* 207, 263). Solutions of sodium malate containing about 54 pts. of the salt to 46 pts. of water are inactive at 20°; stronger solutions are lævorotatory, while more dilute solutions are dextrorotatory (Thomsen, *J. pr.* [2] 35, 153). Malic acid kills algæ (*Zygnemaceæ*) (Loew a. Bokorny, *J. pr.* [2] 36, 272). Malic acid prevents the ppn. of cupric and ferric salts by alkalis; 2 mols. holding 1 mol. of CuO in solution (Hofmeister, *A.* 189, 27; *cf.* Juette, *Fr.* 7, 489). A dilute solution of malic acid or of a malate is not immediately ppd. by lime-water or by $CaCl_2$ either in the cold or on heating; but on the addition of alcohol a white pp. of calcium malate separates (Braconnot, *A. Ch.* [2] 51, 331; H. Rose, *P.* 31, 210). However, a solution of malic acid (1 mol.) mixed with pure milk of lime (2 mols.) may solidify to a pasty mass (Iwig a. Hecht, *A.* 233, 171). A concentrated solution of an alkaline malate is ppd. by $CaCl_2$, but presence of NH_4Cl hinders the ppn., which, however, takes place on adding alcohol. Lead acetate gives a white pp., soluble in excess of malic acid and in ammonia; when the pp. is heated in the mother-liquid it melts to a semifluid translucent mass. Malates are not blackened by heating with fuming H_2SO_4. Dilute HOAc at 60° dissolves lead malate, but not lead tartrate or citrate (Hartsen, *Fr.* 14, 373; *Ar. Ph.* [3] 6, 110). Malic acid may be separated from oxalic and tartaric acids by ppg. the latter with $CaCl_2$, filtering, and ppg. calcium malate by adding alcohol to the filtrate (Barfoed, *Fr.* 7, 403). Ammonium malate may be separated from ammonium citrate, tartrate, and oxalate by solution in alcohol (Barfoed).

Reactions.—1. *Heated* for some hours at 140° it yields water and fumaric acid. At 180° it gives off water and maleïc anhydride, while fumaric acid remains as a solid residue. If the malic acid be suddenly heated to 200° and kept at that temperature a comparatively large quantity of maleïc anhydride is obtained. The maleïc anhydride, combining with the water in the distillate, is partially converted into maleïc acid. Malic acid is carbonised when suddenly exposed to a red heat.—2. By treatment with potash and *bromine*, bromoform is obtained (Cahours, *A. Ch.* [3] 19, 507).—3. *Nitric acid* easily oxidises it to oxalic acid and CO_2.—4. Conc. HIAq at 130° reduces it to succinic acid (Schmitt, *A.* 114, 106). Succinic acid is also formed when calcium malate is *fermented* in contact with yeast (Piria, *A.* 70, 102; Liebig, *A.* 70, 104, 363). Fermentation of calcium malate by certain *Schizomycetes* produces succinic, acetic, butyric, and propionic acids and ethyl alcohol (Fitz, *B.* 11, 1896; 12, 481; *cf.* Dessaignes, *C. R.* 28, 16; Liebig, *A.* 70, 104, 363; Kohl, *A.* 78, 252; Baer, *Ar. Ph.* [2] 69, 147; Winckler, *Jahrb. pr. Pharm.* 22, 300; Rebling, *Ar. Ph.* [2] 67, 300; Béchamp, *C. R.* 70, 999).—5. By slow oxidation in the cold with $K_2Cr_2O_7$ it is converted into malonic acid (Dessaignes, *A.* 107, 251).—6. When boiled in dilute aqueous solution with MnO_2 it yields a distillate containing aldehyde (Liebig, *A.* 113, 14).—7. Heated with KOH it yields acetic and oxalic acid.—8. When calcium malate (1 pt.) is heated with PCl_5 (4 pts.) the chloride of fumaric acid passes over (Perkin a. Duppa, *A.* 112, 24; Liès-Bodart, *A.* 100, 327).—9. Boiling aqueous H_2SO_4 at 135° gives aldehyde, CO_2, water, and CO (Weith, *B.* 10, 1744).—10. The *electrolysis* of potassium malate gives aldehyde, CO_2, and some acetic acid (Bourgoin, *Bl.* [2] 9, 427).—11. *Water* containing a few drops of H_2SO_4 at 160° gives fumaric acid (Markownikoff, *A.* 182, 351).—12. When heated with *phenol* and H_2SO_4 it gives CO and  (Pechmann, *B.* 17, 929, 1649).—13. Long boiling with conc. HClAq gives fumaric acid.—14. Conc. HBr at 100° gives bromo-succinic acid and fumaric acid (Kekulé,

A. 130, 11).—15. *Chloral* at 125° forms

$$CCl_3.CH\left\langle\begin{array}{l}O.CH.CH_2.CO_2H\\ \quad\ \ |\\ O.CO\end{array}\right.$$

[140°]. This forms large crystals, sl. sol. cold water (Wallach, *A.* 193, 42). With PCl_5 it gives the oily chloride $C_6H_4Cl_4O_4$, whence alcohol forms $C_6H_4Cl_3(OEt)O_4$ [46°], and MeOH gives $C_6H_4Cl_3(OMe)O_4$ [85°].—16. *Phenyl hydrazine* at 120° forms $C_{16}H_{18}N_4O_3$ *i.e.* $C_2H_4O(CO.N_2H_2Ph)_2$ [223°], which crystallises from dilute alcohol in plates (Bülow, *A.* 236, 195; *cf.* Fischer a. Passmore, *B.* 22, 2734).—17. Malic acid (3 pts.) heated with *m-amido-benzoic acid* at 150° forms a product whence by washing with hot water and alcohol, dissolving in aqueous NH_3 and ppg. by HCl, there is obtained a white powder $C_2H_4O(CO.NH.C_6H_4.CO_2H)_2$. The ammonium salt of this acid forms with cupric acetate a pp. of $Cu_3(C_{18}H_{13}N_2O_7)_2$. Ac_2O decomposes it, forming $NHAc.C_6H_4.CO_2H$ (Schiff, *G.* 16, 28; *A.* 232, 166).

Salts.—Malic acid has a tendency to form acid salts. At 200° the salts give off water and are converted into fumarates.—NH_4HA'': transparent trimetric prisms. Not hemihedral, but becomes so after fusion and recrystallisation. S.G. $\frac{12.5}{}$ 1·55. S. 32 at 15·7°. $[\alpha] = -6°$. On dry distillation it forms fumarimide, fumaric, and maleïc acids, and active and inactive malic acid. Combines with acid ammonium tartrate. Normal ammonium malate $(NH_4)_2A''$ is v. e. sol. water, and its solution gives off NH_3 to the air, becoming acid. In a solution containing 63 p.c. of the salt $[\alpha]_D = -4·2$. In a 17 p.c. solution $[\alpha]_D = -7·2$ (Schneider, *A.* 207, 276).—KHA'': crystals. Begins to decompose at 100°. Sol. water, insol. alcohol. $[\alpha]_D = -5$ in a 21 p.c. solution; $= -5·7$ in a 9·4 p.c. solution at 20°.—K_2A''. Uncrystallisable and deliquescent mass. $[\alpha]_D = -2·2$ in a 62 p.c. solution; $= -6·8$ in a 9·4 p.c. solution at 20° (Schneider).—$NaHA''$. Crystallisable and permanent in the air; sol. water, insol. alcohol. $[\alpha]_D = +0·15$ in a 60·6 p.c. solution; $= -5·64$ in a 20 p.c. solution at 20° (Schneider). — Na_2A''. Uncrystallisable. $[\alpha]_D = +4·7$ in a 65·5 p.c. solution; $= -8·4$ in a 5·3 p.c. solution.—$^{\times}LiHA''$. Uncrystallisable. $[\alpha]_D = -4·6$ in a 50 p.c. solution; $= -8·4$ in a 10 p.c. solution.—$^{\times}Li_2A''$. Uncrystallisable. $[\alpha]_D = -4·1$ in a 39 p.c. solution; $= -12$ in a 6 p.c. solution at 20° (Schneider, *A.* 207, 273).—$BaA''aq$: thin plates. $[\alpha]_D = +8·2$ in a 9·4 p.c. solution; $= -2·6$ in a 2 p.c. solution at 20°.—$^{\times}BaH_2A''_2$. Uncrystallisable and more soluble than the neutral salt.—$SrA''aq$ (dried at 100°). Crystalline mass, v. sol. water.—$^{\times}SrH_2A''$. Crystalline pp. formed by adding malic acid to a solution of the preceding. Sl. sol. cold, m. sol. hot, water.—$CaA''3aq$. S. ·839 at 15°; ·711 at 45°; ·566 at 58°; ·600 at 65°; ·663 at 72°; ·737 at 86° (Iwig a. Hecht, *A.* 233, 170). Granular crystalline mass. When a solution of malic acid is added to lime water a pasty mass of $A''Ca_2(OH)_2 9aq$ (?) is first formed, but when the theoretical quantity of malic acid has been added this dissolves up again, and the clear liquid deposits nodules of $CaA''3aq$ in the course of 24 hours.—$CaH_2A''_2 6aq$ (Hagen, *A.* 38, 263). Occurs in stems of *Geranium zonale*, the berries of *Rhus glabrum* (Rogers, *Am. S.* 27, 294), and in tobacco. Separates in well-formed trimetric octahedra from a solution of the neutral salt in warm dilute nitric acid. S. (of $CaH_2A''_2$) 1·287 at 15°; 8·514 at 45°; 32·236 at 57°; 13·127 at 68°; 7·437 at 78° (I. a. H.). $[\alpha]_D = +5$ (Bremer, *R. T. C.* 3, 164). When the solution obtained by neutralising malic acid with $CaCO_3$ is boiled a nearly insoluble granular pp. is got, which consists of $CaA''aq$ (Richardson a. Meundorf, *A.* 26, 135), or of CaA'' (Hagen, *A.* 38, 257).—$MgA'' 5aq$. Prisms, which separate from a highly concentrated solution (Liebig, *A.* 5, 148). Alcohol ppts. MgA''.—$MgH_2A''_2 4aq$ (or 3aq). Flattened prisms.—$ZnA''3aq$. Monoclinic crystals (Handl, *J.* 1859, 289). Slowly deposited in the cold from the product of solution of zinc carbonate in aqueous malic acid at 30°. When these substances are boiled together a basic salt $ZnO(ZnA'')_2 4aq$ is deposited as a jelly, changing to a sandy powder, while the filtrate deposits $ZnA'' 3aq$ as hard, four-sided prisms. S. 1·7 at 20°.—$ZnH_2A''_2 2aq$. Elongated octahedra. S. 4 in the cold.—The neutral manganese salt is very soluble and uncrystallisable; by adding malic acid to its solution the acid salt is ppd. as a white powder, S. 2·5. From boiling water it separates in rose-coloured crystals.—The neutral and acid ferric salts are gummy masses, v. sol. water and alcohol.—$CuA''aq$: green gummy mass, v. sol. water.—$CuH_2A''_2 2aq$: blue crystals, obtained by evaporation at 40°.—$CuO(CuA'')_2 4aq$: green insoluble powder obtained by boiling aqueous malic acid with cupric carbonate. If evaporated at 45° dark-green crystals of $CuO(CuA'')_2 6aq$ may be got. H. Schulze (*Ar. Ph.* [2] 57, 273) obtained green crystals of a double salt of cupric malate and ammonium sulphate.—$PbA''3aq$. Obtained by ppg. neutral lead acetate with a solution of calcium or potassium malate, as a white curdy pp., which slowly changes to radiating four-sided needles. Melts in boiling water. V. sl. sol. cold, m. sol. boiling, water, from which it is deposited in needles. Dissolves easily in nitric acid; acetic and malic acids do not dissolve it more readily than water. When dry it does not melt at 170° but at 220° it forms lead fumarate.—$PbA''aq$ (dried at 100°) (Otto, *A.* 127, 175).—$PbO(PbA'')_2$. Obtained by digesting the neutral salt with ammonia, or by dropping a solution of a neutral malate into a boiling solution of lead subacetate. Amorphous pp., not becoming crystalline. Does not melt under water. Melts under hot dilute HOAc, evidently changing to the neutral salt. Nearly insol. water, to which, however, it imparts an alkaline reaction.—Ag_2A''. White granular pp., formed by adding silver nitrate to a solution of neutral or acid ammonium malate. —Aniline malate $C_6H_5NH_3HA''$. [144°]. White prisms (from alcohol). On dry distillation it gives water, aniline, the phenyl-imide of phenyl-aspartic acid [211°], and the phenyl-imide of maleïc acid [91°] (Anschütz a. Wirtz, *Am.* 9, 237; *A.* 239, 140).

Acetyl derivative $C_2H_3(OAc)(CO_2H)_2$ [132°]. From the acetyl derivative of the anhydride and water (Anschütz, *A.* 254, 165).

Di-methyl ether Me_2A''. (122° at 10 mm.). S.G. $\frac{24·6}{24·6}$ 1·2386. Formed, together with $MeHA''$, by passing HCl into a cooled solution of malic acid in MeOH (Demondesir, *A.* 80, 301; *C. R.*

23, 227; Anschütz, *B.* 14, 2790; 18, 1953).—$Ca(MeA'')_2$ is sol. alcohol.

Acetyl derivative of the di-methyl ether $C_2H_3(OAc)(CO_2Me)_2$. (129° at 11 mm.). From the ether and AcCl.

Di-ethyl ether Et_2A''. (128° at 10 mm.). Formed in like manner. Can only be distilled *in vacuo*.—$Ca(EtA'')_2$ is sol. alcohol.

Acetyl derivative of the di-ethyl ether $C_2H_3(OAc)(CO_2Et)_2$. (137° at 12 mm.).

Nitroxyl derivative of the di-ethyl ether $C_2H_3(ONO_2)(CO_2Et)_2$. S.G. $\frac{12}{}$ 1·202. From the ether, fuming HNO_3, and conc. H_2SO_4 (Henry, *B.* 3, 532). Thick oil.

Di-n-propyl ether $C_2H_3(OH)(CO_2Pr)_2$. (151° at 10 mm.) (Anschütz).

Acetyl derivative of the di-n-propyl ether $C_2H_3(OAc)(CO_2Pr)_2$. (157° at 12 mm.).

Mono-isoamyl ether $C_2H_3(OH)(CO_2H)(CO_2C_5H_{11})$. From malic acid and isoamyl alcohol at 120° (Breunlin, *A.* 91, 323).—NH_4A': needles.—CaA'_2aq: plates.

Acetyl derivative of the anhydride

$$\begin{array}{l} CH(OAc).CO\diagdown \\ \;| \qquad\qquad\quad >O. \\ CH_2 ——— CO\diagup \end{array}$$

[54°]. (161° at 14 mm.). Formed, together with maleïc anhydride, by heating malic acid with AcCl (Anschütz, *B.* 14, 2791). Decomposed by distillation under atmospheric pressure into HOAc and maleïc anhydride.

Amide $C_2H_3(OH)(CONH_2)_2$. *Malamide.* When gaseous NH_3 is passed into an alcoholic solution of malic ether crystals of malamide are deposited. Separates from water in well-defined crystals. Resolved by hydrolysis into NH_3 and malic acid.

Amic ether $C_2H_3(OH)(CO_2Et)(CONH_2)$. *Malamic ether.* Formed as a crystalline mass when gaseous NH_3 is passed into malic ether (Pasteur, *J.* 1853, 411).

Di-anilide $C_2H_3(OH)(CONHPh)_2$. [175°]. Formed, together with the phenyl-imide, by boiling aniline (2 mols.) with malic acid ($1\frac{1}{2}$ mols.). The phenyl-imide is extracted by boiling water, and the residue recrystallised from alcohol, using animal charcoal (Arppe, *A.* 96, 106). Colourless scales. Nearly insol. water, dilute acids, and alkalis.

Mono-anilide $C_2H_3(OH)(CO_2H)(CONHPh)$. *Malanilic acid.* [145°]. Obtained by boiling the phenyl-imide with aqueous ammonia; the product is ppd. by baryta, and the Ba salt decomposed by H_2SO_4, avoiding any excess. White granules composed of very minute needles (from alcohol); v. sol. water, m. sol. alcohol, sl. sol. ether. Reddens litmus. Hot dilute H_2SO_4 resolves it into water and the phenyl-imide. Its salts are soluble in water.—AgA′: white pp., crystallising from water in shining scales.

Phenyl-imide $C_2H_3(OH)<\!\begin{smallmatrix}CO\\CO\end{smallmatrix}\!>NPh$. [170°]. Formed by heating malic acid with aniline and crystallising from water. Groups of delicate needles; v. sol. water, alcohol, and ether.

Inactive malic acid

$CO_2H.CH_2.CH(OH).CO_2H$. [c. 108°] (Pictet, *B.* 14, 2648); [c. 114°] (Kekulé); [133°] (Pasteur; Loydl; Bischoff). Occurs as calcium salt in the leaves of the common ash (*Fraxinus excelsior*) (Gintl, *J.* 1868, 800; Garot, *J.* 1853, 409).

Formation.—1. By mixing equal parts of lævo- and dextro- malic acids (Van't Hoff, jun., *B.* 18, 2170; *R. T. C.* 4, 130).—2. By reducing racemic acid with HIAq (Bremer, *Bl.* [2] 25, 6).—3. By the action of nitrous acid on inactive aspartic acid obtained from fumarimide (Pasteur, *A. Ch.* [3] 34, 46; *A.* 82, 330).—4. By the action of moist Ag_2O on bromo-succinic acid (Kekulé, *A.* 117, 126; 130, 24).—5. By heating fumaric acid with a large quantity of water at 150°-200° (Jungfleisch, *Bl.* [2] 30, 147).—6. By heating fumaric acid (1 pt.) with NaOH (4 pts.) and water (40 pts.) for 100 hours at 100° (Linnemann a. Loydl, *A.* 192, 80; *B.* 9, 925).—7. Together with fumaric acid, by treating di-β-chloro-propionic ether with a weak alcoholic solution of KCy, and boiling the product with potash (Werigo a. Tanatar, *A.* 174, 367). Also in like manner from di-β-bromo-propionic acid (Tanatar, *B.* 13, 160).—8. From chloro-ethane tri-carboxylic ether $CO_2Et.CH_2.CCl(CO_2Et)_2$ and dilute alcoholic KOH (Bischoff, *A.* 214, 49).

Properties.—Crystallises more readily than active malic acid, being less soluble in water and not deliquescent, or at any rate less deliquescent than the active acid. V. e. sol. water, v. sol. alcohol, v. sl. sol. ether. When heated at 200° it yields fumaric acid.

Salts.—NH_4HA'': trimetric crystals (Van't Hoff).—$NH_4HA''aq$: monoclinic crystals. $a:b:c$ = ·5856 : 1 : ·5377; $\beta = 68° 12'$.—CaA'': granular pp.; sl. sol. water.—$CaA''aq$.—$CaA'' 2\frac{1}{2}aq$: nodules of transparent crystals (Pasteur). The acid calcium salt resembles that of the active acid except that its crystals exhibit hemihedral faces. The lead salt melts under water, but crystallises less easily than the inactive salt. The lead salt obtained by Tanatar from di-bromo-propionic acid did not melt under water.—Ag_2A''.

By crystallising the cinchonine salt Bremer (*B.* 13, 352) was able to separate it into salts of lævo- and dextro- malic acid.

Ethyl derivative $C_2H_3(OEt)(CO_2H)_2$. [86°]. Obtained by saponifying its di-ethyl ether (Purdie, *C. J.* 39, 348). Transparent crystals (from ether), sol. water. Not ppd. by lead subacetate, but in neutral and feebly acid solution it is ppd. by lead nitrate and, more slowly, by neutral lead acetate. Fuming HI at 120° reduces it to succinic acid.—CaA'': insoluble.—Ag_2A'': sl. sol. water.—$BaA''aq$: hygroscopic; v. sol. water.

Di-ethyl ether of the ethyl derivative $C_2H_3(OEt)(CO_2Et)_2$. (195°-200°) at 250 mm. From fumaric ether and NaOEt, the product being neutralised (Purdie).

Isobutyl derivative $C_2H_3(OC_4H_9)(CO_2H)_2$. Crystalline, deliquescent mass (Purdie).—CaA'': insol. water.—Ag_2A'': flocculent, insol. water.

The following compounds are probably also derivatives of the same inactive malic acid:—

Amic acid $CO_2H.CH_2.CH(OH).CONH_2$. *Malamic acid.* [146°]. Obtained, together with its ether, by boiling the amide of diazo-succinic ether with water (Curtius, *J. pr.* [2] 38, 479). Colourless prisms; v. sol. water, alcohol, and ether.

Methyl ether of the amic acid $CO_2Me.CH_2.CH(OH).CONH_2$. [105°]. Formed,

together with methyl fumaramate, by boiling methyl diazo-succinamate

$CO_2Me.CH_2.CN_2.CONH_2$

with slightly acidified water (Curtius, *J. pr.* [2] 38, 482). Silky plates; v. e. sol. alcohol, ether, and water. With benzoic acid at 150° it forms crystalline $CO_2Me.CH_2.CH(OBz).CONH_2$ [80°]; v. sol. ether.

Benzoyl derivative of the ethyl ether of the amic acid $CO_2Et.CH_2.CH(OBz).CONH_2$. [97°]. Formed by heating ethyl diazo-succinamate with HOBz at 145°. Colourless rhombohedra.

Dextro-malic acid $CO_2H.CH_2.CH(OH).CO_2H$. [c. 100°]. Formed from dextro-asparagine (from sprouting vetch seeds) by treatment with nitrous acid (Piutti, *B.* 19, 1693). The cinchonine salt is obtained by crystallisation from the cinchonine salt of inactive malic acid. Resembles ordinary malic acid, except that it is dextrorotatory.

Isomeride of malic acid $C_4H_6O_5$. [155°–168°]. Formed by heating acetylene dibromide (5 pts.) with KCy (4 pts.) and alcohol (28 pts.) at 100°, and saponifying the resulting nitrile with potash (Sabanejeff, *A.* 216, 275). Crystals; v. sol. water.—Ag_2A''.

Isomalic acid of Kämmerer (*J. pr.* 88, 321; *A.* 139, 257) is identical with citric acid (Ostwald, *B.* 21, 3534).

Paramalic acid is described as DIGLYCOLLIC ACID.

Iso-malic acid $CH_3.C(OH)(CO_2H)_2$. [c. 140°]. From bromo-iso-succinic acid and moist Ag_2O (Schmöger, *J. pr.* [2] 14, 77; 19, 168; 24, 38). Crystals; v. sol. water, alcohol, and ether. At 170° it splits up into CO_2 and lactic acid. Inactive. Its neutral solutions give no pp. with $CaCl_2$ (unlike methyl-tartronic acid, which gives a pp. on warming).—$BaA''2aq$: amorphous pp. S. 1 at 100°. Loses its water of crystallisation at 130° (unlike methyl-tartronic acid).—PbA''. Does not melt under water.—Ag_2A'': needles.

Methyl-tartronic acid $CH_3.C(OH)(CO_2H)_2$. [178°]. Obtained from pyruvic acid by addition of KCy and HCl, the product being boiled with baryta-water (Böttinger, *B.* 14, 148; 17, 144). Rhombohedral crystals. Decomposes on fusion, giving off CO_2. Boiling conc. HClAq splits it up into CO_2 and lactic acid.—$BaA''aq$ (dried at 130°). Heavy crystalline powder, ppd. on boiling. — $ZnA''2aq$: crystalline powder. — $Ag_2A''aq$: white crystalline powder.

Reference.—BROMO-MALIC ACID.

MALLOTOXIN $C_{11}H_{10}O_3$ or $C_{18}H_{16}O_5$. May be extracted by CS_2 from finely-divided kamala, a yellow dye got from the seeds of *Mallotus Phillipensis* (A. G. Perkin a. W. H. Perkin, jun., *B.* 19, 3109). Flesh-coloured needles; insol. water, v. sol. hot alcohol. Dissolves readily in alkalis, forming a yellowish-red solution. Ac_2O yields a di-acetyl derivative.

MALOBIURIC ACID $C_5H_5N_3O_4$ *i.e.* $CO\langle{NH.CO \atop NH.CO}\rangle CH.CO.NH_2$ (?). Formed, as ammonium salt, by heating barbituric acid (malonyl-urea) with urea at 100° (Baeyer, *A.* 135, 312). Formed also by boiling cyanuromalic acid with HClAq (Nencki, *B.* 5, 888). Ppd. by adding HCl to solutions of its salts as a granular pp., which, when quite pure, can be obtained in crystals. Dissolves completely in bromine and water, forming di-bromo-barbituric acid. Nitric acid converts it into nitro-barbituric (dilituric) acid.—KA'aq: long needles. S. 16 in hot water.

MALONAMIC ACID *v.* MALONIC ACID.

MALONAMIDE *v. Amide* of MALONIC ACID.

MALONANILIC ACID *v. Mono-anilide* of MALONIC ACID.

MALONIC ACID $C_3H_4O_4$ *i.e.* $CH_2(CO_2H)_2$. Mol. w. 104. [134°] (Krafft a. Noerdlinger, *B.* 22, 816). S. 109 at 1°; 138 at 16° (Miczynski, *M.* 7, 258); 109 at 15° (Bourgoin, *Bl.* [2] 33, 423). H.F. 212,700 (Stohmann, Kleber a. Langbein, *J. pr.* [2] 40, 206). H.C. v. 207,900. H.C. p. 207,300 (S., K. a. L.); 208,650 (Louguinine, *C. R.* 107, 597). *Heat of solution* = – 4573. *Heat of neutralisation* by NaOH 27,120 (Gal a. Werner, *Bl.* [2] 46, 803); 26,650 (Massol); by KOH 27,300; by NH_3 25,040; by BaO_2H_2 30,135; by CaO_2H_2 27,090 (Massol, *C. R.* 107, 257, 393; 108, 813, 1060; 109, 27). S.H. (0° to 50°) ·2832; (0° to 110°) ·3262 (Hess, *P.* [2] 35, 410).

Occurrence.—In beet-root (Lippmann, *B.* 14, 1183).

Formation.—1. Discovered by Dessaignes (*C. R.* 47, 76) as a product of the slow oxidation of malic acid by cold aqueous $K_2Cr_2O_7$.—2. By the action of alkalis or acids on cyano-acetic acid (semi-nitrile of malonic acid) or cyano-acetic ether (Hugo Müller, *C. J.* 17, 109).—3. By oxidation of allylene or propylene with cold alkaline $KMnO_4$ (Berthelot, *J.* 1867, 335).—4. By boiling barbituric acid with potash (Baeyer, *A.* 130, 143; Heintzel, *A.* 139, 129).—5. By boiling mucobromic acid with baryta-water (Jackson a. Hill).—6. From di-chloro-acrylic ether by treatment with Ag_2O at 125°, and saponifying the product (Wallach a. Hunaeus, *A.* 193, 25).—7. By treating $CBr_3.CO.CH_2.CBr_3$ with fuming HNO_3 (Demole, *B.* 11, 1714).

Preparation.—1. From ethylic, or better from potassic, chloro-acetate. Chloro-acetic acid (100 g.) dissolved in water (200 g.) is neutralised by K_2CO_3 (75 g.), mixed with KCy (70 g.), and warmed. The reaction heats the liquid to boiling and is soon over. KOH (100 g.) is now added, and the liquid boiled as long as NH_3 escapes. The liquid is then acidified with HCl, evaporated to dryness, and the malonic acid extracted by ether (H. v. Miller, *J. pr.* [2] 19, 326; *cf.* Finkelstein, *A.* 133, 338).—2. Chloro-acetic acid (100 pts.) is dissolved in twice its weight of water, and neutralised with potassium carbonate (75 pts.) To the solution is added 75 to 80 pts. potassium cyanide (98 p.c.), and the mixture heated for two hours, with continual renewal of the evaporated water. The remaining mass is decomposed with concentrated potash. When the odour of ammonia has disappeared the solution is neutralised with hydrochloric acid, and ppd. as a calcium salt. This is decomposed with the requisite quantity of oxalic acid, the residue extracted with ether, and the solution evaporated (Conrad, *A.* 204, 121).—3. By dissolving chloro-acetic acid (100 gms.) in double its weight of water, saturating the solution with potassium bicarbonate (110 gms.), adding potassium cyanide (75 gms.), and warming on the water-bath. At the end of the reaction double the volume of concentrated hydrochloric acid is added and the precipitation of potassium chloride rendered complete by passing in a current of HCl gas. The

potassium and ammonium chlorides are filtered off, and the filtrate evaporated. The nearly dry residue is taken up with ether, which on evaporation yields pure malonic acid (70 gms.) (Bourgoin, *A. Ch.* [5] 20, 271).—4. Chloro-acetic ether is boiled with pure KCy dissolved in 70 p.c. alcohol for 4 hours. The alcohol is distilled off, and the residue mixed with dilute HCl and evaporated to dryness. The cyano-acetic ether is extracted with ether and decomposed by fuming HClAq at 100° (Petrieff, *J. R.* 10, 64; *B.* 7, 400).—5. In like manner from bromo-acetic ether (Franchimont, *B.* 7, 216).

Properties.—Triclinic laminæ or prisms. Decomposes a little over its melting-point into CO_2 and acetic acid, but when heated under 10 mm. pressure it may be sublimed. V. sol. water, alcohol, and ether. When heated with Ac_2O, malonic acid gives a reddish-yellow liquid with greenish-yellow fluorescence:—·001 g. is sufficient for this test (Kleemann, *B.* 19, 2030). A small quantity of malonic acid treated with urea and $POCl_3$ yields a product which when evaporated with nitric acid leaves a residue which gives with ammonia the purple colour due to murexide (Grimaux, *C. R.* 88, 85).

Reactions.—1. A solution of the free acid is hardly affected by the passage of an electric current. But the *electrolysis* of a concentrated alkaline solution gives off oxygen, CO, and CO_2 at the positive pole, without any hydrocarbon (von Miller; Bourgoin, *A. Ch.* [5] 20, 80; *C. R.* 90, 608).—2. Malonic acid (5 g.) heated with *bromine* (10 c.c.) and water (12 c.c.) for 18 hours at 120° to 145° gives bromoform, tri-bromo-acetic acid, CO_2, and HBr (Bourgoin, *Bl.* [2] 34, 215).—3. HNO_3 (S.G. 1·53) in the cold gives off CO_2 (2 mols.) (Franchimont, *R. T. C.* 3, 422).—4. PCl_5 gives malonyl chloride and a compound $C_9H_5ClO_6$, crystallising in needles [122°], decomposed by water and alcohol with evolution of CO_2 (Béhal a. Augur, *Bl.* [2] 50, 631).—5. Malonic acid (1 pt.), NaOAc (1 pt.), and Ac_2O (3 pts.) at 100° forms a brownish-yellow acid $C_{11}H_4O_8$. The sodium salt $C_{11}H_3NaO_8$ is v. sol. water, alkalis, and conc. H_2SO_4, m. sol. HOAc. Its solutions exhibit fluorescence, but on heating CO_2 is evolved and the fluorescence disappears. An acetic acid solution of the salt $C_{11}H_3NaO_8$ boiled with a solution of phenyl-hydrazine acetate forms CO_2, NaOAc, and $C_{10}H_4O_4(N.NHPh)_2$, a substance insol. water and ether, v. sol. alcohol and HOAc, forming a green solution in conc. H_2SO_4, and melting with decomposition about 180° (Kleemann, *B.* 19, 2030).—6. *Benzoic aldehyde* and HOAc forms benzylidene-malonic acid $C_6H_5.CH:C(CO_2H)_2$.—7. *Propionic aldehyde* and HOAc gives $CH_3.CH_2.CH:CH.CO_2H$ (Komnenos, *A.* 218, 168).—8. *o-Oxy-benzoic aldehyde* and HOAc at 100° forms coumarin-carboxylic acid (vol. ii. p. 269).—9. *Cinnamic aldehyde* and HOAc at 100° gives phenyl-butinene dicarboxylic acid $C_6H_5.CH:CH.CH:C(CO_2H)_2$ (Stuart, *C. J.* 49, 366).—10. Heated with *phenyl thiocarbimide* it gives acetanilide and the dianilide of malonic acid (Moine, *Ann. Chim. Farm.* [4] 4, 201).

Salts.—The salts, with the exception of those of the alkali metals, are sparingly soluble in water, more soluble in dilute malonic acid, HOAc, or nitric acid (Finkelstein, *A.* 133, 338).—NaHA″ ½aq: well-defined crystals (F.).—NaHA″ aq: trimetric prisms (Shadwell, *J.* 1881, 699).—Na_2A'' aq (Mulder, *Bl.* [2] 29, 532; *cf.* Massol, *C. R.* 107, 393).—KHA″ ½aq: prisms.—KHA″: monoclinic prisms (Haushofer, *J.* 1881, 699).—K_2A''2aq: deliquescent monoclinic crystals. Gives CO_2 and hydrogen on electrolysis (H. von Miller).—K_2A'' aq: monoclinic prisms (H.).—NH_4HA'': very deliquescent crystals. Heat of formation from solid malonic acid and NH_3: 22,780 (Massol, *C. R.* 108, 1060).—$(NH_4)_2A''$: very deliquescent needles. Heat of formation from solid malonic acid and NH_3: 41,015.—BaA″ 2aq: bulky flocculent pp. gradually becoming crystalline. Crystallises from water in long slender needles. At 100° it loses aq, and when heated in a current of hydrogen at 140° it becomes anhydrous. BaA″ aq is not dehydrated by heating in air at 150° (Pinner a. Bischoff, *A.* 179, 84). S. ·14 at 0°; ·20 at 18°; ·32 at 70° (Miczynsky, *M.* 7, 261). Heat of solution: −3830 (Massol, *C. R.* 109, 29).—CaA″ 2aq: monoclinic needles (from water). Ppd. in gelatinous form on adding $CaCl_2$ to a solution of ammonium malonate. S. ·3 at 0°; ·37 at 20°; ·47 at 72° (Miczynski). According to Massol (*C. R.* 108, 813) this salt separates in small brilliant scales on slow evaporation of its solution at 35°.—CaA″ 4aq: silky needles. Obtained by slow evaporation at 15° (Massol). V. sl. sol. water. May be dehydrated in a current of hydrogen at 135°.—SrA″: small brilliant scales (Ossipoff, *C. R.* 108, 815).—MgA″ 2aq, MgA″ aq, and MgA″ ½aq are described by Finkelstein as crystalline powders.—ZnA″ 2aq: monoclinic crystals.—MnA″ 2aq: trimetric prisms.—CoA″ 2aq: monoclinic crystals (Haushofer).—NiA″ 2aq: bluish-green powder.—CdA″: deliquescent.—CdA″ 4aq: monoclinic crystals.—CdA″ 12aq: triclinic (Haushofer, *J.* 1882, 362).—PbA″: crystalline powder, sol. HOAc.—CuA″ 3aq: blue triclinic crystals (H.).—Cu_2OA'': bluish-green pp.—Ag_2A'': crystalline pp., not blackened by boiling water.—Ethylamine salt $NEtH_3HA''$: gives at 180° water and the ethylimide of fumaric acid $\begin{array}{l} CH.CO \\ \| \\ CH.CO \end{array}\!\!>NEt$, whence concentrated caustic potash solution forms $NHEt.CO.CH:CH.CO_2H$ [126°] (Piutti, *C. C.* 1888, 1529).

Methyl ether Me_2A'' (181·5° cor.). S.G. $\frac{15}{15}$ 1·1603; $\frac{25}{25}$ 1·1511 (Perkin, *C. J.* 45, 509); $\frac{0}{0}$ 1·1753 (W.). M. M. 5·28 at 17°. S.V. 137·6 (Wiens, *A.* 253, 297). From silver malonate and MeI (Osterland, *B.* 7, 1286). Oil, sol. alcohol and ether.

Mono-ethyl ether $CO_2Et.CH_2.CO_2H$. When alcoholic KOH (1 mol.) is added to alcoholic malonic ether the liquid forms a crystalline pulp of $CO_2Et.CH_2.CO_2K$ composed of needles (Van't Hoff, *B.* 7, 1571; Freund, *B.* 17, 780). PCl_5 converts it into $CO_2Et.CH_2.COCl$ (170°–180°).

Ethyl ether $CH_2(CO_2Et)_2$. (198° cor.) (Perkin, *C. J.* 45, 508); $\frac{0}{0}$ 1·0761 (Wiens). S.G. $\frac{15}{15}$ 1·0610; $\frac{25}{25}$ 1·0525. M. M. 7·41 at 14°. S.H. ·439 at 0°; ·45 between 10·6° and 82·2° (R. Schiff, *Zeit. Phys. Chem.* 1, 376; *G.* 16, 454). S.V. 185·1 (Wiens, *A.* 253, 297).

Preparation.—1. Calcium malonate is boiled with H_2SO_4 and 4 times the theoretical quantity of alcohol for 24 hours (Conrad, *B.* 12, 749).—

2. Chloro-acetic acid (250 g.) is dissolved in water (500 g.) and K_2CO_3 (187 g.); KCy (175 g.) is added, and the whole heated on a sand-bath until the reaction begins. The product is evaporated until its temperature is 135°, and is then allowed to cool. When cold it is treated with two-thirds of its weight of alcohol and gaseous HCl is passed in. The product is poured into iced water, extracted with ether, dried over $CaCl_2$, and distilled (Venable a. Claisen, *A.* 218, 131). Tricarballylic ether (287°) is obtained as a by-product (Däumichen, *C. C.* 1888, 1347).

Reactions.—1. *Water* at 150° gives CO_2 and acetic ether (Hjelt, *B.* 13, 1949).—2. Boiling with *m-amido-benzoic acid* and a little alcohol forms $CH_2(CO.NH.C_6H_4.CO_2H)_2$, a powder which will not melt and is insol. water, hardly sol. boiling alcohol, sol. dilute NH_3Aq, and dissolves without change in conc. H_2SO_4 (Schiff, *A.* 232, 143; *B.* 17, 403; *G.* 15, 534). The intermediate compound $CO_2Et.CH_2.CO.NH.C_6H_4.CO_2H$ [173°] is also formed at the same time.—3. *Chlorine* forms chloro-malonic ether.—4. Cautious treatment with *nitric acid* (5 pts. of S.G. 1·5) gives nitro-malonic ether (Franchimont a. Klobbie, *R. T. C.* 8, 283).—5. According to Lang (*B.* 19, 2937) *zinc methyl* or *zinc ethyl* act in the cold, forming phloroglucin tricarboxylic ether, methane, and ethane.—6. When a mixture of malonic ether (1 mol.) and EtI (2 mols.) is heated with zinc there is formed ethane and ethyl-malonic ether (90 p.c. of the theoretical amount) (Daimler, *B.* 20, 203). When malonic ether (20 g.), EtI (100 g.), and granulated zinc are heated with inverted condenser at 100° there is formed di-ethyl-malonic ether (Joulowsky, *J. pr.* [2] 39, 446).—7. With *allyl iodide* and *zinc* there is formed di-allyl-malonic ether and propylene (Matvéeff, *J. pr.* 39, 452).—8. When malonic ether (2 mols.) is treated with *glyoxal* (1 mol.) and zinc chloride it forms di-oxy-butane tetracarboxylic ether $(CO_2Et)_2CH.CH(OH).CH(OH).CH(CO_2Et)_2$ (Polonowsky, *A.* 246, 1).—9. With *benzoic aldehyde* and HCl it forms benzylidene-malonic ether $C_6H_5.CH:C(CO_2Et)_2$ (Claisen a. Cremer, *A.* 218, 129).—10. *Furfuraldehyde* and acetic anhydride give furfuryl-methenyl-malonic ether $C_4H_3O.CH:C(CO_2Et)_2$ which boils with slight decomposition at 293°, and gives on saponification the acid ether $C_4H_3O.CH:C(CO_2H)(CO_2Et)$ [102·5°], and finally the acid $C_4H_3O.CH:C(CO_2H)_2$ [187°], which may be reduced by sodium-amalgam to $C_4H_3O.CH_2.CH(CO_2H)_2$ [125°] (Marckwald, *B.* 21, 1081).—11. *Aldehyde* forms $CH_3.CH:C(CO_2Et)_2$ and $CH_3.CH\{CH(CO_2Et)_2\}_2$ (Komnenos, *A.* 218, 145).—12. *Diazobenzene chloride* forms benzene-azo-malonic acid, identical with the phenyl hydrazide of mesoxalic acid (R. Meyer, *B.* 21, 118).

Sodium-malonic ether $CHNa(CO_2Et)_2$. Formed, with evolution of hydrogen, by dissolving sodium in malonic ether. The reaction is stopped by the crust of the sodium compound which forms on the surface of the metal; but this may be removed by adding alcohol (2 vols.) which first forms NaOEt, and this then reacts with the malonic ether. The sodium-malonic ether crystallises on cooling, and may be freed from alcohol by heating to 150° in a current of hydrogen (Conrad, *B.* 12, 750). If, however, it be required merely for synthetical purposes the presence of alcohol is for the most part not injurious, and the mixture of malonic ether and alcoholic NaOEt may be used at once. This reacts upon organic halogen compounds thus:—

$$CHNa(CO_2Et)_2 + XI = CHX(CO_2Et)_2 + NaI,$$

the reaction being energetic at first but often requiring heat to finish it. If the substances are mixed in the right proportion the end of the reaction is recognised by the solution becoming neutral. Water is then added, and if X is a hydrocarbon radicle, $CHX(CO_2Et)_2$ separates as an oil, which may be purified by fractional distillation. The resulting $CHX(CO_2Et)_2$ still contains hydrogen displaceable by sodium, and if it be mixed with alcoholic NAOEt and another halogen compound, say YI, the reaction

$$CNaX(CO_2Et)_2 + YI = NaI + CXY(CO_2Et)_2$$

takes place (Conrad a. Bischoff, *A.* 204, 121). When the substituted malonic ethers are saponified acids are obtained, which at 150° or 160° give off CO_2 and leave derivatives of acetic acid:

$$CHX(CO_2H)_2 = CO_2 + CH_2X.CO_2H$$
$$CXY(CO_2H)_2 = CO_2 + CHXY.CO_2H.$$

Hence malonic ether may be used, like aceto-acetic ether, to effect the synthesis of organic acids of the general formula $CXYH.CO_2H$ where X and Y may be alkyls, groups like $CH_2.CO_2Et$, or other radicles. When it is desired to prepare a di-alkyl-malonic ether it is not necessary to perform the operation in two stages, for the proper quantity of NaOEt (2 mols.) may be added all at once, and then the alkyl iodide (2 mols.). By the action of AcCl on sodio-malonic ether in ethereal solution it may be converted into acetyl-malonic ether (120° at 17 mm.), which is soluble in KOHAq; the yield is 55 p.c. of its weight. This ether forms an oxim and a phenyl-hydrazide. and therefore appears to be $CH_3.CO.CH(CO_2Et)_2$. When sodio-aceto-acetic ether is acted upon by chloroformic ether $ClCO_2Et$ the same ketonic ether $CH_3.CO.CH(CO_2Et)_2$ should be formed; but the product is found to be insol. conc. KOHAq, and to boil at a higher temperature (127° at 17 mm.). It is decomposed by cold dilute KOH, and gives CO_2 and alcohol. The latter compound would therefore appear to be $CH_3.C(OCO_2Et):CH.CO_2Et$ (Michael, *Am.* 10, 158; *J. pr.* [2] 37, 473; *cf.* Lange, *B.* 20, 1325).

Reactions.—1. EtI gives ethyl-malonic ether. 2. *Benzyl chloride* gives mono- and di- benzyl-malonic ether and regenerated malonic ether (Bischoff a. Siebert, *A.* 239, 94).—3. Malonic ether (32 g.), sodium (9·2 g.), dry alcohol (200 g.) and chloroform (12 g.) react thus (Conrad a. Guthzeit, *A.* 222, 250). $2CNa_2(CO_2Et)_2 + CHCl_3 = 3NaCl + CNa(CO_2Et)_2.CH:C(CO_2Et)_2$ forming sodium di-carboxy-glutaconic ether (*q. v.*).—4. *Trimethylene bromide* reacts with formation of $(CO_2Et)_2.C{<}{\scriptstyle CH_2 \atop CH_2}{>}CH_2$ (Perkin, jun., *C. J.* 51, 1, 702, 820).—5. NaOEt, allyl iodide, and isobutyl iodide gives an acid $C_{10}H_{14}O_4$ instead of allyl-isobutyl-malonic acid.—6. *Chloro-formic ether* $ClCO_2Et$ forms methane tricarboxylic ether $CH(CO_2Et)_3$ (Conrad a. Bischoff, *A.* 214, 31; Claisen, *B.* 21, 3567).—7. *Tri-bromo-di-nitro-benzene* dissolved in ether reacts with formation of $C_6H_2Br(NO_2)_2CH(CO_2Et)_2$ [75°], although bromo-benzene does not react (Jackson a. Robinson, *B.* 21, 2034).—8. *Phthalyl chloride* (1 mol.) added to sodium-malonic ether (2 mols.) dissolved in ether forms phthalyl-malonic ether $C_{15}H_{14}O_6$

[75°], phthalyl-dimalonic ether $C_{22}H_{26}O_{10}$ [48·5°], and 'phthaloxyl-dimalonic' ether $C_{22}H_{24}O_9$ 116·5°] (Wislicenus, *A.* 242, 23).—9. Treatment with the *chloride of mono-ethyl phthalate* $CO_2Et.C_6H_4.COCl$ dissolved in benzene forms $(CO_2Et.C_6H_4.CO)_2C(CO_2Et)_2$ [above 180°] (Zelinsky, *B.* 20, 1012).—10. In alcoholic solution it is probably converted by carbonic acid gas into $(CO_2Et)_2CH.CO_2Na$ (Michael, *J.pr.* [2] 35, 453).—11. *Carbon disulphide* added to an alcoholic solution of sodium-malonic ether gives yellow plates of $(CO_2Et)_2CNa.CS_2Na$.—12. SO_3 acts according to the equation $SO_3 + CHNa(CO_2Et)_2 + HOEt = CH_2(CO_2Et)_2 + NaO.SO.OEt$.—13. *Resorcin* dissolved in alcoholic sodium malonic ether gives a greenish-blue fluorescence, when after a few days the liquid is poured into water and acidified a small pp. of needles of a condensation product $C_{11}H_8O_5$ [191°] is got. A little above its melting-point it is split up into CO_2 and (β)-methyl-umbelliferone of which it is probably the carboxylic acid (Michael, *J. pr.* [2] 37, 469).—14. *Sulphur* dissolves in alcoholic sodium-malonic ether, and at 100° crystals separate. From these, acids liberate a stinking oil (thiotartronic ether?).—15. With alcohol and *cinnamic ether* at 100° it forms $C_{18}H_{21}O_6$ (305°–310°). It is probably $Ph.CH(CHNa.CO_2Et).CH(CO_2Et).CO_2Et$, for on saponifying and heating the resulting acid, phenyl-glutaric acid $CO_2H.CH_2.CHPh.CH_2.CO_2H$ is got (Michael, *J. pr.* [2] 35, 349).—16. *Phenyl cyanate* PhNCO acts violently upon an alcoholic solution of sodium-malonic ether with formation of $(CO_2Et)_2CH.CONHPh$ [124°] and the salt of an acid $C_{12}H_9NO_3$ [172°] (Michael, *J. pr.* [2] 35, 452).—17. *Phenyl thio-carbimide* forms crystalline $C_{14}H_{15}NaSNO_4$, whence acids separate $NHPh.CS.CH(CO_2Et)_2$ [60°] (Michael, *Am.* 9, 124).—18. *Urea* dissolves in malonic ether and rhombic prisms of $CHNa{<}{CO-NH \atop CO-NH}{>}CO$ separate, whence acids liberate barbituric acid (Michael, *J. pr.* [2] 35, 456).—19. *Thio-urea* gives similarly flat plates of sodium thio-barbiturate $CHNa{<}{CO-NH \atop CO-NH}{>}CS$, whence acids liberate thiobarbituric acid, which crystallises in six-sided plates from water.—20. *Acetamide* forms crystalline $C_7O_4N_2Na_2H_8$, the reaction which occurs being $2CHNa(CO_2Et)_2 + 2CH_3.CO.NH_2 = C_7O_4Na_2N_2H_8 + CH_2(CO_2Et)_2 + 2HOEt$.—21. $CSCl_2$ forms $CS{:}C(CO_2Et)_2$, which crystallises in flesh-coloured needles [178°] (Bergreen, *B.* 21, 337).—22. *Iodine* forms $(CO_2Et)_2CH{:}CH(CO_2Et)$. 23. *Di-bromo-maleïc ether* yields 'di-malonyl-maleïc' ether [75°], whence by saponification the corresponding acid $C_{10}H_8O_{12}$ [148°] may be obtained. This acid, the formula of which is $(CO_2H)_2CH.C(CO_2H){:}C(CO_2H).CH(CO_2H)_2$, may be better called butylene hexa-carboxylic acid. It crystallises in plates, v. sol. water, and forms the salts, Na_6A^{vi} 10aq and Ag_6A^{vi}, and the ethers Me_6A^{vi} [129°] and Et_6A^{vi} [75°] (Pum, *M.* 9, 450). When the acid is heated it splits up into CO_2 and butylene tetracarboxylic acid $CO_2H.CH_2C(CO_2H){:}C(CO_2H).CH_2CO_2H$. [176°]. 24. Dry *cyanogen chloride* forms cyano-malonic ether (Haller, *A. Ch.* [6] 16, 419).

Di-sodium-malonic ether $CNa_2(CO_2Et)_2$. Obtained by ppg. malonic ether (1 mol.) with NaOEt (2 mols.) (Bischoff a. Rach, *B.* 17, 2782). Very unstable. Iodine converts it into $(CO_2Et)_2C{:}C(CO_2Et)_2$.

Ethyl propyl ether EtPrA″. (211°). S.G. $\frac{0}{0}$ 1·0498. S.V. 207·8 (Wiens, *A.* 253, 297).

Propyl ether Pr_2A''. (228°). S.G. $\frac{0}{0}$ 1·0271. S.V. 234·6 (Wiens, *A.* 253, 297). S.H. (from 11·6° to 82·3°) ·453 (R. Schiff, *G.* 17, 286).

Butyl ether $(C_4H_9)_2A''$. (251·5°). S.G. $\frac{0}{0}$ 1·0049. S.V. 269·1 (Wiens, *A.* 253, 297).

Chloride $CH_2(COCl)_2$. (58° at 27 mm.). From malonic acid and $CSCl_2$ heated above 100° (Béhal a. Auger, *Bl.* [2] 50, 594). Liquid. Smells slightly like chloral.

Amide $CH_2(CONH_2)_2$. [170°] (Van't Hoff, *Ar. Néerl.* 10, 274). S. 8·3 at 8° (Henry, *Bl.* [2] 43, 618). From malonic ether (50 c.c.) by shaking with strong aqueous NH_3 (150 c.c.) (Osterland, *B.* 7, 1286; Freund, *B.* 17, 133). The yield, in 2 days, is 75 p.c. Silky needles (from dilute alcohol), insol. alcohol and ether. Boiling aqueous NH_3 converts it into ammonium malonamate. Salt.—$CH_2{<}{CO.NH \atop CO.NH}{>}Hg$: white amorphous powder, insol. alcohol and ether, sl. sol. hot water, v. sol. HClAq (Freund).

Di-methyl-amide $CH_2(CO.NHMe)_2$. [128°] (F.); [125°] (Henry); [136°] (Franchimont, *R. T. C.* 4, 199). Formed by the action of methylamine on malonic ether (Freund, *B.* 17, 133). Small flat needles. V. e. sol. water and alcohol, sl. sol. ether. Fuming HNO_3 converts it into $CH_2(CO.N(NO_2)Me)_2$ [150°].

Di-ethyl-amide $CH_2(CO.NHEt)_2$. [149°]. Six-sided tables (Wallach a. Kamenski, *B.* 14, 170).

Ethylene diamide $CH_2{<}{CO.NH \atop CO.NH}{>}C_2H_4$. Formed by heating malonic ether or malonamide with ethylene-diamine (Freund, *B.* 17, 137). Crystalline solid. V. sol. water, nearly insol. alcohol.

Amide-anilide $CONH_2.CH_2.CONHPh$. [163°]. Obtained by heating malonamide with 1 mol. of aniline for ½ hour at 200°–220° (Freund, *B.* 17, 135). Fine white felted needles. Sol. hot water and alcohol.

Mono-anilide $CO_2H.CH_2.CO.NHPh$. *Phenyl-malonamic acid. Malonanilic acid. Malonphenylamic acid.* [132°]. Formed by boiling the amide-anilide with milk of lime (Freund, *B.* 17, 135). Formed also by heating sodium acetyl-phenyl-carbamate $C_6H_5NAc.CO_2Na$ for 5 or 6 hours at 130°–140° under pressure (Seifert, *B.* 18, 1359), and by heating malonic acid (1 mol.) with aniline (1 mol.) at 105° (Rügheimer, *B.* 17, 737). Large colourless monoclinic crystals, or slender needles. At its melting-point it breaks up quantitatively into CO_2 and acetanilide. — A′Ag: small white needles. — A'_2Ca 4½aq: large needles.

Ethyl ether of the mono-anilide $CO_2Et.CH_2.CONHPh$. [39°]. From aniline and $CO_2Et.CH_2.COCl$, both dissolved in benzene (Rügheimer a. Hoffmann, *B.* 17, 739). Crystals (from ether-ligroïn). Insol. water and ligroïn, v. e. sol. alcohol and benzene.

Anilide $CH_2(CONHPh)_2$. [223°]. Obtained by boiling malonic ether or malonamide with aniline (Freund, *B.* 17, 134). White needles. Insol. water and ether, e. sol. hot alcohol.

Tri-bromo-anilide $CH_2(CO.NH.C_6H_2Br_3)_2$. [146°]. White silky needles, sl. sol. alcohol, insol. water (Freund, *B.* 17, 780).

Methyl-anilide $CH_2(CO.NMePh)_2$. [109°]. Obtained by boiling malonic ether with an excess of methyl-aniline (Freund, *B.* 17, 137). Colourless trimetric prisms. V. sol. alcohol.

Mono-o-toluide [2:1] $CH_3.C_6H_4.NH.CO.CH_2.CO_2H$. *o-Tolyl-malonamic acid.* Colourless needles, v. sol. water and alcohol. Melts about 140°, giving off CO_2.—CaA'_2 3aq: small needles, m. sol. water.—BaA'_2 aq: needles, v. sol. water.—CuA'_2 2aq: prisms (Rügheimer a. Hoffmann, *B.* 18, 2971).

Ethyl ether of the o-*toluide* EtA'. [74°]. Long needles, sol. ether and ligroïn.

Mono-m-toluide [3:1] $CH_3.C_6H_4.NH.CO.CH_2.CO_2H$. [101°].

Mono-p-toluide [4:1] $CH_3.C_6H_4.NH.CO.CH_2.CO_2H$. Obtained by heating malonic acid with *p*-toluidine (Rügheimer a. Hoffmann, *B.* 17, 740; 18, 2971). Long colourless needles, sol. water, alcohol, ether, and chloroform. At 150° it gives off CO_2. PCl_5 converts it into tri-chloro-methyl-quinoline [134°].—CaA'_2 4½aq: long needles, m. sol. water. —BaA'_2 5aq: needles.—AgA': cheesy white pp. or needles, sl. sol. water.—CuA'_2 2aq: minute needles, sl. sol. hot water.—ZnA'_2: glistening plates, m. sol. water.

Ethyl ether of the *p-Toluide.* EtA': plates, v. sol. alcohol.

Mono-phenyl hydrazide $PhN_2H_2.CO.CH_2.CO_2H$. [154°]. Formed from malonic acid and aqueous phenyl-hydrazine acetate at 100° (Fischer a. Passmore, *B.* 22, 2734). Needles, v. sol. water. Its phenyl-hydrazine salt $PhN_2H_2.CO.CH_2.CO_2N_2H_4Ph$ is converted at 200° into $CH_2<\substack{CO\\CO}>N_2HPh$, crystallising in white needles, [128°], v. sol. alcohol.

Di-phenyl dihydrazide $CH_2(CO.N_2H_2Ph)_2$. [187°]. From malonic ether or the amide of malonic acid and phenyl-hydrazine at 200° (Freund a. Goldsmith, *B.* 21, 1241). Plates (from dilute alcohol). With $COCl_2$ it gives $C_{17}H_{12}N_4O_4$, which crystallises from HOAc in laminæ [205°].

Semi-nitrile $CO_2H.CH_2.CN$ *v.* Cyano-acetic acid.

Nitrile $CH_2(CN)_2$. *Methylene cyanide.* [30°]. (219°) (H.); (223°) (Berthelot a. Petit, *A. Ch.* [6] 17, 131). H.F. –43200. Obtained by heating cyano-acetamide $CN.CH_2.CONH_2$ with P_2O_5 (Henry, *C. R.* 102, 1394, 1481). White solid. Appears to be polymerised by prolonged action of heat. Sol. water, v. sol. alcohol and ether. Burns with a purple-edged flame. Conc. HClAq dissolves it with evolution of heat and formation of malonic acid. HClAq at 150° in sealed tubes forms CO_2 and chloro-acetic acid. With ammoniacal $AgNO_3$ it gives a white pp. $CAg_2(CN)_2$ (?), which explodes when heated.

References.—Amido-, Bromo-, Chloro-, Cyano-, Nitro-, Methyl-, Ethyl-, Propyl-, Methyl-ethyl-, and Benzyl- Malonic acid.

MALONYL-UREA *v.* Barbituric acid.

Isomalonylurea $CO<\substack{NH.CH\\NH.CO}>C.OH$ is formed, together with amido-uracil, by reducing nitro-uracil (Behrend, *A.* 229, 39; *B.* 21, 999). It is converted by bromine into an acid isomeric with dialuric acid. The acetyl derivative $C_4H_3N_2O_3Ac$ crystallises from hot water in prisms.

MALONOXYL-AMIDO-BENZENE *v.* Carboxy-phenyl-malonamic acid.

MALTOBIONIC ACID $C_{12}H_{22}O_{12}$. Formed by oxidising maltose (1 pt.) by bromine (1 pt.) in water (7 pts.) (E. Fischer a. Meyer, *B.* 22, 1941). Almost colourless syrup. V. sol. water, sl. sol. alcohol, insol. ether. It reduces Fehling's solution. By heating with dilute sulphuric acid it is split up into dextrose and gluconic acid.

Salt.—CaA'_2: hard shining mass, v. sol. water.

MALTONIC ACID. Identical with Gluconic acid (*q. v.*)

MALTOSE *v.* Sugar.

MALYL UREÏDE, so-called, *v.* Uramido-succinic acid.

MANDELAMIDINE $C_8H_{10}N_2O$ *i.e.* $C_6H_5.CH(OH).C(NH_2):NH$. [110°]. From the hydrochloride of mandelic imido-ether and alcoholic NH_3 (Beyer, *J. pr.* [2] 31, 387). Needles, v. sol. water and alcohol, sl. sol. ether. Very unstable.—B'HCl. [214°]. Prisms (from cold water).

MANDELAMIDOXIM $C_8H_{10}N_2O_2$ *i.e.* $C_6H_5.CH(OH).C(NH_2):NOH$. [159°]. From the nitrile of mandelic acid and hydroxylamine (base) (Tiemann, *B.* 17, 126). Crystals (from alcohol). Insol. benzene, sl. sol. cold, v. sol. hot, water. V. e. sol. aqueous acids and alkalis. $FeCl_3$ colours its aqueous solution blood-red. It does not reduce Fehling's solution.

Reactions.—1. The hydrochloride, mixed with conc. aqueous *potassium cyanate* forms $C_6H_5.CH(OH).C(NOH).NH.CO.NH_2$ [127°].—2. *Phenyl cyanate* forms the corresponding $Ph.CH(OH).C(NOH).NH.CO.NHPh$ [155°].—3. Excess of AcCl, or a mixture of Ac_2O and NaOAc forms $C_6H_5.CH(OAc)C<\substack{N.O\\N}>C.CH_3$ [52°].—4. $COCl_2$, added to its benzene solution, forms $(C_6H_5.CH(OH).C(NH_2):N.O)_2CO$ [131°].—5. *Chloroformic ether*, $ClCO_2Et$, gives the compound $C_6H_5.CH(OH).C(NH_2):N.O.CO_2Et$ [107°].

Salts.—NaA': needles.—HA'HCl (Gross, *B.* 18, 1074).

Ethyl ether EtA'. [89°]. Slender needles; sl. sol. cold water. With phenyl cyanate it forms $Ph.CH(OH).C(NOEt).NH.CO.NHPh$ [119°].

Benzyl ether $C_6H_5CH_2A'$. [103°]. From mandelamidoxim, NaOEt, and benzyl chloride (Gross, *B.* 18, 1080). Needles.

Acetyl derivative $C_6H_5.CH(OH).C(NH_2):NOAc$. [140°]. From mandelamidoxim and Ac_2O. Crystals (from alcohol). Insol. cold water; sol. alcohol, ether, and benzene. With water at 100° it forms $C_6H_5.CH(OH).C<\substack{NO\\N}>C.CH_3$ [65°].

Di-acetyl derivative $C_6H_5.CH(OAc).C(NH_2):NOAc$. [113°]. From mandelamidoxim and a slight excess of AcCl. Laminæ (from alcohol).

Benzoyl derivative $C_6H_5.CH(OH).C(NH_2):NOBz$. [149°]. From mandelamidoxim and BzCl (1 mol.). With

AcCl it gives $C_6H_5.CH(OAc).C(NH_2):NOBz$ [165°] (Gross).

MANDELIC ACID $C_8H_8O_3$ *i.e.* $C_6H_5.CH(OH).CO_2H$. *Phenyl-glycollic acid. Oxy-phenyl-acetic acid.* Mol. w. 152. [115°] (Müller, *Ar. Ph.* [3] 2, 385); [118°] (Claisen, *B.* 10, 847; Lewkovitch, *B.* 16, 1568). S.G. $\frac{\pm}{}$ 1·361 (Schröder, *B.* 12, 1612). S. 16 at 20°. *Heat of solution*: −3100. *Heat of neutralisation* by NaOH: +13860 (Berthelot, *A. Ch.* [6] 7, 185).

Formation.—1. Discovered by Winckler (*A.* 18, 310), who obtained it by heating bitter almond water with HCl, the benzoic aldehyde reacting with the HCy present (Liebig, *A.* 18, 319).—2. By heating amygdalin with fuming HClAq (Wöhler, *A.* 66, 238).—3. By boiling the compound of benzoic aldehyde with $KHSO_3$ for several hours with KCy and alcohol. The nitrile $C_6H_5.CH(OH).CN$ thus formed is saponified by dilute HClAq (O. Müller, *B.* 4, 980).—4. By reducing phenyl-glyoxylic acid $C_6H_5.CO.CO_2H$ with sodium-amalgam (Schwebel, *B.* 10, 2045).—5. From di-bromo-acetophenone $C_6H_5.CO.CHBr_2$ by boiling with dilute KOHAq (1:20), the compound $C_6H_5.CO.CH(OH)_2$ being a theoretical intermediate product (Engler a. Wöhrle, *B.* 20, 2202).—6. In small quantity, by boiling pseudo-phenyl-hydantoïn with baryta (Pinner, *B.* 21, 2327).—7. By boiling α-chloro-phenyl-acetic acid with alkalis (Spiegel, *B.* 14, 239).

Preparation. — Benzoic aldehyde (100 g.), water (3500 c.c.), fuming HClAq (200 g.), and 4 times the calculated quantity of hydrogen cyanide are boiled for 36 hours. The product is evaporated at 100°, the residue extracted with ether, the extract evaporated, and the mandelic acid left recrystallised from water (Wallach, *A.* 193, 38; *cf.* Strecker, *A.* 75, 27).

Properties.—Large trimetric crystals; v. sol. water, alcohol, and ether. Inactive to light. By crystallisation of the cinchonine salt it can be separated into equal quantities of the dextro- and lævorotatory acids. If *Penicillium glaucum* is grown in it the lævorotatory acid is destroyed, leaving the dextrorotatory (Lewkowitsch, *B.* 16, 1568).

Reactions.—1. $KMnO_4$ and KOH convert it, in the cold, into phenyl-glyoxylic acid (R. Meyer a. A. Baur, *A.* 220, 39).—2. Dry *distillation* yields benzoic aldehyde.—3. Boiling with MnO_2 and H_2SO_4 yields benzoic aldehyde and CO_2.—4. Fuming HBrAq converts it slowly in the cold, quickly at 125°, into α-bromo-phenyl-acetic acid, whence alcoholic NaOEt forms the ethyl derivative of mandelic acid (Glaser a. Radziszewsky, *Z.* [2] 4, 140).—5. Fuming HClAq at 140° gives α-chloro-phenyl-acetic acid.—6. *Phosphorus* and HI reduce it to phenyl-acetic acid.—7. When taken internally it passes unaltered into the urine (Schotten, *H.* 8, 68).—8. Cannot be nitrated. Conc. NHO_3 forms benzoic aldehyde (Liebig, *A.* 18, 321), dilute HNO_3 forms phenyl-glyoxylic acid (Zincke a. Hannäus, *B.* 10, 1488).—9. Dilute H_2SO_4 in sealed tubes at 130° converts mandelic acid nearly quantitatively into benzoic aldehyde and formic acid (Biedermann, *B.* 19, 638). 10. *Chloral* at 120° forms

$$C_6H_5.CH{<}\begin{matrix}O\text{———}\\CO.O\end{matrix}{>}CH.CCl_3$$

which forms large transparent crystals [83°]; insol. water, sol. alcohol and chloroform (Wallach, *A.* 193, 1).—11. *Phenyl-hydrazine* forms a compound [182°], crystallising in needles and almost insol. boiling water (Reissert a. Kayser, *B.* 22, 2928).

Salts.—The ammonium and potassium salts are very soluble and difficult to crystallise. The Ba salt forms small needles. S. 8 at 24°; 16 at 100° (Zinin, *Z.* 1868, 710). The lead salt is a crystalline powder, scarcely sol. water.—CuA'_2 (dried at 100°).—AgA′: crystalline pp. May be crystallised from water.

Methyl ether MeA′. [48°]. Small laminæ (from benzene-ligroïn) (Zincke a. Breuer, *B.* 13, 636).

Ethyl ether $Ph.CH(OH)CO_2Et$. (254°). Formed by the action of water on the hydrochloride of mandelic imido-ether (*q.v.*). Solidifies in a freezing mixture, but is liquid at ordinary temperatures (Beyer, *J. pr.* [2] 31, 389). But Naquet and Luguinin (*A.* 139, 300), who prepared it from silver mandelate and EtI, say it melts at 75°.

Methyl derivative $Ph.CH(OMe)CO_2H$. [72°]. Formed from $Ph.CHCl.CO_2Me$, MeOH, and NaOMe (R. Meyer a. H. Boner, *A.* 220, 44; *B.* 14, 2392). Needles grouped concentrically (on solidifying) or thick tables (from light petroleum). V. sol. alcohol or ether, sl. sol. cold water or cold petroleum. KOH and $KMnO_4$ forms phenyl-glyoxylic acid.

Salts. — NaA′2aq. — $BaA'_2$2aq. — CaA'_2. — $CuA'_2$2aq.—AgA′.

Methyl ether of the methyl derivative $Ph.CH(OMe).CO_2Me$. (246° cor.).

Ethyl derivative $C_6H_5.CH(OEt).CO_2H$. From $C_6H_5.CHBr.CO_2H$ and alcoholic KOEt. Viscid mass.—AgA′: pulverulent pp.

Phenyl derivative $Ph.CH(OPh).CO_2H$. [108°]. From methyl α-chloro-phenyl-acetate and sodium phenate (R. Meyer a. H. Boner, *A.* 220, 51). Radiating groups of slender needles (from water). V. sl. sol. cold water, v. e. sol. alcohol or ether. KOH and $KMnO_4$ convert it into phenyl-glyoxylic acid. HNO_3 forms picric acid and benzoic aldehyde.—$NaA'_2$3aq.—CuA'_2.—AgA′.

Acetyl derivative of the ethyl ether $C_6H_5.CH(OAc).CO_2Et$. [74°]. From mandelic acid by successive treatment with AcCl and alcohol (Naquet a. Luguinin, *A.* 139, 302). Slender needles (from ether). Insol. water, v. sol. alcohol and ether.

Amide $C_6H_5.CH(OH).CONH_2$. [132°]. S. 3 at 24°. S. (boiling 93 p.c. alcohol) 100 (Z.). Formed, together with benzoic aldehyde, by heating the compound $(C_6H_5.CHO)_2CNH$ with water or alcohol at 180° (Zinin, *Z.* [2] 4, 709). Formed also by allowing a mixture of the nitrile with fuming HClAq to stand in the cold (Tiemann a. Friedländer, *B.* 14, 1967). Likewise obtained by the action of NH_3 on mandelic ether, and by heating mandelic imido-ether (C. Beyer, *J. pr.* [2] 31, 386). Prismatic needles or plates. Sol. hot, sl. sol. cold, water; sl. sol. ether, v. sol. alcohol. Decomposed by acids and alkalis with production of mandelic acid. A polymeride (?) melts at 190°.

Nitrile $C_6H_5CH(OH).CN$. [−10°]. S.G. 1·124. Obtained by adding fuming HClAq to a mixture of benzoic aldehyde and KCy (Spiegel, *B.* 14, 239; Völkel, *A.* 52, 361). Oil; sol. alco-

hol and ether. Dissolved in ether, mixed with alcohol (1 equivalent), and treated with HCl gas it forms C_6H_5.CH(OH).C(OEt):NH,HCl [125°]. This is decomposed by water, forming NH_4Cl and mandelic ether (Beyer, *J. pr.* [2] 28, 190). At 170° mandelonitrile splits up into benzoic aldehyde and HCy. Boiling aqueous HCl gives NH_4Cl and mandelic acid. Fuming HClAq forms the amide in the cold, but on heating it gives α-chloro-phenyl-acetic acid. NH_3 in the cold forms $C_6H_5.CH(NH_2).CN$. Methylamine yields C_6H_5.CH(NHMe).CN. Phenyl-hydrazine produces the phenyl-hydrazide of benzoic aldehyde (Reissert, *B.* 17, 1451).

(*dextro*)-**Mandelic acid** [133° cor.]. $[\alpha]_D$ at 20° = +156. Prepared by converting inactive mandelic acid into the cinchonine salt and adding a crystal of cinchonine dextro-mandelate to the aqueous solution when the dextro- salt crystallises out, leaving the lævo- salt in solution. It can be also obtained by growing Penicillium glaucum in the inactive acid, which destroys the lævorotatory acid, leaving the dextrorotatory (Lewkowitsch, *B.* 16, 1568). Resembles the lævo-acid, having the same solubility in water.

(*lævo*)-**Mandelic acid** [133°]. S. 8·64 at 20° $[\alpha]_D$ at 20° = −158. Prepared by heating amygdalin with strong HCl for several hours on the water-bath. It can also be obtained from inactive mandelic acid, which can be separated into equal quantities of the lævo- and dextrorotatory acids by crystallisation of the cinchonine salt (Lewkowitsch, *B.* 16, 1565; *cf.* Wöhler, *A.* 66, 240).

Nitro-mandelic acid *v.* NITRO-OXY-PHENYL-ACETIC ACID.

MANDELIC IMIDO-ETHER Ph.CH(OH)C(NH)OEt. [72°].

Preparation. — Benzoic aldehyde (100 g.) treated with KCN, dilute HCl and ether forms the cyanhydrin Ph.CH(OH)CN which is dissolved by the ether. If this is mixed with an equivalent of alcohol and dry HCl be passed in, the liquid being cooled, needles of the hydrochloride of mandelic imido-ether (80 g.) are formed (C. Beyer, *J. pr.* [2] 31, 381). Ph.CH(OH).CN + EtOH + HCl = PhCH(OH).C(NH).OEt,HCl. These melt at [125°]. The free ether is got by shaking these simultaneously with conc. KOH and ether. After evaporating the ether the residue is crystallised from ligroïn.

Properties. — White needles. Extremely soluble in ether, alcohol, and benzene.

Reactions.—1. At 140° the hydrochloride splits up thus: PhCH(OH)C(NH)OEt,HCl = EtCl + PhCH(OH)$CONH_2$, forming mandelamide.—2. Alcoholic NH_3 converts the hydrochloride into the hydrochloride of the amidine, Ph.CH(OH)C(NH)NH_2,HCl. This forms prisms [211°]. Shaken with ether and potash, the free mandel-amidine, ×Ph.CH(OH)C(NH)NH_2, is dissolved by the ether. It forms feathery needles of narcotic odour, melting at [110°].—3. *Water* quickly converts the hydrochloride into mandelic ether (*q. v.*) C_6H_5CH(OH).C(NH).OEt,HCl + H_2O = C_6H_5CH(OH).CO.OEt + NH_3,HCl.

MANDRAGORINE $C_{17}H_{23}NO_3$. [c. 79°]. Extracted from powdered mandragora root by alcohol. The extract is evaporated and the residue treated with very dilute acid. The alkaloid is liberated from the acid solution by

adding K_2CO_3 and shaking with ether (Ahrens, *A.* 251, 312). Hygroscopic brittle mass. Picric acid gives with a solution of mandragorine hydrochloride light-yellow needles of the picrate. Iodine in KIAq gives an oily periodide. K_4FeCy_6 gives no pp. Phosphotungstate gives a white pp. The sulphate is crystalline and very deliquescent. Dropped into the eye, its solution causes enlargement of the pupil.—B'$HAuCl_4$: [155°]; yellow plates; sol. hot water and HClAq. —$B'_2H_2PtCl_6$. [194°]. Red nodules or yellow plates (from hot water).—B'HCl4$HgCl_2$. [160°]. Plates or needles (from water) or long slender needles (from alcohol). V. sol. alcohol (Ahrens, *B.* 22, 2161).

Mandragora root also contains a second alkaloid of which the platinochloride [181°] and aurochloride [147°–153°] are crystalline (Ahrens).

MANGANATES. Salts of the form $M^I_2MnO_4$ derived from the hypothetical acid H_2MnO_4; *v.* MANGANESE, OXYACIDS OF, p. 185.

MANGANESE. Mn. At. w. 55. Mol. w. probably same as At. w. (*v. infra*). [c. 1800°–1900°]. S.G. 6·85 to 8·01; according to Glatzel, S.G. of pure Mn is 7·3921 at 22° (*B.* 22, 2857). S.H. 14° to 97° ·1217 (Regnault, *A. Ch.* [3] 67, 427; specimen contained Si). Chief lines in emission-spectrum are 6521, 6016, 6013, 4823, 4783, 4765, 4762, 4753, 4235, 4027 (Thalén). For absorption-spectrum of Mn vapour *v.* Lockyer a. Roberts (*Pr.* 23, 344).

Occurrence.—The metal does not occur uncombined. Mn compounds are widely distributed; the chief are *pyrolusite* MnO_2, *braunite* Mn_2O_3, *manganite* $Mn_2O_3.H_2O$, *hausmannite* Mn_3O_4, *psilomelane* $(Mn,Ba,K_2)O.4MnO_2$, *manganese-spar* $MnCO_3$, *manganese-blende* MnS. Small quantities of Mn compounds are found in sea-water (Forchhammer, *Pr.E.* 2, 303); in many mineral waters (Buchanan, *Pr.* 24, 593); in blood (Cottereau, *J.* 1849. 530; Burin de Buisson, *J.* 1852. 377; Campani, *B.* 5, 287); in the liver (Béchamp, *C. R.* 49, 895); in milk (Polacci, *Naturforscher*, 4, 122); in human urine (Horsford, *J.* 1851. 602); in wines, cereals, most vegetables used as human food, and in considerable quantities in tea (Maumené, *C. R.* 98, 1056, 1416). Mn also occurs in the sun's atmosphere (Cornu, *C. R.* 86, 315, 530).

Manganese dioxide was recognised as a compound of a distinctive metal by Scheele in 1774; it had previously been looked on as a compound of iron. The metal Mn was first isolated by Gahn. Native MnO_2 was long known as *magnesia nigra* (probably because of its supposed magnetic properties); a new medicine was introduced in the early years of the eighteenth century, and was called *magnesia alba*, seemingly in contra-distinction to *magnesia nigra*; when *magnesia nigra* was shown to contain a distinctive metal, this metal was called sometimes *magnesium* and sometimes *manganesium*; finally the name *magnesium* was retained for the metal of *magnesia alba*, and the name *manganesium* (hence *manganese*) was given to the metal of *magnesia nigra*.

Formation.—1. By reducing the oxides by C at a white heat.—2. By reducing MnF_2 or $MnCl_2$ by Na or by Mg.—3. By heating Mn amalgam in a stream of H; the amalgam is made by the reaction of Na amalgam with $MnCl_2$Aq (Giles,

P. M. [4] 24, 328; Roussin, *Bl.* 6, 93).—4. By electrolysing $MnCl_2Aq$ in a porous cell placed in a carbon crucible containing HClAq (Bunsen, *P.* 91, 619).

Preparation. — 1. Crystallised $MnCl_2$ is thoroughly dried by heating; it is then finely powdered and 100 grams are intimately mixed with 200 grams well dried and powdered KCl; the mixture is packed into a Hessian crucible which is loosely covered and heated in an air-furnace until the contents melt (the temperature must not be raised so high that white vapours begin to come off); the lid is removed and 15 grams Mg are thrown into the crucible in four or five portions, each weighing 3 to 4 grams, two to three minutes being allowed to elapse between the entrance of each piece; the lid is now replaced and the crucible is strongly heated for a few minutes, and then allowed to cool very slowly in the furnace. About 20 to 25 grams Mn are thus obtained as a compact regulus. If the temperature of the final heating is not sufficiently high, the regulus does not form a compact mass; if the temperature is too high and the heating is unduly prolonged, the KCl is vaporised and the surface of the Mn is oxidised (Glatzel, *B.* 22, 2857).—2. Brunner (*P.* 101, 264) recommends the following method:—2 pts. MnF_2 (obtained by dissolving moist $MnCO_3$ in HFAq, evaporating and drying at 100°) and 1 pt. Na are arranged in alternate thin layers in a Hessian crucible, the mixture is pressed down and covered with NaCl over which is placed a layer of CaF_2 in small pieces (to prevent spirting); the crucible is covered and heated in an air-furnace, at first gently, and then to near a white heat for about $\frac{1}{4}$ an hour; the crucible is then allowed to cool very slowly in the furnace. — 3. For an account of the older methods of preparing Mn from MnO_2, *v.* John (Gehlen's *Journ. Chem. Phys.* 3, 452), and Deville (*A. Ch.* [3] 46, 182). Tamm describes a method for obtaining approximately pure metal (99·91 p.c. Mn, ·05 p.c. Fe, ·115 p.c. Si, and ·025 p.c. C) from MnO_2 (*C. N.* 26, 73, 111).

Properties.—A white-grey, lustrous, metal; very hard; brittle; may be highly polished; non-magnetic (Glatzel). According to Glatzel (*B.* 22, 2857), Mn prepared by reducing $MnCl_2$ by Mg (*v. Preparation* No. 1) is unchanged by keeping for months in a bottle closed with a glass stopper; but in moist air the surface undergoes slight oxidation. Mn is usually described as very easily oxidised in ordinary air, and as capable of decomposing water, with evolution of H, almost as rapidly as K. Mn obtained by Brunner (*v. Preparation* No. 2) by reducing MnF_2 by Na was scarcely oxidised in cold water. According to Bullock (*C. N.* 60, 20), Mn prepared by reducing the oxides by C is very easily oxidised, while specimens obtained by reducing $MnCl_2$ by Na are no more oxidisable than iron. It is probable that some specimens have contained small traces of Si and C which have affected the properties of the metal. Mn melts at a very high temperature (c. 1800°–1900°), and is said to volatilise at a full white heat.

The atomic weight of Mn has been determined (1) by estimating Cl in $MnCl_2$ (Arfvedson, *S.* 42, 202; Dumas, *A. Ch.* [3] 55, 151; Berzelius, *P.* 18, 71); (2) by dissolving Mn in HNO_3, evaporating, and calcining the nitrate (Berzelius, *P.* 8, 185); (3) by oxidising MnO to Mn_3O_4 by heating in air (v. Hauer, *W. A. B.* 25, 133); (4) by reducing Mn_3O_4 in H, and weighing H_2O produced (Rawack, *P.* 107, 605, 616); (5) by analysing MnC_2O_4 (Schneider, *P.* 107, 605); (6) by reducing $AgMnO_4$ and estimating Ag produced (Dewar a. Scott, *Pr.* 35, 44); (7) by determining S.H. (Regnault, *A. Ch.* [3] 67, 427).

Molecular weight of manganese.—Ramsay (*C. J.* 55, 521) has determined the lowering of the vapour pressure of Hg produced by dissolving Mn in Hg; the results render it probable that the molecular weight of Mn is the same as the atomic weight. This conclusion assumes the accuracy of Van't Hoff's law that equal volumes of dilute solutions contain equal numbers of molecules of the dissolved substances, and it also supposes the molecular weight of liquid Hg to be the same as the atomic weight of Hg.

Mn is metallic in its physical, and some of its chemical, properties; but in many of its reactions it behaves as a non-metal. The oxides MnO and Mn_2O_3 are basic, forming salts, such as $MnSO_4$ and $Mn_2(SO_4)_3$, of which the manganous salts, corresponding with MnO, are much the more stable. The oxide MnO_2 reacts as a basic peroxide, *e.g.* with H_2SO_4 it forms $MnSO_4$ and O; it also reacts with some positive oxides, *e.g.* CaO, to produce salts of the form $xMO.yMnO_2$; when this oxide is treated with molten KOH in presence of O the salt K_2MnO_4 is formed, in which Mn forms part of the acidic radicle. The oxides MnO_3 and Mn_2O_7 have also been isolated; both are very unstable; both react with water to form manganic acid $HMnO_4$, the former (MnO_3) at the same time also producing MnO_2; these oxides are distinctly acidic. The acid $HMnO_4$ has been isolated, and many salts derived from the hypothetical acid H_2MnO_4 are known.

Mn shows marked analogies with the iron metals Fe, Ni, and Co; it is also related, although less distinctly, to the halogens; and it is also related to the chromium metals, Cr, Mo, W, and U. In the classification of the elements based on the periodic law, Mn occupies a position different from that of any known element: it is placed in the same group as the halogens (Group VII.), and in the same family (even-series members) as F, but no member of this family coming after Mn (*i.e.* with a greater atomic weight than Mn) has yet been isolated; Mn finds a place in series 4 (K, Ca, Sc, Ti, V, Cr, Mn), all the members of which are metallic, and it is immediately followed by Fe, Ni, Co, and Cu. The strongly marked negative character of the halogens is impressed on Mn, but this is counterbalanced by the positive characteristics of the metals which come before and after Mn in order of atomic weights (*v.* HALOGEN ELEMENTS, vol. ii. p. 666; also IRON GROUP OF ELEMENTS, this vol. p. 65).

The atom of Mn is divalent in the gaseous molecule $MnCl_2$.

Reactions.—1. Mn is oxidised in *air* or *oxygen*, forming MnO.—2. Mn reacts energetically with *dilute mineral acids* forming salts of MnO. 3. Fused with *potassium nitrate* or *chlorate* $KMnO_4$ is produced.—4. Heated in *bromine* $MnBr_2$ is formed.—5. When Mn is heated in a stream

of *hydrogen chloride* $MnCl_2$ is produced.—6. Mn decomposes *water* readily, with evolution of H. The reactions of the metal have not been much examined.

Combinations.—Mn forms alloys with many metals, and compounds with most of the non-metals, but few have been formed by the direct union of their elements.

Detection and estimation.—Mn is usually detected by the colour its compounds impart to a borax-bead, and by the ppn. of buff-coloured MnS by addition of NH_4 sulphide to an alkaline or neutral solution of Mn salts. Mn is usually estimated gravimetrically by ppn. with NH_3Aq, heating the pp. in air, and weighing as Mn_3O_4. As MnO_2 is much used in technical chemistry it is necessary to have accurate and rapid methods for determining the quantity of this oxide in specimens of Mn ores; for descriptions of these methods, and also for other methods for estimating Mn, reference must be made to *Manuals of Analysis*.

Manganese, alloys of. Several alloys of Mn have been prepared; none has been made by directly alloying Mn with other metals.

1. With *aluminium*. Wöhler a. Michel (*A.* 115, 102) obtained a crystalline powder, having the composition $MnAl_3$, by fusing together $MnCl_2$, Al, and a mixture of NaCl and KCl.

2. With *copper*. Alloys of Mn and Cu are obtained by reducing mixtures of MnO_2 and Cu with charcoal; an alloy containing 25 p.c. Mn is white, fairly hard, very elastic, and tolerably easily melted (Allen, *C. N.* 22, 184). Alloys containing from 3 to 20 p.c. Mn resemble bronze (Valenciennes, *C. R.* 70, 607; *v.* also Schrötter, *D. P. J.* 210, 355; Prieger, *ibid.* 177, 303; Gintl, *ibid.* 224, 653).

3. With *iron*. Alloys of Mn and Fe, containing from 8 to 80 p.c. Mn, are used in the manufacture of steel, under the names of *spiegeleisen* and *ferromanganese*. These alloys are prepared by heating MnO_2 with iron filings and charcoal in the blast-furnace, or in graphite crucibles, or by reducing a mixture of FeO and $MnCO_3$ on the hearth of a Siemens' furnace, and then fusing under a reducing flame.

4. With *mercury*. An amalgam of Mn is obtained by reducing $MnCl_2Aq$ by Na-amalgam (Giles, *P. M.* [4] 24, 328); also by electrolysing $MnCl_2Aq$ in contact with Hg (Ramsay, *C. J.* 55, 532; Moissan, *Bl.* [2] 31, 149). Alloys of Mn with Pb, Sn, and Zn are described by Allen (*l.c.*) and Valenciennes (*l.c.*).

Manganese, arsenates of; *v.* vol. i. p. 309.

Manganese, arsenide of. Mn and As combine when heated together to redness. An arsenide, approximately As_3Mn_4, occurs native (Kane, *P.* 19, 145).

Manganese, arsenite of; *v.* vol. i. p. 306.

Manganese, boride of. By heating Mn_3C (*v. Manganese, carbides of*) with B_2O_3 in a graphite crucible, Troost and Hautefeuille obtained small greyish-violet crystals of MnB_2 (*C. R.* 81, 1263). This compound decomposes water at 100° and dissolves in acids with evolution of H; it reacts with moist $HgCl_2$ to produce $MnCl_2$, boric acid, and HCl.

Manganese, bromides of. Only one bromide, $MnBr_2$, has been isolated; the tetrabromide also perhaps exists in solution.

Manganous bromide, $MnBr_2$. *Manganese dibromide.* The hydrate $MnBr_2.4H_2O$ is obtained as clear, red, deliquescent, crystals, by dissolving $MnCO_3$ in HBrAq, or by digesting Mn with Br (Balard, *J. pr.* 4, 178; Marignac, *Ann. M.* [5] 12, 7); crystallises in monoclinic forms, $a:b:c = \cdot645:1:1\cdot165$ (Marignac). The anhydrous salt $MnBr_2$ is obtained by heating powdered Mn in Br vapour; it forms a rose-red deliquescent mass; heated in air it gives Br and Mn_3O_4. Thomsen gives the thermal data:—$[Mn, Br^2, Aq] = 106{,}120$ (*Th.* 3, 271).

Manganic bromide, $MnBr_4$. (*Manganese tetrabromide*). This compound perhaps exists in the green solution obtained by treating Mn_3O_4 or MnO_2 with HBr gas and dry ether; the solution is easily decomposed with formation of $MnBr_2$ (Nicklès, *C. R.* 60, 79).

Manganese, carbides of. According to Brown (*J. pr.* 17, 492), the compound MnC is obtained by heating $Mn(SCy)_2$, and MnC_2 by heating $MnCy_2$. Troost and Hautefeuille obtained graphite-like, lustrous, crystals of Mn_3C by melting Mn in a charcoal crucible, and cooling slowly (*C. R.* 80, 960).

Manganese, chlorides of. The only chloride of Mn which has been isolated is $MnCl_2$. A solution of MnO_2 or Mn_2O_3 in conc. cold HClAq very probably contains Mn_2Cl_6, perhaps also some $MnCl_4$. The existence of $MnCl_7$, described by Dumas, is very doubtful.

Manganous chloride, $MnCl_2$. Mol. w. 125·74. Rose-coloured crystals of $MnCl_2.4H_2O$ are obtained by dissolving $MnCO_3$, or any oxide of Mn, in HClAq, and evaporating; by heating the dried crystals in a stream of dry HCl, the anhydrous salt, $MnCl_2$, is obtained. $MnCl_2$ is also formed by heating Mn, $MnCO_3$, or Mn_3O_4, in a stream of dry HCl. By heating very finely powdered MnO_2 with half its weight of NH_4Cl gradually to redness, $MnCl_2$ is formed. $MnCl_2$ is very deliquescent; Brandes (*P.* 22, 263) gives S. at 10° = 62·16, at 31·25° = 85·72, at 62·5° = 122·22, at 87·5° = 122·22, and at 106·25° = 123·81. S. in alcohol at 11° = 50. S.G. of $MnCl_2 = 2\cdot478$ (Schröder), of $MnCl_2.4H_2O = 1\cdot913$ (Schröder), 2·015 (Boedeker). The tetrahydrated salt is isomorphous with $FeCl_2.4H_2O$; monoclinic, $a:b:c = 1\cdot1409:1:1\cdot6406$ (Marignac, *Ann. M.* [5] 15). All water is removed at 100°. Thomsen gives the thermal data: $[Mn,Cl^2] = 111{,}990$; $[MnCl^2,Aq] = 16{,}010$; $[MnCl^2,4H_2O] = 14{,}470$ (*Th.* 3, 270). Heated in O, a crystalline oxide containing 37 p.c. MnO_2 is produced (Schulze, *J. pr.* [2] 21, 407). $MnCl_2$ melts, in absence of air, at a red heat and sublimes at higher temperature. Scott found V.D. at c. 1200°–1500° to be 132·3 (*Pr. E.* 14, 410).

$MnCl_2$ forms double salts with the alkali chlorides, of the composition $MnCl_2.2XCl.3H_2O$. The best examined are those in which X = NH_4, Rb, and Cs; the NH_4 salt contains one H_2O only according to Rammelsberg (*J. pr.* 65, 181; confirmed by Pickering, *C. J.* 35, 672). The double salts are obtained by mixing $MnCl_2Aq$ or a solution of an oxide of Mn in HClAq, with the alkali chloride, and evaporating slowly (*v.* Godeffroy, *B.* 8, 9; v. Hauer, *J. pr.* 63, 436). Another double salt $MnCl_2.3CuO.3H_2O$, is formed by boiling $MnCl_2Aq$ with powdered CuO, filtering, and cooling (André, *C. R.* 106, 854). The double

salt $MnCl_2.HgCl_2.4H_2O$, is described by Bonsdorff (*P.* 17, 131).

MANGANIC CHLORIDE, Mn_2Cl_6; and MANGANESE TETRACHLORIDE, $MnCl_4$. Neither of these chlorides has been isolated. Mn_2O_3 and MnO_2 dissolve in cold conc. HClAq to form deep-brown liquids, which slowly evolve Cl and after a time contain $MnCl_2$. Nicklès (*A. Ch.* [4] 5, 161), by passing HCl into ether in which MnO_2 was suspended, obtained a green liquid, of varying composition and very unstable; one analysis gave results approximately agreeing with the formula $MnCl_4.12C_4H_{10}O.2H_2O$. These results are quite inconclusive of the formation of $MnCl_4$ (*cf.* Pickering, *C. J.* 35, 672). Fisher's experiments (*C. J.* 33, 409) led him to conclude that a solution of MnO_2 in cold conc. HClAq contains $MnCl_4$; but the more complete experiments of Pickering (*C. J.* 35, 654) make it very probable that Mn_2Cl_6, and not $MnCl_4$, is produced when either Mn_2O_3 or MnO_2 is dissolved in cold conc. HClAq. When the solutions are decomposed by adding water, the pp. varies in composition but may always be expressed as $xMnO_2.yMnO$, x varying from 16 to 36 and y being usually 5. Pickering expresses the reactions of HClAq with Mn_2O_3 and MnO_2, and the decomposition of the solutions by H_2O, in the following equations:—

$$Mn_2O_3 + 6HClAq = Mn_2Cl_6Aq + 3H_2O$$
$$2MnO_2 + 8HClAq = Mn_2Cl_6Aq + Cl_2 + 4H_2O.$$
$$\left\{\begin{array}{l} xMn_2Cl_6Aq + 2H_2O = MnO_2 + MnCl_2Aq + 4HClAq \\ yMn_2Cl_6Aq + 3H_2O = Mn_2O_3 + 6HClAq \end{array}\right\}.$$

The average values of x and y are 4 and 1 respectively. Christensen (*J. pr.* [2] 35, 57) thinks that Mn_2Cl_6 is the product of the reaction of cold HClAq with MnO_2; he supposes that some $MnCl_4$ is produced at 10°. According to C., ether holding HCl in solution produces a solution of Mn_2Cl_6 when shaken with Mn_2O_3. According to Vernon (*C. S. Proc.* 1890. 58), a solution of MnO_2 in conc. HClAq evolves less than half the Cl, at ordinary temperatures, required by the equations given by Pickering (*supra*); at −18° Cl is evolved very slowly, and at −26° only ·35 p.c. of the available Cl comes off when air is drawn through the solution for two hours. Vernon thinks that $MnCl_4$ is the only higher chloride formed by dissolving MnO_2, Mn_2O_3, or Mn_3O_4 in cold conc. HClAq.

Franke (*J. pr.* [2] 36, 38) obtained *chloromanganic acid*, H_2MnCl_6, by adding $KMnO_4$ to ether containing HCl, shaking with dry ether, and surrounding the deep-blue liquid thus produced with a freezing mixture.

MANGANESE HEPTACHLORIDE, $MnCl_7$ (?). Dumas (*B. J.* 7, 112; 8, 177) described a greenish gas, condensing at − 15° to − 20° to a green-brown liquid, produced by adding excess of conc. H_2SO_4 to $KMnO_4$ and throwing in small pieces of fused KCl or NaCl; he gave the formula $MnCl_7$ to this substance. Aschoff's analyses of the compound proved the presence of O in it, and led to the formula MnO_3Cl (*J. pr.* 81, 29). The exact composition of the substance is not yet settled.

Manganese, chromate of; *v.* vol. ii. p. 155.

Manganese, cyanides of; *v.* vol. ii. p. 342.

Manganese, ferri- and ferro-cyanides of; *v.* vol. ii. pp. 335, 339.

Manganese, fluorides of. Two fluorides of Mn have been certainly isolated, MnF_2 and Mn_2F_6. The existence in solution of MnF_4 is doubtful. Wöhler obtained a gas by the reaction of H_2SO_4 with a mixture of K_2MnO_4 and KF. To this gas he assigned the composition MnF_7, but the composition of the substance cannot be regarded as settled. Nicklès asserts the existence of Mn_3F_8.

MANGANOUS FLUORIDE, MnF_2 (*Manganese difluoride*). A reddish crystalline powder, obtained by dissolving $MnCO_3$ in excess of HFAq, and evaporating; undecomposed by heating to redness (Berzelius).

MnF_2 forms double compounds with SiF_4, &c. (Berzelius; Stolba, *C. C.* 1883. 292; Marignac, *J. pr.* 83, 202). These compounds, better regarded as silicofluoride, titanofluoride, &c., of Mn, have the composition $MnXF_6.6H_2O$, where X = Si, Ti, or Sn; they are isomorphous, crystallising in hexagonal forms, $a:c$ = 1: ·515 (Marignac, *Ann. M.* [5] 15). There is also a zircofluoride of Mn, $MnZnF_6.5H_2O$, which crystallises in monoclinic forms, $a:b:c$ = 2·09:1:1·2515 (M. *l.c.*).

MANGANESE SESQUIFLUORIDE, Mn_2F_6. Crystals of $Mn_2F_6.6H_2O$ were obtained by Christensen (*J. pr.* [2] 35, 57) by dissolving artificially prepared MnO_2 in HFAq, filtering through spongy Pt, evaporating, and placing over H_2SO_4. Boiling or diluting the solution of MnO_2 in HFAq produces an oxyfluoride.

The double salts $Mn_2F_6.4KF.2H_2O$, $Mn_2F_6.4NH_4F$, $Mn_2F_6.4NaF$, and $Mn_2F_6.2AgF.8H_2O$ are described by Christensen (*l.c.* and *ibid.* p. 161). They are obtained by adding solution of the alkali fluoride to solution of Mn_2O_3 or MnO_2 in HFAq, washing with water containing HF, and drying on Pt; the Ag salt is obtained by dissolving freshly ppd. Ag_2CO_3 in HFAq, adding Mn_2F_6 in HFAq, and evaporating. According to Christensen, the salt $Mn_2F_6.4KF.2H_2O$ is identical with the compound to which Nicklès gave the formula $MnF_4.2KF$ (*C. R.* 65, 107).

MANGANESE TETRA- and HEPTA- FLUORIDES, MnF_4 and MnF_7 (?). The former compound was supposed by Nicklès to exist in the solution of MnO_2 in HFAq (*C. R.* 65, 107); by adding KF or NaF the double salts $MnF_4.2K(Na)F$ were said to be formed. The investigations of Christensen (*J. pr.* [2] 35, 57, 161) have made it very probable that Mn_2F_6, and not MnF_4, is formed when MnO_2 or Mn_2O_3 is dissolved in HFAq (*v. supra*; *cf. Manganic chloride, supra*).

The formula MnF_7 was given by Wöhler (*P.* 9, 619) to a purple-yellow gas obtained by adding conc. H_2SO_4 to a mixture of 2 parts commercial K_2MnO_4 and 1 part CaF_2 in a Pt retort. The gas dissolves in water to form $HMnO_4Aq$ and HFAq, and on evaporation HF and O are evolved, and MnF_2 remains. The composition of the gas is still very doubtful; no analyses are given in Wöhler's paper.

MANGANO-MANGANIC FLUORIDE, Mn_3F_8. According to Nicklès (*C. R.* 67, 448), brown crystals, having the composition $Mn_3F_8.10H_2O$, are obtained by reacting on MnO_2 with warm HFAq and evaporating.

Manganese, haloid compounds of. The compounds MnX_2 (X = F, Cl, Br, I) have been isolated. Mn_2F_6 has also been obtained in definite form. There are very strong reasons in favour of the existence of Mn_2Cl_6 in the solutions obtained by dissolving Mn_2O_3 or MnO_2 in cold conc. HClAq.

The existence, even in solution, of tetra-haloid compounds, MnX_4, is doubtful. Niclès claims to have obtained mangano-manganic fluoride Mn_3F_8, corresponding with Mn_3O_4. The only haloid compound of Mn which has been gasified is $MnCl_2$. The general formula MnX_2 probably expresses the atomic composition of the molecules of the more stable haloid compounds of Mn; the formula Mn_2X_6 may or may not be molecular. The existence of hepta-haloid compounds MnX_7 might be expected from the position of Mn in the periodic scheme of classification; but the existence of these compounds is extremely doubtful.

Manganese, hydroxides of, *v. Manganese, oxides and hydrated oxides of*; for $HMnO_4$ *v. Manganese, oxyacids of.*

Manganese, iodide of. MnI_2. Obtained, with $4H_2O$, in rose-red deliquescent crystals, isomorphous with $MnCl_2.4H_2O$, by dissolving $MnCO_3$ in HIAq, and evaporating. Turns brown when exposed to air and light; heated in absence of air, it is not decomposed; heated in O it burns like tinder, evolving vapours of I. Thomsen gives the thermal data $[Mn, I^2, Aq] = 75,700$ (*Th.* 3, 271).

Manganese, oxides and hydrated oxides of. The oxides MnO, Mn_3O_4, Mn_2O_3, MnO_2, probably also MnO_3 and Mn_2O_7, have been isolated. A number of oxides intermediate between Mn_2O_3 and MnO_2, having the general form $xMnO_2.yMnO$, also exist. Hydrates of most of these oxides exist, but their stability is generally small. $Mn_2O_7.H_2O = H_2Mn_2O_8$ is known; it is an acid. The acid corresponding to MnO_3 (H_2MnO_4) has not been isolated, but salts of this acid (manganates) are known. The oxides MnO, Mn_3O_4, and Mn_2O_3 are basic. MnO reacts with acids to form manganous salts MnX_2 ($X = NO_3$, $\frac{1}{2}SO_4$, &c.); Mn_2O_3 forms manganic salts Mn_2X_3, which are readily reduced to MnX_2; Mn_3O_4 does not form corresponding salts, but with acids yields MnX_2 and Mn_2X_3, or in some cases MnX_2 and MnO_2. Niclès, however, asserts the production of Mn_3F_8 by the action of HFAq on Mn_3O_4 (*v. Mangano-manganic fluoride*, p. 180). MnO_2 reacts with acid to form manganic salts Mn_2X_3 or manganous salts MnX_2, according to temperature. It is possible that a few salts corresponding with MnO_2 may exist, but their isolation is doubtful. MnO_2 also combines with some oxides more basic than itself to form *manganites*, salts of the form $xMO.yMnO_2$. MnO_3 is very unstable; it does not form salts. The existence of $(MnO_3)_2SO_4$ is probable. With water MnO_3 forms $H_2Mn_2O_8Aq$ and MnO_2. Mn_2O_7 is very unstable; with water it forms permanganic acid, $H_2Mn_2O_8$.

The molecular weight of none of the oxides of Mn is known with certainty, as none has been gasified.

Manganous oxide, MnO. (*Manganese monoxide* or *protoxide.*) S.G. 5·09, crystalline (Rammelsberg); 5·18, *manganosite* (Blomstrand, *B.* 8, 130).

Occurrence.—In small quantities, as *manganosite*, in bright green hexagonal forms (Blomstrand, *l.c.*).

Preparation.—1. By heating to redness in a Pt vessel a mixture of equal parts $MnCl_2$ and Na_2CO_3, with a little NH_4Cl; $MnCO_3$ is formed and then decomposed, the formation of higher oxides is prevented by the NH_4Cl; the residue is washed and dried (Liebig a. Wöhler, *P.* 21, 578). 2. By heating any of the higher oxides of Mn, very finely divided, to redness in a stream of H until the powder is green. According to Wright a. Menke (*C. J.* 37, 28), pure MnO can be thus obtained, even from specimens of MnO_2 containing c. 10 p.c. of potash.—3. $MnCO_3$ or MnC_2O_4 is strongly heated in absence of air, and the product is then heated in H (Liebig, *A.* 95, 116).—4. Deville (*C. R.* 53, 199) obtained MnO in bright green regular octahedra by heating MnO_2 in H containing a very little HCl.

Properties and Reactions.—A grass-green powder; Deville's crystalline specimen (*v. supra*) formed lustrous, diamond-like, green regular octahedra. According to Moissan (*A. Ch.* [5] 21, 199, 251), MnO prepared by reduction of higher oxides by CO at 140° is pyrophoric. When pure, MnO does not oxidise by exposure to air (Wright a. Menke, *C. J.* 37, 28 *note*); but if it contains minute quantities of potash oxidation occurs. Heated in air or O, Mn_3O_4 is produced; if the heating is done carefully till the weight is constant at dull redness, Mn_2O_3 is produced (*v.* Gorgeu, *C. R.* 106, 743). MnO melts at white heat in absence of air. It is not reduced by heating in H or CO, or with C at 500°-600° (Wright a. Luff, *C. J.* 33, 523). When heated in H_2S, MnS and H_2O are formed. MnO reacts with acids to form manganous salts, MnX_2 ($X = NO_3$, ClO_3, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c.).

Hydrate of manganous oxide, $MnO.H_2O$. Occurs in small quantities in Sweden, in white crystalline tablets, as *pyrochroïte.* Prepared, as small white hexagonal prisms, by adding 300 grm. KOH in 500 c.c. air-free water to an air-free solution of 15–17 grm. crystallised $MnCl_2$ in 15 c.c. air-free water, in a vessel filled with H or coal-gas, heating to 160°, and allowing to cool (A. de Schulten, *C. R.* 105, 1265). Rapidly oxidises in air. When a manganous salt is present the compound $2MnO.MnO_2.xH_2O$ is formed; when exposed to O for several years the product is $MnO_2.MnO$ (Gorgeu, *C. R.* 108, 948). When NH_3Aq is added to solution of a manganous salt, $MnO.H_2O$ is not ppd., as it is soluble in NH_3Aq; but this solution rapidly absorbs O from the air, and after a time all the Mn is ppd. as hydrates of Mn_2O_3. The presence of NH_4 salts hinders the oxidation process; solutions of double NH_4-Mn salts are scarcely changed in air if free NH_3 is absent. Thomsen gives the thermal data: $[Mn,O,H^2O] = 94,770$; $[MnO^2H^2,O] = 21,560$; $[MnO^2H^2,H^2SO^4Aq] = 26,480$ (*Th.* 3, 271).

Mangano-manganic oxide, Mn_3O_4. (*Red oxide of manganese.*)

Occurrence.—As *hausmannite*, in small brownish-black tetragonal forms, $a:c = 1:1·1537$; S.G. 4·8.

Preparation.—1. Pure $MnCl_2Aq$ is ppd. by Na_2CO_3Aq, the pp. is thoroughly washed, dried, and then heated to whiteness for some time until the weight is constant (*cf.* Wright a. Luff, *C. J.* 33, 520, with Reissig, *A.* 103. 27).—2. By strongly heating MnC_2O_4 in air (Lassaigne, *A. Ch.* [3] 40, 329).—3. Crystals of *hausmannite* were obtained by Debray by strongly heating a mixture of $MnSO_4$ and K_2SO_4 in a Pt crucible (*C. R.* 52, 985); also by passing a very slow stream of HCl

over amorphous Mn_3O_4 heated to redness (Deville, *C. R.* 53, 199); also by keeping molten $MnCl_2$ in an atmosphere laden with moisture (Gorgeu, *C. R.* 96, 1044); also by melting amorphous Mn_3O_4 with borax (Nordenskjöld, *P.* 114, 112; *v.* also Debray, *Ann. M.* [5] 1, 124; Sidot, *C. R.* 69, 201; v. Hauer, *J. pr.* 63, 425; Ebell, *D. P. J.* 220, 64, 155).

It is generally stated that Mn_3O_4 is produced by heating any of the other oxides of Mn to redness in air; according to the experiments of Dittmar (*C. J.* 1864. 294) the composition of the product of heating MnO_2 in a mixture of O and N varies according to the pressure of the O; if the pressure of the O is about ·19 atmos. the product is approximately Mn_3O_4, while if the pressure of the O is greater than about ·26 atmos. the product approximates more or less closely to Mn_2O_3. The experiments of Wright and Luff (*C. J.* 33, 520), on the effect of heating $MnCO_3$ in air, showed that unless the heating is continued for a long time and the temperature is kept very high the product contains more O than Mn_3O_4. According to Gorgeu (*C. R.* 106, 743), finely powdered Mn_3O_4 can be oxidised to $xMnO_2.yMnO$, finally to Mn_2O_3, by heating in air.

Properties and Reactions.—A reddish-brown solid powder; crystalline Mn_3O_4 is brown. S.G. crystalline 4·856, amorphous 4·918. Mn_3O_4 is not changed when heated to a very high temperature. It is reduced to MnO by H, CO, and C (Bell, *C. N.* 23, 258; Müller, *P.* 136, 160); reduction by CO begins at c. 100°, by H at c. 240°, and by C at c. 420° (Wright a. Luff, *C. J.* 33, 520). Mn_3O_4 with conc. H_2SO_4 forms a solution containing $MnSO_4$ and $Mn_2(SO_4)_3$; when the acid is hot, only $MnSO_4$ is formed and O is evolved. With boiling HNO_3Aq, $Mn(NO_3)_2$ and MnO_2 are produced. Hot conc. HClAq produces $MnCl_2$ and evolves Cl. Fused with alkalis, alkaline manganate is formed. Cl in presence of an alkaline solution reduces an alkaline permanganate. The reactions of Mn_3O_4 with acids, KIAq, &c., suggest the constitution $2MnO.MnO_2$ (Pickering, *C. J.* 35, 657).

Hydrates of mangano-manganic oxide, $Mn_3O_4.xH_2O$. Such hydrates appear to exist, but their composition varies. Gorgeu (*C. R.* 84, 177) says a yellowish-green hydrate is formed by shaking an aqueous solution of a manganese salt with alkali in presence of air. Hydrates of Mn_3O_4 are also said to be formed by placing finely-powdered MnO_2 in excess of an ammoniacal solution of $MnCl_2$ and heating (*cf.* J. Otto, *A.* 93, 372). Veley (*C. J.* 41, 63) obtained a substance nearly agreeing in composition with the formula $8Mn_3O_4.3H_2O$, by heating $xMnO_2.yMnO.zH_2O$ in H to 200°.

Manganic oxide, Mn_2O_3. (*Sesquioxide of manganese.*)

Occurrence.—As *braunite* in quadratic octahedra; S.G. 4·752 (Rammelsberg, *P.* 124, 513). The hydrate $Mn_2O_3.H_2O$ occurs native as *manganite.*

Preparation.—1. The pp.—approximately $MnO_2.xH_2O$—obtained by passing Cl into Na_2CO_3Aq holding finely-powdered $MnCO_3$ in suspension, is made into a thin cream with conc. H_2SO_4 and slowly heated on an oil-bath to 100°, at which temperature O is suddenly evolved, and the mass becomes thicker and greyish-violet in colour; it is then heated to 138° until it is dark green. The impure $Mn_2(SO_4)_3$ thus produced is placed on a warm porous plate, by which H_2SO_4 is absorbed; it is then rubbed with conc. HNO_3Aq, free from HNO_2, again dried on a porous tile, and then warmed to 130°. The $Mn_2(SO_4)_3$ thus produced is exposed to air, when it rapidly deliquesces to form a violet solution, which afterwards becomes turbid from separation of $Mn_2O_3.H_2O$ ($Mn_2(SO_4)_3 + 4H_2O = Mn_2O_3.H_2O + 3H_2SO_4$). The brown solid which separates is washed, dried at 100° and then gently heated until the water is removed (Carius, *A.* 98, 53).—2. According to Schreider (*P.* 107, 605), Mn_2O_3 is obtained by heating MnO_2, MnO, or Mn_3O_4 in O (but *v.* account of Dittmar's experiments under *Mangano-manganic oxide, supra*). Moissan says that artificially prepared MnO_2 goes to Mn_2O_3 when heated in O to 230° (*A. Ch.* [5] 21, 232). According to Berthelot (*A. Ch.* [5] 15, 185) and Knab, Mn_2O_3 is obtained by heating $MnCl_2$, $MnBr_2$, or MnI_2 in air or O. This oxide is also said to be formed, with evolution of O, by passing H_2O vapour over heated K_2MnO_4. Gorgeu (*C. R.* 108, 1106) obtained Mn_2O_3 by allowing ppd. $MnCO_3$ to remain in contact with aërated water for 10 years; also by exposing $MnO.H_2O$ to O in presence of excess of a manganous salt; also by exposing solutions of $MnSO_4$, $MnCl_2$, and $Mn(C_2H_3O_2)_2$ to sunlight.

Properties and Reactions.—A black powder, S.G. 4·325; the mineral *braunite* forms brownish-black, very hard, lustrous quadratic octahedra, S.G. 4·752. Deoxidised at white heat to Mn_3O_4. Soluble in conc. H_2SO_4, forming a reddish liquid, which evolves O on warming, and then contains $MnSO_4$; boiled with dilute H_2SO_4Aq or HNO_3Aq, MnO_2 is separated, and manganous sulphate or nitrate goes into solution (Christensen, *J. pr.* [2] 28, 1). Soluble in cold conc. HClAq, forming a brown liquid, which most probably contains Mn_2Cl_6 (*v. Manganic chloride*, p. 180).

Mn_2O_3 is a basic oxide; the corresponding salts are not numerous, they are readily reduced to manganous salts. $Mn_2(SO_4)_3$ combines with alkali sulphates to form alums. Mn_2O_3 reacts with hot HClAq, with KIAq, and other reagents, as if it were $MnO.MnO_2$ (Pickering, *C. J.* 35, 657). Laugier (*C. R.* 104, 1508) describes several compounds of Mn_2O_3 with SeO_2, prepared by the reaction of MnO_2 with H_2SeO_3Aq.

Hydrate of manganic oxide, $Mn_2O_3.H_2O$. Occurs native as *manganite*; S.G. 4·335; isomorphous with *göthite* and *diaspore*, the corresponding Fe and Al compounds. The preparation of $Mn_2O_3.H_2O$ is described under *Manganic oxide* (*v. supra*); it forms a brownish-black powder. Warmed with conc. H_2SO_4 to c. 100°, $Mn_2(SO_4)_3$ is formed without evolution of O (Carius, *A.* 98, 53). According to Carius (*l.c.*), $Mn_2O_3.H_2O$ is not dissolved by dilute H_2SO_4Aq even on gently warming, but if a little MnO is present solution occurs in the cold. $Mn_2O_3.H_2O$ is said by Hermann (*P.* 74, 303) to dissolve in tartaric acid, forming a brownish-red liquid, from which manganous tartrate separates on standing, the liquid becoming colourless and now containing formic acid and CO_2. In a stream of H_2S, a little $MnSO_4$ and also MnS

and Mn_2O_3 are formed (Wagner, *D. P. J.* 195, 532). When moist $Mn_2O_3.H_2O$ is shaken with *magnesia alba*, K_2CO_3, or Na_2CO_3, or even with water, and much air, nitrates are produced according to Reichardt (*Henneberg's J. für Landwirthsch.* 26, 167).

MANGANESE PEROXIDE, MnO_2. (*Manganese dioxide.*)

Occurrence.—As *pyrolusite*; in iron-black, opaque, rather brittle trimetric crystals, $a:b:c$ = ·776:1:1·066; S.G. 4·82 to 4·97. The name is supposed to have been given from the use of the mineral to remove the colour from glass coloured by compounds of iron (πῦρ = fire, and λύειν = wash out).

Preparation.—Pure $MnCO_3$ is dissolved in as small a quantity as possible of dilute HNO_3Aq, the solution is evaporated to a syrup, which is heated to 160°–165° for some hours; the product is thoroughly washed with boiling water, then dried over H_2SO_4, and heated to c. 180°–200°, until every trace of water is removed. Pure MnO_2 is thus obtained, exactly resembling *pyrolusite* (Gorgeu, *C. R.* 88, 796; Wright a. Menke, *C. J.* 37, 45; *cf.* Schlösing, *C. R.* 55, 284; and Kuhlmann, *D.P.J.* 211, 25). Even if the $Mn(NO_3)_2$ used contain a large quantity of KNO_3, MnO_2 practically free from K_2O is obtained by this method.

Very many attempts have been made to obtain pure MnO_2 by ppn. from Mn salts; *e.g.* by ppg. with BrAq in presence of Na acetate, by passing Cl into an alkaline solution containing $MnCO_3$ in suspension, by reacting on a Mn salt solution with $KMnO_4Aq$, &c. The various methods have been examined by Gorgeu (*C. R.* 88, 796; *A. Ch.* [3] 66, 153); Guyard (*Bl.* [2] 1, 89); Hannay (*C. J.* 33, 269; *cf.* Beilstein a. Jawein, *B.* 12, 1530); Pickering (*C. J.* 35, 654); Volhard (*A.* 198, 318); Kessler (*Fr.* 18, part 1); Pattinson (*C. J.* 35, 365); Veley (*C. J.* 37, 581); Wright a. Luff (*C. J.* 33, 504); and Wright a. Menke (*C. J.* 37, 22). The outcome of the work is that pure MnO_2 cannot be obtained by any of the ppn. methods; either the pp. is $xMnO_2.yMnO$, or, if all the Mn is present as MnO_2, the pp. contains also K_2O or some other base besides H_2O. Volhard's method—adding excess of $KMnO_4Aq$ to $MnSO_4Aq$ in presence of HNO_3 (exact quantities are given by V.)—gave all the Mn as MnO_2 accompanied by a small quantity of K_2O (c. 3 p.c.), which could not be removed by washing (W. a. M., *l.c.*).

Properties.—A black, or brownish-black, hard, crystalline powder. S.G. 5·02. Heated to moderate redness, Mn_2O_3 is formed; heated to whiteness, Mn_3O_4 remains (*cf. Mangano-manganic oxide*; *Preparation*, p. 182). MnO_2 is a conductor of electricity; it is strongly electro-negative to the metals. Reacts with acids to form salts corresponding with MnO; with cold conc. HClAq most probably forms Mn_2Cl_6.

Reactions.—1. *Heated*, gives Mn_2O_3 at moderate redness, and Mn_3O_4 at white heat.—2. *Heated in hydrogen*, or *carbon monoxide*, is reduced to MnO; reduction in H begins at c. 190°, and in CO at c. 87°; when *heated with carbon* reduction begins at c. 390° (Wright a. Luff, *C. J.* 33, 518).—3. Heated with *potassium chlorate*, O is evolved and MnO_2 and KCl remain; a little Cl is evolved, and at one stage of the change $KMnO_4$ is produced. The reaction between MnO_2 and $KClO_3$ probably produces $KMnO_4$, Cl, and O; the $KMnO_4$ then decomposes to K_2MnO_4, MnO_2, and O; and the K_2MnO_4 reacts with Cl to form KCl, MnO_2, and O. The following equations are given by McLeod as expressing approximately the various changes:
(1) $2MnO_2 + 2KClO_3 = 2KMnO_4 + Cl_2 + O_2$;
(2) $2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$;
(3) $K_2MnO_4 + Cl_2 = 2KCl + MnO_2 + O_2$ (*v.* McLeod, *C. J.* 55, 184; Hodgkinson a. Lowndes, *C. N.* 59, 63; Fowler a. Grant, *C. J.* 57, 272; Baudrimont, *J. Ph.* [4] 14, 84, 161; Warren, *C. N.* 58, 247; Veley, *T.* 1888 [1], 271; Spring a. Prost, *Bl.* 1889. 340).—4. With hot conc. *sulphuric acid*, $MnSO_4$ is formed and O evolved.—5. With cold conc. hydrochloric acid, Mn_2Cl_6 is very probably produced; on warming, Cl is evolved and $MnCl_2$ remains (*cf. Manganic chloride*, p. 180).—6. Heated with *sulphuric acid and oxidisable bodies*, MnO_2 acts as an oxidiser; *e.g.* $H_2C_2O_4$ is thus oxidised to CO_2 and H_2O.—7. Not acted on by moderately dilute *nitric acid alone*; but in *presence of an oxidisable body*, $Mn(NO_3)_2$ and oxidised products are formed, *e.g.* with HNO_3 and HCl, Cl is evolved.—8. Compounds of Mn_2O_3 with SeO_2 were obtained by Laugier (*C. R.* 104, 1508), by heating ppd. MnO_2 with *selenious acid.*—9. With *hydrogen peroxide and an acid*, forms a salt of MnO and H_2O and evolves O; with *hydrogen peroxide alone*, O is evolved and the same quantity of MnO_2 remains as was originally used (*v.* HYDROGEN PEROXIDE; *Reactions* 11 and 19, vol. ii. pp. 723, 724).—10. Heated with *magnesium chloride*, $MnCl_2$ and MgO are formed and Cl is evolved.—11. *Fused with alkalis in presence of air or oxygen*, manganates, $M^I_2MnO_4$, are formed (*v. Manganates* under *Manganese, oxyacids of*, p. 185).

12. MnO_2 combines with a number of *basic oxides* to form salts of the form $xMO.yMnO_2$, known as *manganites*. According to Gorgeu (*A. Ch.* [3] 66, 153) MnO_2 decomposes neutral solutions of many salts of Ca, Ba, Ag, and Mn, making the solutions acid to litmus and combining with the bases. From dilute solutions of K_2CO_3 and Na_2CO_3 MnO_2 withdraws and combines with 7 p.c. K_2O, and 4·1 p.c. Na_2O, respectively, according to Gorgeu; the *manganites* thus produced approximately correspond with the formula $M_2O.15MnO_2$. According to Jolles (*Chem. Zeitung*, 11, 1394) K_2MnO_3 is obtained, as a brown-yellow solid, by mixing equivalent quantities of K_2MnO_4 and C_2H_6O. Wright and Menke (*C. J.* 37, 22) have examined the *potassium manganites* formed by ppg. MnO_2 in presence of K salts, by passing Cl into K_2CO_3Aq holding $MnCO_3$ in suspension, by adding $MnSO_4Aq$ to $KMnO_4Aq$, &c.; they conclude that the amount of K_2O ppd. in combination with MnO_2 varies according to the relative masses of the reacting bodies, the temperature, the quantity of free acid present, &c., and that it tends to the maximum $5MnO_2.K_2O$. W. a. M. failed to obtain $8MnO_2.K_2O.3H_2O$ described by Stingl a. Morawski (*J. pr.* [2] 18, 91) as produced by acting on $KMnO_4Aq$ with a reducing agent such as SO_2, glycerin, or alcohol; they say that K_2O is ppd. in combination with MnO_2, but that the ratio of K_2O to MnO_2 varies much. Weldon (*C. N.* 20,

109) gave the formulæ $CaO.MnO_2$ and $CaO.2MnO_2$ to the *manganites* formed by oxidising $MnO.H_2O$ by air in presence of lime. *Manganites* of the form $MO.5MnO_2$, where M = Ca, Ba, Sr, Zn, and Pb, are described by Risler (*Bl.* [2] 30, 110) as produced by heating $KMnO_4$ with slight excess of various metallic chlorides, and washing with water. By heating metallic chlorides with MnO_2, and then adding $MnCl_2$, Rousseau obtained *manganites*, which he classes as $MO.5MnO_2$, $MO.MnO_2$, and $2MO.MnO_2$ (*C. R.* 101, 167; *cf.* also Post, *B.* 12, 1484, 1537; Rammelsberg, *B.* 8, 233; Rousseau, *C. R.* 102, 425, 615; 103, 261; 104, 786, 1796). Various compounds of MnO with MnO_2 seem to exist; these may be regarded as *manganese manganites*; *v. Oxides intermediate between manganic oxide and manganese peroxide, infra.*

13. While MnO_2 reacts as an acidic oxide towards the oxides of the more positive metals, it also reacts as a basic oxide with some acids. The usual reactions of MnO_2 with acids are those of a basic peroxide (*v. Reactions*, 3 to 6, *supra*). The salt $MnO_2.SO_3$ is said by Fremy to be formed by carefully reacting on $MnO_2.xH_2O$ with conc. H_2SO_4, and allowing to stand in air (*C. R.* 82, 475). By adding $MnSO_4$ to a freshly prepared solution of Pb_3O_4 in acetic acid, as long as $PbSO_4$ was ppd., Schönbein (*J. pr.* 74, 325) obtained a deep brownish-red liquid, which had strongly oxidising properties, and from which MnO_2 separated on standing, or more quickly on boiling. Schönbein thought that this liquid contained an acetate of MnO_2, but he did not succeed in isolating this salt.

Hydrates of manganese peroxide. When approximately pure MnO_2 is ppd., by oxidising manganous salts in alkaline solutions, or by reactions between manganous salts and permanganates, or by decomposing $KMnO_4Aq$ by H_2SO_4 or HNO_3, the pp. always contains water; but it is very doubtful whether any definite, and fairly stable, hydrate of MnO_2 exists. When the process of formation results in ppn. of all the Mn as MnO_2 the composition of the pp. approximates to $MnO_2.H_2O$, but this body loses water in dry air (*v.* Wright a. Menke, *C. J.* 37, 22). When the whole of the Mn is not ppd. as MnO_2, the pp. consists of compounds of the form $xMnO_2.yMnO.zH_2O$ containing variable quantities of metallic oxides according to the conditions of formation. It appears to be possible to obtain hydrates which are stable for many hours within definite limits of temperature, but these hydrates are of the form $xMnO_2.yMnO.zH_2O$ (*v.* Veley, *C. J.* 37, 581; 41, 56).

References.—The following papers contain the chief experiments bearing on the formation and composition of supposed hydrates of MnO_2:—Rammelsberg, *B.* 8, 233; Fremy, *C. R.* 82, 1231; Van Bemmelen, *B.* 13, 1466; Gorgeu, *A. Ch.* [3] 66, 154; *C. R.* 108, 948; Von Hauer, *W. A. B.* 13, 453; Reisig, *A.* 103, 206; Böttcher, *J. pr.* 76, 235; Guyard, *Bl.* 6, 81; Morawski a. Stingl, *J. pr.* [2] 18, 90, 97; Volhard, *A.* 198, 318; Suckow, *D. P. J.* 177, 231; Wernicke, *P.* 141, 116; Veley, *C. J.* 37, 581; 41, 56; Pickering, *C. J.* 35, 654; Wright a. Luff, *C. J.* 33, 504; Wright a. Menke, *C. J.* 37, 22; Franke, *J. pr.* [2] 36, 166, 451.

Oxides intermediate between manganic oxide and manganese peroxide. These oxides belong to the general formula $xMnO_2.yMnO$. The composition of the pp. obtained by adding water to solutions of MnO_2 or Mn_2O_3 in cold conc. HClAq varies between $16MnO_2.5MnO$ and $36MnO_2.5MnO$ (Pickering, *C. J.* 35, 659). By passing Cl for a limited time into solution of Mn acetate, Veley obtained a pp. approximating in composition to $5MnO_2.MnO.xH_2O$ (*C. J.* 37, 581; 41, 56); by heating this pp. in a current of air, the compound $11MnO_2.MnO.H_2O$ was produced; and by heating the first compound in O, the body produced had the composition $23MnO_2.MnO.2H_2O$. Wright a. Menke (*C. J.* 37, 22) obtained a number of bodies $xMnO_2.yMnO.xH_2O$ by various processes of oxidising manganous salts, and reducing permanganates; in every case, however, K_2O, or other alkali, was held in combination. Further accounts of these intermediate oxides, many of which were probably mixtures of the better defined oxides of Mn, will be found in the memoirs referred to under Hydrates of manganese peroxide (*v. supra*), especially in the memoirs of Gorgeu.

Manganese trioxide, MnO_3. This compound is formed, in very small quantities, by slowly dropping a solution of $KMnO_4$ in cold conc. H_2SO_4 (c. 6 grams $KMnO_4$ in 100 c.c. H_2SO_4) on to dry Na_2CO_3. The Na_2CO_3 is placed in a distilling flask surrounded by cold water. The flask is connected with a U-tube filled with fragments of glass, and surrounded by a mixture of ice and salt, and this tube is connected with another U-tube containing a little dilute H_2SO_4Aq. As each drop of the green solution of $KMnO_4$ in H_2SO_4 falls on to the Na_2CO_3, a pink cloud is formed; the cloud partly condenses in the first U-tube, and part of it passes on and is dissolved in the H_2SO_4 in the second tube (Franke, *C. J.* [2] 36, 31, 166; *v.* also Thorpe a. Hambly, *C. J.* 53, 175). Only a very small quantity of MnO_3 can be obtained. It appears as a reddish, amorphous, deliquescent mass. It slowly decomposes at ordinary temperatures, but is fairly stable if surrounded by ice and salt (T. a. H., *l. c.*). MnO_3 is decomposed by water yielding $HMnO_4Aq$ and MnO_2 (T. a. H.); according to Franke, H_2MnO_4 is produced, but quickly decomposes to MnO_2, O, and $HMnO_4$, and probably also $H_2Mn_2O_7$. MnO_3 dissolves in conc. H_2SO_4, forming a green solution. Franke thinks this liquid contains $(MnO_3)_2SO_4$. MnO_3 dissolves in KOHAq, forming K_2MnO_4. MnO_3 liberates I from KI, and acts on Hg similarly to ozone (T. a. H.).

Manganese heptoxide, Mn_2O_7. (*Permanganic anhydride.*) This oxide was obtained by Thenard (*C. R.* 42, 382). Its composition was determined by Aschoff (*J. pr.* 81, 34). Pure $KMnO_4$, free from Cl compounds, is added little by little to conc. H_2SO_4, S.G. 1·845, kept cold by a freezing mixture. To the green solution thus obtained a few drops of water are added, when Mn_2O_7 slowly separates in dark reddish-brown oily drops. If acid of the composition $H_2SO_4.H_2O$ (S.G. c. 1·78) is used, oily drops of Mn_2O_7 are formed without addition of water. According to Franke (*J. pr.* [2] 36, 31), a solution of $KMnO_4$ in conc. H_2SO_4 contains $(MnO_3)_2SO_4$, and this is decomposed by a little water, giving Mn_2O_7 and H_2SO_4.

Terreil (*Bl.* 1862. 40) prepares Mn_2O_7 by dissolving $KMnO_4$ in well-cooled H_2SO_4, containing water in the ratio $H_2SO_4{:}\frac{1}{2}H_2O$, placed in a stoppered retort, the beak of which passes into a glass balloon surrounded by a freezing mixture. Corks or organic material must not be used in any part of the apparatus. He heats the retort to 60°–65° (not over 70°), when purple-red vapour is evolved and condensed to a thick greenish-black liquid, which is Mn_2O_7. Only a few drops of Mn_2O_7 can thus be prepared at a time. As soon as a certain quantity collects in the balloon, decomposition occurs, with slight detonation (*v.* also Spiess, *J. pr.* [2] 1, 421).

P. Thenard (*J. pr.* 69, 58) describes Mn_2O_7 as a dark olive-green liquid, with a smell recalling Cl compounds and ozone. Aschoff (*J. pr.* 81, 34) describes it as dark brownish-red oily drops, which do not solidify at −20°. Mn_2O_7 slowly decomposes in air at ordinary temperatures, with evolution of O. It may be heated to 60°–65°, under reduced pressure, without volatilising; at a somewhat higher temperature it is suddenly and violently decomposed to MnO_2 and O. Mn_2O_7 is very hygroscopic. It dissolves in water to form a purple liquid, probably containing $HMnO_4$. This liquid is slowly decomposed on warming into MnO_2 and O. Mn_2O_7 dissolves in cold conc. H_2SO_4, apparently without decomposition, to form an olive-green liquid (this liquid contains $(MnO_3)_2SO_4$ according to Franke, *J. pr.* [2] 36, 31). Mn_2O_7 is at once decomposed by contact with small quantities of MnO_2, Ag_2O, or HgO (Aschoff, *l. c.*). Mn_2O_7 is a powerful oxidiser. It inflames paper or alcohol.

Manganese tetroxide (?). Franke (*J. pr.* [2] 36, 31, 166) states that a blue gas is obtained by leading air or CO_2, saturated with water at 40°–50°, over the green liquid formed by dissolving $KMnO_4$ in well-cooled conc. H_2SO_4. To this blue gas he gives the formula MnO_4. Thorpe and Hambly repeated Franke's experiments (*C. J.* 53, 178), but failed to obtain any indications of the formation of a blue gas.

Manganese, oxyacids of, *and their salts.* Two series of salts derived from oxyacids of Mn are known—the *manganates* $M^I_2MnO_4$ and the *permanganates* M^IMnO_4. The acid corresponding to the manganates, viz. H_2MnO_4, has not been isolated, but its anhydride MnO_3 is known. The anhydride of permanganic acid, viz. Mn_2O_7, is known, and the acid itself has also probably been isolated.

Manganates, $M^I_2MnO_4$, derived from the hypothetical acid H_2MnO_4. The anhydride of this acid, viz. MnO_3, is known. A solution of this oxide in water perhaps contains H_2MnO_4, but it decomposes almost at once to $HMnO_4$ and MnO_2 (*v. Manganese trioxide*, p. 184). When an acid is added to solution of a manganate, the manganic acid produced at once decomposes to permanganic acid and MnO_2. This change occurs even when CO_2 is passed into solution of a manganate. The manganates are isomorphous with the sulphates.

The fact that the product of fusing together pyrolusite, potash, and saltpetre dissolved in water to form a green liquid, which became blue, violet, and then red, on addition of much water, was known to Scheele. To the green substance Scheele gave the name '*Chamæleon minerale.*' Chevillot and Edwards, in 1817, showed that the green substance was a definite compound of potash with an acid of Mn (*A. Ch.* [2] 4, 287; 8, 337). Forchhammer (*Annals of Phil.* 16, 310; 17, 150) and Fromherz (*P.* 31, 677) investigated the manganates. Mitscherlich, in 1830, showed that two salts are obtained by the action of alkali on pyrolusite in presence of air or alkali nitrate (*P.* 25, 287).

Manganates of the alkalis and alkaline earths are obtained by heating MnO_2 with KOH, CaO_2H_2, &c., to c. 150° in absence of air, or to higher temperatures in presence of air, or by strongly heating any Mn salt with KOH, CaO_2H_2, &c., in presence of O or an oxidiser, *e.g.* $KClO_3$. K_2MnO_4 and Na_2MnO_4 dissolve without decomposition in water containing alkali. In pure water, $KMnO_4$ or $NaMnO_4$ is formed and MnO_2 ppd. Solutions of the alkali manganates are decolourised, with ppn. of MnO_2, by easily oxidised bodies, *e.g.* SO_2Aq, As_2O_3Aq, H_2SAq, or ferrous salts. Ba and Sr manganates are insoluble in water.

Barium manganate $BaMnO_4$. A dark-green powder. S.G. 4·85. Insol. water. Unchanged in air; decomposed by acids. Prepared by calcining $Ba(NO_3)_2$ with MnO_2, or by projecting finely-powdered MnO_2 into a molten mixture of $KClO_3$ and BaO_2H_2, washing with hot water, and drying. By heating MnO_2 with $Ba(NO_3)_2$, $BaMnO_4$ is obtained as a green powder consisting of minute hexagonal crystals (Forchhammer, *Annals of Phil.* 16, 130; 17, 150; Rosenstiehl, *J. Ph.* 46, 544; Schafavik, *J. pr.* 90, 16). The salt is also obtained by digesting $Ba(MnO_4)_2$ with BaOAq.

Didymium manganate $Di_2(MnO_4)_3$. A black powder; insol. water. Obtained by heating for 30 minutes 1 pt. MnO_2 with 4 pts. $Di3NO_3$ and washing with water (Frerichs a. Smith, *A.* 191, 353).

Lanthanum manganate $La_2(MnO_4)_3$. Resembles the Di salt; prepared similarly (F. a. S. *l.c.*).

Potassium manganate K_2MnO_4.

Formation.—1. A mixture of equal parts of finely-powdered MnO_2 and KOH is heated to bright redness in air, or in O; $3MnO_2 + 2KOH = K_2MnO_4 + Mn_2O_3 + H_2O$. K_2MnO_4 is formed by heating MnO_2 and KOH in absence of O to c. 150° (Beketoff, *Bl.* 1, 43); the reaction occurs in N at c. 180° (Elliot a. Storer, *P. Am. A.* 5, 192). If the mixture is heated above 180° O must be present, because at c. 190° K_2MnO_4 is decomposed with re-formation of MnO_2.—2. By boiling conc. $KMnO_4Aq$ with KOHAq; $2KMnO_4Aq + 2KOHAq = 2K_2MnO_4Aq + H_2O + O$ (Aschoff, *J. pr.* 81, 29). According to Thenard (*J. pr.* 69, 58), this reaction only occurs when the KOH contains some oxidisable substances, *e.g.* a little organic matter.—3. By long-continued heating $KMnO_4$ to 240°; $2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$ (Thenard, *l.c.*).—4. By fusing any oxide of Mn with KOH in presence of O, or an oxidiser such as $KClO_3$.

Preparation.—2 pts. KOH are dissolved in the smallest quantity of water, 1 pt. $KClO_3$ and 2 pts. very finely-powdered MnO_2 are added, the mixture is dried, and then heated, nearly to redness, for a long time in a Pt dish; the fused mass when cold is treated with a little water,

the conc. green solution is decanted, after standing until quite clear, and evaporated *in vacuo* over H_2SO_4.

Properties and Reactions.—Dark-green crystals; isomorphous with K_2SO_4 and K_2CrO_4. Soluble in water containing KOH without decomposition; dissolves in pure water with decomposition to $KMnO_4Aq$ and MnO_2. Dilute acids, even CO_2, quickly decompose K_2MnO_4, forming K permanganate and a manganous salt; *e.g.* with H_2SO_4;—$5K_2MnO_4Aq + 4H_2SO_4Aq = 2K_2Mn_2O_8Aq + MnSO_4Aq + 3K_2SO_4Aq + 4H_2O$. Heated in CS_2, MnS, CO_2, and polysulphides of K are formed (Müller, *P.* 127, 404). Heated in a stream of water-vapour, Mn_2O_3, KOH, and O are produced ($2K_2MnO_4 + 2H_2O = Mn_2O_3 + 4KOH + 3O$). By fusing MnO_2 with KOH in air, and then passing water-vapour over the product, then again fusing the products together, and repeating these processes, O may be obtained from the atmosphere.

Sodium manganate $Na_2MnO_4.10H_2O$. Obtained by long-continued heating equal pts. finely-powdered MnO_2 and $NaNO_3$, boiling with water, filtering, and allowing to cool (Gentele, *J. pr.* 82, 58). Said to form colourless crystals, resembling Glauber's salt, and to dissolve in water with partial decomposition to form a green solution.

PERMANGANIC ACID and PERMANGANATES. The acid $HMnO_4$, or $H_2Mn_2O_8$, has probably been isolated; a series of salts derived from this acid is known. Permanganic anhydride, Mn_2O_7, is a very unstable liquid; it dissolves in water to form $HMnO_4Aq$, which slowly decomposes to MnO_2 and O. Permanganic acid and its salts readily part with O, and hence act as energetic oxidisers. The permanganates are isomorphous with the perchlorates M^IClO_4; they are purple red; all are soluble in water, the least soluble is the Ag salt. These salts are produced by the action of dilute acids, or of Cl, on the manganates; or by the reaction of several oxidisers, *e.g.* Pb_3O_4 and dilute HNO_3Aq, on Mn salts:—(Tamm, *J.* 1872. 910; Fresenius, *Fr.* 11, 415, 425; Crum, *A.* 60, 219; Gibbs, *Am. S.* [2] 14, 204; Chatard, *C. N.* 24, 196; Pichard, *C. R.* 75, 1821; Deshayes, *Bl.* [2] 29, 541; Volhard, *A.* 198, 354; Rose, *P.* 105, 289). $KMnO_4$ is reduced to K_2MnO_4 by boiling conc. $KMnO_4Aq$ with potash (*cf.* POTASSIUM MANGANATE, *Formation* No. 2, p. 185). Solutions of permanganates are decomposed by NH_3Aq with separation of $xMnO_2.yMnO$; they are reduced to manganous salts by HNO_3Aq, fairly conc. HClAq, SO_2Aq, $Na_2S_2O_3Aq$, many organic compounds, &c. H_2SO_4 decomposes solid permanganates with separation of MnO_2 and evolution of O. Solutions of $HMnO_4$ and $KMnO_4$ absorb the green and yellow-green rays of the spectrum; the absorption-spectrum has been examined by Lecoq de Boisbaudran (*Spectres lumineux*, p. 108). According to Vogel (*B.* 8, 1534) $\frac{1}{2500000}$ pt. of Mn may be detected, in presence of Cu and Fe compounds, by boiling with PbO_2 or Pb_3O_4 and dilute HNO_3Aq free from Cl compounds, and examining the absorption-spectrum of the solution (of permanganate) produced.

Ammonium permanganate NH_4MnO_4. Resembles $KMnO_4$, with which it is isomorphous; v. sol. water; decomposed by gently heating. Prepared by rubbing together $AgMnO_4$ and NH_4ClAq in the ratio $AgMnO_4$:NH_4Cl, filtering, and evaporating at the ordinary temperature over H_2SO_4; also by decomposing $BaMnO_4$ by $(NH_4)_2SO_4$ (Böttger, *N. R. P.* 25, 115).

Barium permanganate $BaMnO_4$. Small, hard, rhombic octahedra; almost black, with violet sheen. Prepared by adding excess of H_2SiF_6Aq to $KMnO_4Aq$, filtering from K_2SiF_6 through asbestos, saturating with BaOAq containing BaO_2H_2 in suspension ($BaCO_3$ should not be used as it causes ppn. of $MnO_2.xH_2O$), decanting from $BaSiF_6$, and evaporating (Rousseau a. Bruneau, *C. R.* 93, 229). Böttger (*N. R. P.* 25, 115) prepares $BaMnO_4$ by dissolving in water the product of the fusion of 2 pts. KOH and 1 pt. MnO_2, filtering, and adding $BaCl_2Aq$ until the green colour of the liquid disappears; he collects the violet-blue pp., and washes it with cold water till the washings begin to appear reddish; he heats this pp., which is $Ba(MnO_4)_2$, with water, passes in CO_2 till the liquid is purple-red, filters from MnO_2, and evaporates.

Calcium permanganate $CaMnO_4.5H_2O$. A crystalline, deliquescent mass; prepared by decomposing $AgMnO_4$ by $CaCl_2Aq$, following directions given for obtaining NH_4MnO_4 (*v. supra*).

Cobalt permanganate does not seem to have been isolated; but Klobb has prepared several *luteo-cobaltic permanganates*, viz. $Co_2(NH_3)_{12}(MnO_4)_6$, $Co_2(NH_3)_{12}Cl_4(MnO_4)_2$, $Co_2(NH_3)_{12}Br_4(MnO_4)_2$ (*C. R.* 103, 384; *Bl.* [2] 48, 240).

Potassium permanganate $KMnO_4$.

Formation.—1. By fusing together KOH and an oxide of Mn in the air or with $KClO_3$, dissolving the K_2MnO_4 in water, passing in CO_2, filtering from MnO_2, and evaporating ($3K_2MnO_4Aq + 2CO_2 = 2KMnO_4Aq + 2K_2CO_3Aq + MnO_2$).—2. By warming solution of a Mn salt with K_2CO_3 and KClOAq.—3. By melting MnO_2 with KHO, making a conc. solution of the fused mass, adding saturated $MgSO_4Aq$, and filtering

$$3K_2MnO_4Aq + 2MgSO_4Aq = 2KMnO_4Aq + 2K_2SO_4Aq + 2MgO + MnO_2$$

(Tessié du Mothay, *D. P. J.* 186, 231).—4. By passing Cl into a solution of the fused mass obtained as in 1 and 3, and evaporating (Städeler, *J. pr.* 103, 107) ($2K_2MnO_4Aq + Cl_2 = 2KClAq + 2KMnO_4Aq$).

Preparation.—A mixture of 2 pts. KOH and 1 pt. $KClO_3$ is melted in a thin sheet-iron crucible; the crucible is removed from the lamp, and 2 pts. very finely powdered and sifted MnO_2 are added, little by little; heating is then continued, with stirring, until the mass gets quite hard; the temperature is then raised for a short time to full redness; when cold, the mass is broken up, and boiled with so much water that no crystals separate on cooling (c. 40 pts. water for 1 pt. $KClO_3$ used); a rapid stream of well-washed CO_2 is passed into the boiling liquid until a drop placed on paper makes a red stain (showing no green at the edges), the outer part of which soon becomes brown. After cooling, the greater part of the liquid is poured off, the rest is filtered (from MnO_2) through glass-wool, and the whole is evaporated until a drop placed on a cold surface quickly deposits crystals.

After standing 12 to 24 hours the greater part of the $KMnO_4$ separates out; a little is obtained by further evaporating the mother-liquor. 100 grms. pyrolusite give about 30 grms. $KMnO_4$ (Böttger, *J. pr.* 90, 156; for modification of this method, *v.* Gräger, *J. pr.* 96, 169; Wöhler, *P.* 27, 626; Gregory, *J. Ph.* 21, 312; Mitscherlich, *P.* 25, 287; Elliot a. Storer, *P. Am. A.* 5, 192). Béchamp (*A. Ch.* [3] 57, 293) heats MnO_2 with KOH, and oxidises by passing O over the fused mass; he then dissolves in water, passes in CO_2, and evaporates.

Properties.—Dark purple-red, almost black, rhombic crystals; $a:b:c = \cdot79523:1:\cdot6478$. S.G. 2·71 (Kopp). Isomorphous with $KClO_4$. S. at $15° = 6\cdot25$ (Mitscherlich). Decomposed by heat, giving K_2MnO_4 and O. Pure conc. $KMnO_4Aq$ can be boiled without change; in presence of oxidisable bodies $KMnO_4Aq$ is quickly reduced.

Reactions.—1. Heated to 240°, MnO_2, K_2MnO_4, and O are produced (Chevillot a. Edwards, *A. Ch.* [2] 4, 290). At higher temperatures $xMnO_2.yK_2O$ is formed (Rousseau, *C. R.* 104, 786).—2. *Sulphuric* or *nitric acid* separates $HMnO_4$, which decomposes with evolution of O and ppn. of MnO_2, Mn_2O_3, or $xMnO_2.yMnO$; with considerable excess of warm H_2SO_4Aq or HNO_3Aq, $MnSO_4$ or $Mn(NO_3)_2$ is produced. Cold conc. H_2SO_4 dissolves $KMnO_4$, forming a green liquid, from which a few drops of water cause separation of Mn_2O_7 (*cf. Manganese heptoxide*, p. 184; *v.* also *Manganese trioxide*, p. 184).—3. *Hydrochloric acid* in excess forms $MnCl_2$ and evolves Cl. Dry HCl evolves Cl, and forms H_2O, KCl, $Mn_2O_3.xH_2O$, $MnCl_2$, and probably Mn_2Cl_6 (Thomas, *C. J.* 33, 372).—4. *Sulphuric acid* and *oxidisable bodies* either separate MnO_2, or $xMnO_2.yMnO$, the oxidisable body being simultaneously oxidised; or if there be enough acid to prevent ppn. of $xMnO_2.yMnO$, $MnSO_4$ is formed. With $H_2C_2O_4$ and H_2SO_4, CO_2 and H_2O (besides K_2SO_4 and $MnSO_4$) are produced (*cf.* Berthelot, *A. Ch.* [5] 21, 176; Harcourt, *C. J.* [2] 5, 460; Jones, *C. J.* 33, 95). Harcourt (*l.c.*) represents the reaction thus:

$$2KMnO_4Aq + 3H_2SO_4Aq + 5H_2C_2O_4Aq$$
$$= K_2SO_4Aq + 2MnSO_4Aq + 10CO_2 + 8H_2O.$$

Jones (*l.c.*) says that H_2O, $K_2C_2O_4$, and MnC_2O_4 are at first produced on adding $KMnO_4Aq$ to $H_2C_2O_4Aq$, and that further addition of $KMnO_4Aq$ forms K_2CO_3, ppts. Mn_2O_3, and evolves CO_2 and O. Alcohol gives K acetate and a pp. containing MnO_2, MnO, and K_2O; glycerin gives a similar pp. and forms K_2CO_3 (Morawski a. Stingl, *J. pr.* [2] 18, 78; *cf.* Berthelot, *l.c.*).—5. According to Aschoff (*J. pr.* 81, 29) conc. $KMnO_4Aq$ is reduced to K_2MnO_4 by boiling with *potash solution* ($2KMnO_4Aq + 2KOHAq = 2K_2MnO_4Aq + H_2O + O$); Thenard (*J. pr.* 69, 58) says that this action does not occur unless traces of oxidisable substances, *e.g.* organic matter, are present.—6. $KMnO_4Aq$ acidified by H_2SO_4 reacts with *hydrogen peroxide* to form H_2O, O, and $MnSO_4$. At low temperatures, c. 12°, the $KMnO_4$ is decolourised, but O is not evolved, according to P. Thenard (*C. R.* 75, 177); Berthelot (*A. Ch.* [5] 21, 176) thinks that H_2O_3 (?) is formed (*v.* also Swiontrowski, *A.* 141, 205; Aschoff, *P.* 111, 217).—7. $KMnO_4Aq$ is decomposed with separation of MnO_2, Mn_2O_3, or $xMnO_2.yMnO$, by *ammonia* (Cloëz a. Guignet, *C. R.* 47, 710; Wöhler, *A.* 136, 256; Wanklyn a. Gamgee, *C. J.* [2] 6, 25; Tamm, *C. N.* 25, 47); by *hydrogen* (Jones, *C. J.* 33, 96; Wanklyn a. Cooper, *P. M.* [5] 6, 288); by *phosphine*, *arsine* and *stibine* (Jones, *l.c.*; Schobig, *J. pr.* [2] 14 289; Parsons, *C. N.* 1877. 236); by *chlorine dioxide* [ClO_2] (Fürst, *A.* 206, 75).—8. With *potassium sulphocyanide*, K_2SO_4 and KCNO are produced (Morawski a. Stingl, *J. pr.* [2] 18, 78).—9. *Sodium thiosulphate* in boiling solution is wholly oxidised to Na_2SO_4 by fairly conc. $KMnO_4Aq$; if the $KMnO_4Aq$ is very dilute from 1 to 2½ p.c. $Na_2S_2O_3$ remains (Gläser, *M.* 7, 651).

Combination.—From conc. mixed solutions of $KMnO_4$ and K_2MnO_4 the salt $KMnO_4.K_2MnO_4$ separates in small, six-sided, monoclinic tablets (Gorgeu, *J. pr.* 80, 123).

Sodium permanganate $NaMnO_4.3H_2O$. Formed similarly to $KMnO_4$; or by the reaction between $AgMnO_4$ and NaClAq. V. sol. water, and hence obtained in crystals with difficulty.

Silver permanganate $AgMnO_4$. Monoclinic crystals. S. ·91 in cold water. Obtained by mixing conc. warm $KMnO_4Aq$ with $AgNO_3Aq$, and allowing to cool (Dewar a. Scott, *Pr.* 35, 44). Klobb (*C. R.* 103, 384) obtained $AgMnO_4.2NH_3$ by saturating $KMnO_4Aq$ with NH_3, and then adding an equivalent quantity of $AgNO_3$.

Permanganates of *copper*, *didymium* (Frerichs a. Smith, *A.* 191, 354), *lanthanum* (F. a. S., *l.c.*), *lead*, *lithium*, *magnesium*, *strontium*, and *zinc*, have been isolated.

Permanganic acid, $HMnO_4$. The solution obtained by decomposing powdered $Ba(MnO_4)_2$ by an exactly equivalent quantity of H_2SO_4Aq, contains this acid. Hünefeld (*Schweigger's Jahrb. der Chem. und Phys.* 30, 133) says that the acid can be obtained, in indigo-like crystals, by washing $Ba(MnO_4)_2$ with hot water, whereby it is decomposed to MnO_2 and $BaMnO_4$, filtering, adding exactly enough phosphoric acid to decompose the Ba salt, heating to 60°–100°, filtering, and evaporating at a low temperature. (No analyses are given.)

Manganese, oxychlorides of. Several oxychlorides of Mn appear to exist, but they have not been satisfactorily examined. P. de Saint-Gilles (*C. R.* 55, 329) says that $MnCl_2.3Mn_2O_3$ is formed as a black powder, resembling MnO_2, by heating to 280°, in a partially closed vessel, a mixture of $MnCl_2$ and $NaNO_3$. Gorgeu (*A. Ch.* [6] 4, 515) obtained an oxychloride, to which he provisionally assigned the formula $MnCl_2.MnO$ by heating $MnCl_2$ in water vapour. According to Aschoff (*J. pr.* 81, 29) the gas which Dumas obtained by adding pieces of fused KCl or NaCl to a mixture of $KMnO_4$ and conc. H_2SO_4, and which he said was $MnCl_7$, is probably an oxychloride having the composition MnO_3Cl.

Manganese, oxyfluoride of. According to Nicklès (*C. R.* 65, 107) the compounds $MnOF.KF$ and $Mn_2OF_2.2KF$ are ppd., when solution of MnO_2 in ethereal HCl is poured into boiling KFAq or NaFAq. Christensen (*J. pr.* [2] 35, 57), however, asserts that the double compound obtained as described above is $MnOF_2$.

Manganese, oxysulphide of. The compound MnO.MnS is said to be formed, by Arfvedson (*P.* 1, 50), by heating $MnSO_4$ in H; it is a green solid, which dissolves in acids with evolution of H_2S; heated in air it burns to Mn_3O_4.

Manganese, phosphides of. Several compounds of Mn with P have been described. Mn_3P: an amorphous powder, S.G. 4·94, obtained by heating Mn and P together to low redness (Schrötter, *J. pr.* 51, 385). Also formed, according to H. Rose, by heating $MnCl_2$ in PH_3. By heating Mn pyrophosphate mixed with sugar-charcoal, in a crucible filled up with charcoal, Struve (*J. pr.* 81, 321) obtained a brittle substance resembling pig-iron, the composition of which varied between Mn_3P_2 and Mn_2P. Merkel and Wöhler (*A.* 86, 371) obtained a crystalline, greyish, regulus, S.G. 5·95, by heating together 10 parts MnO_2, 10 parts well-burnt bones, 5 parts quartz-sand, and 3 parts lamp-black. The composition agreed with the formula Mn_5P_2; but as part was soluble, and part insoluble, in HClAq, they regarded the substance as a mixture of two phosphides, Mn_3P_2 (soluble in HClAq) and Mn_7P_2 (insoluble in HClAq).

Manganese, salts of. Compounds obtained by replacing the H of acids by Mn. Mn forms two series of salts: *manganous salts*, MnX_2, and *manganic salts*, Mn_2X_3; $X = NO_3$, ClO_3, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c. One or two salts of the form MnX_4—*e.g.* $Mn(SO_4)_2$—are also said to exist. The manganous salts are considerably more stable than the manganic salts. A number of double salts of manganic sulphate are known; those with the alkali sulphates are alums, *e.g.* $Mn_2(SO_4)_3.K_2SO_4.24H_2O$. The manganous salts form a fair number of double salts and a few basic salts. The chief salts of Mn are the following: *antimonates*, *arsenates* and *arsenite*, *borate*, *carbonates*, *chlorate* and *perchlorate*, *chromates*, *ferri-* and *ferro-cyanides*, *iodate*, *molybdate*, *nitrates* and *nitrites*, *phosphates* and *phosphites*, *selenates* and *selenites*, *silicates*, *sulphates* and *sulphites*, *thiosulphate*, *tungstate*, *vanadate*: *v.* CARBONATES, NITRATES, SULPHATES, &c.

Manganese, selenide of. Said to be produced in combination with H_2O as a red powder, decomposed in air, by adding an alkali selenide solution to solution of a manganous salt.

Manganese, silicides of. Mn and Si combine when heated together (Troost a. Hautefeuille, *C. R.* 81, 264). Silicides of Mn, containing from 6·5 to 13 p.c. Si, have been obtained by Wöhler (*A.* 106, 54) by fusing together MnF_2, Na, K silicate, and cryolite; or $MnCl_2.2NaCl$, CaF_2, and K silicate; or $MnCl_2$, CaF_2, K_2SiF_6, and Na. These silicides form hard, brittle masses; they dissolve in HClAq with evolution of H and SiH_4.

Manganese, silicofluoride of. $MnSiF_6.6H_2O$. Hexagonal crystals, $a:c = 1:·515$; S.G. at 17·5° = 1·9038 (Stolba, *C. C.* 1883. 292). Formed by dissolving $MnCO_3$ or MnF_2 in H_2SiF_6Aq, and evaporating. When heated, the crystals give off water, and then SiF_4, and leave MnF_2 (Berzelius).

Manganese, sulphides of. Two sulphides are known, MnS and MnS_2.

MANGANOUS SULPHIDE, MnS. Occurs native, as *manganese-blende*, in hexagonal crystals, S.G. 3·95. Produced by heating together MnO or $MnCO_3$ and S, *not* by heating S with Mn. Also formed by heating Mn in CS_2 (Gautier a. Hallopeau, *C. R.* 108, 806); also by heating various Mn compounds in H_2S (Carnot, *Bl.* [2] 32, 162). Sidot (*J.* 1868. 229) obtained MnS in hexagonal crystals by heating the amorphous substance in a stream of H_2S. MnS is ppd. from solutions of Mn salts by NH_4 sulphide, as a pale buff-coloured amorphous solid, which quickly oxidises in air; if this pp. is rapidly dried and then warmed in H_2S, pure MnS is obtained. MnS is a greenish solid; decomposed by weak acids, *e.g.* acetic acid, with evolution of H_2S. Heated in air, SO_2 is evolved and Mn_3O_4 remains (P. W. Hofmann, *D. P. J.* 181, 364). Heated in H_2O vapour, H_2S and H are given off and Mn_3O_4 is formed. MnS is slowly decomposed by Cl with formation of $MnCl_2$ and S_2Cl_2.

There appear to be two forms of MnS obtainable by ppn. from Mn salts by NH_4 sulphide: the pp. from conc. $MnCl_2Aq$ or $MnSO_4Aq$ is rose-coloured; if NH_4Cl is present the pp. is greenish and consists of small 8-sided plates. The green sulphide is not produced when K_2S or Na_2S is used as pptant. (Fresenius, *J. pr.* 82, 265; Muck, *Z.* 1869. 580; de Clermont a. Guyot, *Bl.* 27, 353; Geuther, *Z.* 1865. 347). The rose-coloured sulphide is said to be changed to the green sulphide by heating with a little water; but it may be heated to 305° with much water without changing. The change from rose to green is accomplished by heating with NH_3Aq to 250° in a closed tube, and the reverse change by heating in NH_3 gas. The rose sulphide is not changed by heating alone to 250° but in presence of H_2S the green sulphide is formed at 220° (De C. a. G., *l.c.*). The green sulphide is thought by Muck to be an oxysulphide of Mn.

Double compound, $3MnS.K_2S$. Obtained by heating a mixture of 1 pt. dry $MnSO_4$, $\frac{1}{3}$ pt. lamp-black, and 3 pts. K_2CO_3 and S, and treating the fused mass with water; the compound remains insoluble in water, forming small lustrous dark-red tablets (Voelcker).

MANGANIC SULPHIDE, MnS_2. Occurs native as *hauerite*, in large, brown-black, lustrous, regular octahedra, S.G. 3·463. Said to be obtained as a red amorphous powder, by heating $MnSO_4Aq$ with solution of K polysulphides to 160°–180° in a closed tube (Senarmont, *J. pr.* 51, 385). Not changed in air; decomposed by acids.

Manganese, sulphocyanide of, *v.* vol. ii. p. 350. M. M. P. M.

MANGANITES. Salts in which MnO_2 acts as the acidic radicle; *v. Manganese peroxide, Reactions* 12, under MANGANESE, *Oxides and hydrated oxides of*, p. 183.

MANGANOCYANIDES *v.* vol. ii. p. 342.

MANGOSTIN $C_{20}H_{22}O_5$. [c. 190°]. Contained in the husk of the fruit of *Garcinia mangostana*. The dry husks are boiled with water to extract tannin, then treated with hot alcohol, and the alcoholic extract left to evaporate. The mangostin which is deposited is dissolved in alcohol and ppd. by lead subacetate. The pp. is decomposed by water and the mangostin finally crystallised from dilute alcohol (Schmid, *A.* 93, 83). Thin golden laminæ without taste or smell. Insol. water, v. sol. alcohol and ether. Warm dilute acids dissolve it without alteration. Hot conc. HNO_3 gives oxalic acid. Alkalis dissolve it with yellowish-brown colour. Reduces chloride of gold solution. $FeCl_3$ gives a dark greenish-black solution, decolourised by acids. Its solution is not ppd. by any metallic salt except lead subacetate.—$(C_{20}H_{22}O_5)_4 5PbO$ (dried at 100°); ppd. by adding alcoholic lead acetate and ammonia to an alcoholic solution of mangostin.

MANNITE $C_6H_{14}O_6$ *i.e.* $CH_2(OH).CH(OH).CH(OH).CH(OH).CH(OH).CH_2(OH)$. Mol. w. 182 (181 by Raoult's method, Brown a. Morris, *C. J.* 53, 620). [165°]. S.G. 1·5. $[\alpha]_D = -·25$. S. 15·6 at 18° (Berthelot, *A. Ch.* [3] 47, 301); 13 at 14° (Krusemann, *B.* 9, 1467); 16 at 16·5° (Wanklyn a. Erlenmeyer, *J.* 1862. 480). S. (alcohol) ·07 at 14°. H.C. v. 728,200. H.C. p. 728,500 (Berthelot a. Vieille, *Bl.* [2] 47, 868; *A. Ch.* [6] 10, 456). H.F. 318,500 (B. a. V.); 287,000 (Von Rechenberg).

Occurrence.—Discovered by Proust (*A. Ch.* [1] 57, 143). Occurs to the extent of 30 to 60 p.c. in manna, the dried juice which exudes from the manna ash (*Fraxinus Ornus*). Mannite occurs in many other plants, *e.g.*: the roots of *Aconitum napellus*; celery, *Apium graveolens*; *Meum athamanticum*; *Œnanthe crocata*; *Polypodium vulgare*; *Scorzonera hispanica*, and *Triticum repens*; and in the root-bark of *Tunica granatum*. Mannite also occurs in the bark of *Canella alba* (8 p.c.), and of *Fraxinus excelsior*; in the leaves and young twigs of *Syringa vulgaris*; in the leaves of *Ligustrum vulgare* and of *Cocos nucifera*, and in the fruit of *Laurus Persea* and of *Cactus opuntia*. Mannite also occurs in *Laminaria saccharina*, in olives, and in several fungi, *e.g.*: *Lactarius vellereus*, *L. turpis*, *L. pyrogalus*, and *L. pallidus*. *Agaricus integer* contains 20 p.c. of its dry substance. It also occurs in the cambium layer of *Coniferæ* (Payen, *A.* 12, 60; Meyer a. Reiche, *A.* 47, 234; Stenhouse, *A.* 51, 349; Knop a. Schnedermann, *A.* 49, 293; Döpping a. Schlossberger, *A.* 52, 117; Müntz, *C. R.* 76, 649; 82, 210; Smith, *J.* 1850, 535; Roussin, *J.* 1851, 550; Ludwig, *J.* 1857, 503; De Luca, *J.* 1861, 740; 1862, 505; Thörner, *B.* 12, 1635; Reinsch, *J.* 1863, 612; Bourquelot, *C. R.* 108, 568; Kaehler, *M.* 7, 410).

Formation.—1. In the lactic fermentation of sugar (Liebig, *J.* 1847, 466; Pasteur, *J.* 1857, 511; Dragendorff, *Ar. Ph.* [3] 15, 47).—2. In the viscous fermentation of sugar, 100 pts. of sugar yielding 51 pts. mannite and 46 pts. gum (Pasteur, *J.* 1861, 728).—3. In the spontaneous fermentation of the juice of the sugar-cane in tropical climates (Marcano, *C. R.* 108, 955).—4. By reducing glucose, lævulose, or invert-sugar with sodium-amalgam (Linnemann, *A.* 123, 136; Dewar, *P. M.* [4] 39, 345; Bouchardat, *Bl.* [2] 16, 38; Krusemann, *B.* 9, 1465; Scheibler, *B.* 16, 3010).—5. By reducing mannose (E. Fischer, *B.* 21, 1808), or 'glucosone' (E. Fischer, *B.* 22, 94), with sodium-amalgam.—6. From the dilactone of meta-saccharic acid by treating with water and sodium-amalgam (3 p.c.), acidifying with H_2SO_4 (Kiliani, *B.* 20, 2714; *v.* LEVO-MANNITE, *infra*).

Preparation.—1. Manna is extracted with boiling dilute alcohol, and the crystals which separate on cooling are recrystallised from water.—2. Manna (2 pts.) is boiled with water (1 pt.) after addition of a little white of egg. The crystals which separate from the filtrate are boiled with water (6 pts.) to which some animal charcoal has been added, and the filtrate is allowed to crystallise (Ruspini, *A.* 65, 203).

Properties.—Needles or four-sided prisms. V. sol. water, v. sl. sol. alcohol, insol. ether. An aqueous solution, does not become syrupy on spontaneous evaporation (difference from sugar). Only slightly sweet to the taste. It has little, if any, action on light, but if borax be added to the solution it becomes dextrorotatory. Thus in a 10 p.c. solution containing 12·8 g. borax $\alpha = +22·5°$, so that $[\alpha]_D =$ c. $+225°$ (Vignon, *A. Ch.* [5] 2, 433; *C. R.* 77, 1191; Müntz a. Aubin, *C. R.* 83, 1213; Pasteur, *C. R.* 77, 1192; Bouchardat, *C. R.* 80, 120; 84, 34). Arsenic acid slowly develops lævorotation in a solution of mannite. Salts of the alkalis and alkaline earths develop dextrorotation. Free alkalis render the solution lævorotatory. A solution containing 8 g. mannite and 8 g. NaOH in 100 c.c. gives $\alpha = -3·4°$, so that $[\alpha]_D = -42°$. A solution of 12 g. mannite and 4 g. sodium tungstate made up to 100 c.c. shows $\alpha = +0° 40'$ (Klein, *C. R.* 89, 484). These rotations vary with the amount of dissolved substances. The mannite may be recovered from these solutions without having undergone any change in optical properties. Mannite renders a borax solution acid, forming boracic acid and sodium metaborate (Dunstan, *Ph.* [3] 13, 257; 14, 41; Lambert, *C. R.* 108, 1016). Mannite does not reduce Fehling's solution. It hinders the ppn. of ferric and cupric salts by potash. It is not turned brown by boiling KOHAq. With a solution of ammonio-sulphate of copper it gives a blue pp., sol. in ammonia, forming a blue solution which is not affected by boiling (Guignet, *C. R.* 109, 528, 645). Mannite does not reduce boiling solutions of silver or mercurous nitrates, of $HgCl_2$, or of chloride of gold; but it reduces Ag_2O and silver acetate (Hirzel, *A.* 131, 50). When alcohol is added to a solution of mannite mixed with lime, strontia, or baryta-water, pps. $(C_6H_{14}O_6)_4 3CaO$, $(C_6H_{14}O_6)_1 SrO$, and $(C_6H_{14}O_6)_2 BaO$ are formed (Hirzel, *A.* 131, 50; *cf.* Ubaldini, *A. Ch.* [3] 57, 213). Ammoniacal lead acetate gives a pp. On adding to an aqueous solution of mannite (1 mol.) and of lead nitrate (2 mols.) sufficient ammonia to neutralise two-thirds of the nitric acid present in the salt, a voluminous white pp. separates, which, if filtered off and dried over calcium chloride, forms a white crystalline powder $C_6H_8O_6Pb_4(NO_3)_2 2H_2O$, S. 1·10 at 14°; decomposing with explosion on heating, and separated into its constituents on long boiling with water and by carbonic anhydride with formation of lead carbonate (Smolka, *M.* 6, 198).

Reactions.—1. Mannite begins to sublime at c. 200°; in a sealed tube it is unaltered at 250°. At 280° it splits up into water and mannitan $C_6H_{12}O_5$. When distilled *in vacuo* it yields isomannide $C_6H_{10}O_4$.—2. A mixture of HNO_3 and H_2SO_4 forms the nitrate, so-called 'nitro mannite' (Flores Domonte a. Menard, *J.* 1847, 1145).—3. *Nitric acid* oxidises it to saccharic, racemic, and oxalic acids, no mucic acid being formed (Backhaus, *J.* 1860, 522; Carlet, *J.* 1861, 367).—4. Boiling HIAq gives *sec*-hexyl iodide (Wanklyn a. Erlenmeyer; Domac, *M.* 2, 309; *cf.* Le Bel a. Wassermann, *C. R.* 100, 1589).—5. Boiling conc. HClAq slowly forms mannitan.—6. *Potash-fusion* yields formic, acetic, and propionic and oxalic acids and acetone (Gottlieb, *A.* 52, 122).—7. On oxidation with $KMnO_4$ in alkaline solution it gives oxalic acid, formic acid, a little tartaric acid, a sugar which reduces Fehling's solution, and erythric acid $C_4H_8O_5$, which forms

the salts CaA'_2 2aq, BaA'_2 2aq, and $C_4H_6BaO_5$ 2aq (Hecht a. Iwig, *B.* 14, 1760; 19, 468; *cf.* Pabst, *C. R.* 91, 728, who states that he obtained a dibasic acid $C_6H_8O_9$, which he names dioxyisocitric acid).—8. *Air* and *platinum black* yield mannitic acid $C_6H_{12}O_7$ and mannitose $C_6H_{12}O_6$.—9. MnO_2 and H_2SO_4 give formic acid and acroleïn (Backhaus).—10. When mannite (2 pts.) is heated with 80 p.c. formic acid (5 pts.) for 8 hours a mixture of formyl derivatives of mannitan appears to be formed. This mixture yields on distillation CO, CO_2, isomannide $C_6H_{10}O_4$, a liquid $C_6H_{10}O_3$ (?) (157° at 17 mm.) and a liquid C_6H_8O (108°), S.G. $\frac{0}{4}$ ·9396; $[\alpha]_D = -168°$; almost insol. water, and smelling like a carbamine and mustard oil (Fauconnier, *C. R.* 100, 914; *cf.* Henninger, *B.* 7, 264).—11. Distillation with *oxalic acid* yields formic acid, a formyl derivative of mannite or of mannitan being probably first formed (Lorin, *Bl.* [2] 24, 437).—12. *Electrolysis* of a solution of mannite acidulated by H_2SO_4 yields hydrogen, CO_2, CO, oxygen, tri-oxy-methylene (? formic paraldehyde or mannitose), formic acid, oxalic acid, and a small quantity of an acid whose calcium salt is $C_6H_6CaO_8$ 2aq. This acid having reducing properties may be

$CO_2H.CO.(CH.OH)_3.CO_2H$

(Rénard, *A. Ch.* [5] 17, 316).—13. PCl_5 gives tetra-chloro-hexinene (Bell, *B.* 12, 1273).—14. PI_2 forms methylene iodide (Butlerow, *A.* 111, 247).—15. *Organic acids* (*e.g.* acetic and butyric) heated with mannite at 200° form alkoyl derivatives of mannitan. — 16. Mannite heated with *water* suffers no change below 280°, but at that temperature a viscid product is got containing 'mannitic ether' $C_{12}H_{26}O_{11}$ ($[\alpha]_j = -5·6$) and 'mannitone,' a crystalline isomeride of mannitan. Both bodies are reconverted into mannite by heating with water at 295° (Vignon).—17. Mannite does not react when heated with acetic, valeric, or benzoic aldehydes (Lochert, *A. Ch.* [6] 16, 65). But when *acetic aldehyde* is passed into a solution of mannite in H_2SO_4 or HClAq the aldehyde is absorbed and there is formed a compound crystallising in needles [174°]; insol. cold water. S. 1 at 95°. It is sl. sol. cold, v. sol. hot, alcohol. Boiling dilute (2 p.c.) H_2SO_4 resolves it into aldehyde and mannite. Paraldehyde gives the same compound. When a mixture of acetic and benzoic aldehydes is used the above product is formed first (Meunier, *C. R.* 108, 408).—18. When a mixture of mannite (10 g.), absolute alcohol (20 g.), and fused $ZnCl_2$ (5 g.) is saturated with HCl, left for two days, and then mixed with benzoic aldehyde, there is formed 'tribenzoic mannitoïd' $C_6H_8O_3(C_7H_6O)_3$ [207°]. This crystallises from benzene, and is insol. water, sl. sol. alcohol. It is not affected by boiling alcoholic KOH, but dilute H_2SO_4 yields mannite and benzoic aldehyde (Meunier, *C. R.* 106, 1425, 1732). A solution of mannite in HClAq or H_2SO_4 also reacts with benzoic aldehyde (Meunier, *C. R.* 107, 910).—19. A solution of mannite in alcohol containing $ZnCl_2$ and saturated with HCl reacts with BzCl, forming di-benzoyl-mannide $C_6H_8O_2(OBz)_2$ [132°] (Meunier, *C. R.* 107, 346). 20. *Valeric aldehyde*, $ZnCl_2$ and HCl convert mannite in alcoholic solution into $C_6H_8O_3(C_5H_{10}O)_3$, which is deposited as silky needles [91°] (Meunier).—21. Not *fermented* by yeast. In contact with water, chalk, and cheese at 40° it gives alcohol, carbonic, lactic, butyric, and acetic acids, and hydrogen, but no sugar or glycerin (Berthelot, *J.* 1856, 664). When the fermentation is induced by a slit testicle a fermentible sugar is produced. Upon fermentation by Schizomycetes in presence of $CaCO_3$ and ammonium phosphate there is formed alcohol, *n*-butyl alcohol, butyric, lactic, acetic, hexoic, and succinic acids (Fitz, *B.* 10, 281; 11, 43). *Bacillus butyricus* gives similar products. Under other conditions formic acid is among the products of fermentation (Fitz, *B.* 11, 1895; 15, 876; 16, 845).—22. Heating with phenyl cyanate forms $C_6H_8(OH)(O.CONHPh)_5$ [260°] (Tessmer, *B.* 18, 968).

Pentanitrate $C_6H_9(ONO_2)_5O$. *Pentanitroxyl derivative.* [79°]. S. ·2 at 60°. S. (alcohol, S.G. ·81) 150 at 12·8°. S. (ether) 130 at 9°. Formed, together with nitro-mannitan, by passing NH_3 into an ethereal solution of the hexanitrate (Tichanovitch, *J.* 1864, 582). Long needles. Dextrorotatory. Explodes when struck, and also, more feebly, when heated. Ammonium sulphide reduces it to mannite.

Hexanitrate $C_6H_8(ONO_2)_6O$. *Nitro-mannite.* Mol. w. 452. [113°] (Socoloff). S.G. $\frac{0}{}$ 1·604. S. (alcohol of S.G. ·81) 3 at 12·8°. S. (ether) 5 at 9° (Tichanovitch). $\alpha = +12·4$ in a 3 p.c. solution, so that $[\alpha]_D = +400°$ (Müntz a. Aubin). Prepared by treating mannite (1 pt.) with HNO_3 (5 pts. of S.G. 1·5) at 0°, and adding H_2SO_4 (10 pts.). The product is collected on a filter, washed with water and aqueous Na_2CO_3, and recrystallised from alcohol (Domont a. Menard, *J.* 1847, 1145; Sobrero, *A.* 64, 397; Strecker, *A.* 73, 62; Socoloff, *J. R.* 11, 136). Beautiful white needles, insol. water, sol. alcohol and ether. Explodes violently on being struck—it also explodes when suddenly heated; but if carefully heated it may be decomposed without explosion. Ammonium sulphide converts it into mannite (Dessaignes, *A.* 81, 251). Iron and acetic acid and HIAq also convert it into mannite (Béchamp, *A. Ch.* [3] 46, 354; Mills, *J.* 1864, 584). NH_3 passed into its ethereal solution forms crystalline $C_6H_8O(NH_2)_4$ (Tichanovitch).

Di-sulphuric acid $C_6H_8(SO_4H)_2(OH)_4$. From mannite and conc. H_2SO_4 (Favre, *B. J.* 25, 560). The free acid is decomposed by boiling water. It gives no pp. with $BaCl_2$ or $CaCl_2$.—$Pb_2C_6H_{10}S_2O_{12}2PbO$: insoluble pp.

Tri-sulphuric acid $C_6H_8(SO_4H)_3(OH)_3$. From mannite and conc. H_2SO_4 (Knop a. Schnedermann, *A.* 51, 135). Both the acid and its salts are decomposed by water into mannite and H_2SO_4.—Na_3A'''.—K_3A''': deliquescent gummy mass; insol. alcohol.—$Ba_3A'''_2$: crystalline powder, sol. water, insol. alcohol.—$Pb_3A'_2$: amorphous deliquescent mass.

Tetra-sulphuric acid $C_6H_8(SO_4H)_4(OH)_2$. $[\alpha]_D = +9°$. Obtained when, in the preparation of the hexa-sulphuric acid, the neutralisation with $BaCO_3$ is delayed for two days.—Ba_2A^{iv}.

Hexa-sulphuric acid $C_6H_8(SO_4H)_6$. $[\alpha]_D = +21°$. Formed by adding mannite in small portions to chloro-sulphuric acid ($ClSO_3H$). The product is dropped upon ice, and the ice-cold solution neutralised with $BaCO_3$—Ba_3A^{vi} 5aq. When alcohol is added to its solution this salt is thrown down as an oil, which

presently changes to a crystalline mass insol. water. The other salts are very soluble, and do not behave thus (Claesson, *J. pr.* [2] 20, 10).

Boric acid. When mannite (4 pts.) is heated with boric acid (3 pts.) for eight hours at 145°, and the product is dissolved in water and neutralised by $BaCO_3$, a filtrate is obtained which deposits barium borate on evaporating, after which alcohol gives a pp. which, when dried at 100°, has the composition $(C_6H_{13}B_2O_9)_2Ba$ (Klein, *Bl.* [2] 29, 363).

Hexa-acetyl derivative $C_6H_8(OAc)_6$. [119°]. $[\alpha]_D = +18°$ (Bouchardat, *C. R.* 84, 34). From mannite (18 pts.) and Ac_2O (80 pts.) at 180°, with or without addition of a little $ZnCl_2$ (Bouchardat, *A. Ch.* [5] 6, 107; Schützenberger, *A.* 160, 94; Franchimont, *B.* 12, 2059). Limit of etherification from mannite (1 mol.) and HOAc (6 mols.): 26·4 (Menschutkin, *B.* 13, 1814). Trimetric crystals (from HOAc). Insol. water, cold alcohol, and ether, sl. sol. hot alcohol. Dextrorotatory. May be sublimed in a current of CO_2.

Penta-benzoyl derivative $C_6H_9(OBz)_5(OH)$. [c. 80°]. From mannite (3 g.), water (15 g.), BzCl (20 g.), and NaOHAq. The product is extracted with ether (Skraup, *M.* 10, 394). Amorphous mass.

Hexa-benzoyl derivative $C_6H_8(OBz)_6$. [149°]. From the preceding and BzCl. Crystalline grains, v. sl. sol. alcohol.

Mannite dichlorhydrin $C_6H_8(OH)_4Cl_2$. *Di-chloro-tetra-oxy-hexane.* [174°]. S. 4·5 at 14°. $[\alpha]_D = -3·7$. Formed by heating mannite (1 pt.) with conc. HClAq (6 pts.) at 100° for eight hours (Bouchardat, *C. R.* 75, 1187; 76, 1550; *Bl.* [2] 19, 199). Formed also by heating isomannide with fuming HClAq at 100° in sealed tubes (Fauconnier, *Bl.* [2] 41, 119). Prepared by heating mannite (1 pt.) with fuming HClAq (10 pts.) at 106°; evaporating at low temperatures; dissolving the crystals in water: filtering the solution through animal charcoal; and re-crystallising from hot alcohol (Siwoloboff, *A.* 233, 368).

Properties.—Monoclinic crystals. Lævorotatory. Its aqueous solution is neutral and tasteless, and is not ppd. by $AgNO_3$. Insol. alcohol and ether. Decomposed on fusion.

Reactions.—1. Boiling water or conc. NaOHAq rapidly convert it into $C_6H_8O(OH)_3Cl$.—2. A mixture of HNO_3 and H_2SO_4 gives $C_6H_8(ONO_2)_4Cl_2$, which crystallises from hot alcohol in needles [145°], insol. water.—3. *Sodium-amalgam* removes HCl in two stages, forming mannitan chlorhydrin, and finally (β)-mannide [119°].

Mannite dibromhydrin $C_6H_8(OH)_4Br_2$. [178°]. Obtained by heating mannite with conc. HBrAq for 2 hours at 100° (Bouchardat, *A. Ch.* [5] 6, 120). Small colourless plates (from hot water). Decomposed on fusion. Insol. cold water, alcohol, and ether. Converted by a mixture of HNO_3 and H_2SO_4 into $C_6H_8(ONO_2)_4Br_2$, which crystallises in long needles, sol. hot alcohol, insol. water.

Mannitan $C_6H_{12}O_5$ *i.e.* $C_6H_8O(OH)_4$. *First anhydride of mannite.* According to Alechin (*J. R.* 16, 383) the various mannitans described below are mixtures of isomannide and other bodies.

(*a*) *Berthelot's mannitan* $C_6H_{12}O_5$. Obtained in small quantity by heating mannite at 200°. A better method is by protracted boiling of mannite with conc. HClAq (Berthelot, *A. Ch.* [3] 47, 306). Slightly sweetish syrup. Differs from mannite in being soluble in absolute alcohol. V. sol. water, insol. ether. Slightly dextrorotatory (Bouchardat, *A. Ch.* [5] 6, 102). When exposed to the atmosphere it is partially reconverted into mannite. Boiling alkalis or dilute acids accelerate the change. Above 140° it partly volatilises.

(*b*) *Vignon's mannitan* $C_6H_{12}O_5$. $[\alpha]_j = +36·5°$. Prepared by heating mannite for an hour or two with half its weight of water at 295°. Also by heating mannite (2 pts.) with conc. H_2SO_4 (1 pt.) at 120°, saturating with $BaCO_3$, exhausting with alcohol, and evaporating (Vignon, *A. Ch.* [5] 2, 433). Deliquescent mass, v. e. sol. water and absolute alcohol, insol. ether. Does not ferment with yeast. Boiling dilute H_2SO_4 or baryta-water does not reconvert it into mannite. A mixture of mannitan (1 pt.), H_2SO_4 (10 pts.), and HNO_3 (4½ pts. of S.G. 1·5) forms in the cold $C_6H_8O_2(OH)(ONO_2)$, which is obtained on pouring into water and extracting with ether. It is dextrorotatory, $[\alpha]_j = +53°$.

(*c*) *Vignon's mannitone* $C_6H_{12}O_5$. $[\alpha]_j = -25°$. Obtained by heating mannite with water for 3 hours at 280° and extracting the viscid product with alcohol (Vignon, *A. Ch.* [5] 2, 433). Crystals (from alcohol). Has a sweet taste. Lævorotatory. Does not reduce Fehling's solution. In the preparation of this body the syrupy mother-liquor yields a viscid mass, which appears to be the anhydride of mannite or 'mannitic ether' $C_{12}H_{26}O_{21}$; it does not reduce Fehling's solution, and is lævorotatory, $[\alpha]_j = -5·6°$. This mannitic ether is not converted into mannite or mannitan by boiling dilute acids or alkalis.

(*d*) *Crystalline mannitan* $C_6H_{12}O_5$. S. 25 at 15°. When Berthelot's mannitan is allowed to stand for some months in a dry atmosphere it deposits a solid variety (Bouchardat). This crystallises in monoclinic tables. It is strongly lævorotatory. Sl. sol. cold alcohol. Boiling water quickly converts it into mannite. This variety of mannitan is probably identical with Vignon's.

Mannitan tetra-nitrate $C_6H_8O(ONO_2)_4$. Precipitated by adding water to the alcoholic mother-liquor from which mannite pentanitrate has separated (Tichanovitch, *J.* 1864, 583). Syrup, v. sol. alcohol and ether, insol. water. Explodes when struck. Alcoholic KOH converts it slowly into syrupy mannitan.

Di-acetyl derivative $C_6H_8O(OH)_2(OAc)_2$. $[\alpha] = +22·6$. From mannite and HOAc at 210° (Berthelot). Mannite dissolves in boiling Ac_2O, and on cooling crystals of $C_{12}H_{23}AcO_{10}$ separate. Further action of Ac_2O yields hexa-acetyl-mannite and di-acetyl-mannitan (Schützenberger, *A.* 160, 74; Grange, *C. R.* 68, 1326). Extremely bitter substance, v. sol. water, HOAc, and alcohol. Dextrorotatory. Boiling baryta-water converts it into acetic acid and mannitan.

Tetra-acetyl derivative $C_6H_8O(OAc)_4$. Formed, together with hexa-acetyl-mannite, by heating mannite with Ac_2O at 180° (Bouchardat, *A. Ch.* [5] 6, 110). Amorphous viscid mass, which partially crystallises on long standing.

Insol. water, v. e. sol. alcohol, ether, and HOAc. Dextrorotatory. Aqueous alkalis at 100° decompose it into acetic acid and mannitan. Ac_2O forms hexa-acetyl-mannite. A mixture of HNO_3 and H_2SO_4 has no action in the cold.

Di-butyryl derivative $C_6H_8O(OC_4H_7O)_2(OH)_2$. From mannite and butyric acid at 200° (Berthelot, *C. R.* 38, 673; *A. Ch.* [3] 47, 319). Semi-solid, partly crystalline, mass. Insol. water, v. sol. alcohol and ether.

Tetra-butyryl derivative $C_6H_8O(OC_4H_7O)_4$. From mannite and excess of butyric acid at 200°–250°. Oil.

Di-benzoyt derivative $C_6H_8O(OBz)_2(OH)_2$. From mannite and HOBz at 200° (Berthelot, *Chimie organique*, 2, 193). Soft resin; v. e. sol. alcohol and ether.

Di-ethyt derivative $C_6H_8O(OH)_2(OEt)_2$. From mannite, KOH, and EtBr at 100° (Berthelot). Syrup, v. sl. sol. water, sol. alcohol, v.e. sol. ether.

Mannitan chlorhydrin $C_6H_8O(OH)_3Cl$. From mannite dichlorhydrin by boiling for two hours with 100 pts. of water, neutralising with K_2CO_3, evaporating, and extracting with ether (Bouchardat, *A. Ch.* [5] 6, 118). Solid mass, v. e. sol. water, alcohol, and ether. Dextrorotatory. Conc. HClAq at 100° reconverts it into mannite dichlorhydrin. Boiling water converts it into HCl and mannitan.

Mannitan dichlorhydrin $C_6H_8O(OH)_2Cl_2$. From mannite (1 pt.) and fuming HClAq (15 pts.) by heating for 3 days at 100° (Berthelot, *J.* 1856, 661). Crystals, sol. ether. KOHAq converts it into mannitan.

Mannitan bromhydrin $C_6H_8O(OH)_3Br$. From mannite dibromhydrin by boiling with water. V. e. sol. water, alcohol, and ether. Dextrorotatory.

Mannide $C_6H_{10}O_4$. *Second anhydride of mannite.*

(*a*) *Berthelot's mannide* $C_6H_{10}O_4$. (297°–317°). Obtained by heating mannite with butyric acid at 200°–250° (Berthelot, *A. Ch.* [3] 47, 312; Liebermann, *B.* 17, 874). Thick deliquescent syrup, v. e. sol. cold water and alcohol. Decomposes partially on distillation. In contact with the air it partially forms mannite.

(*b*) (β)-*Mannide* $C_6H_{10}O_4$. [119°]. (212° at 16 mm.). S. 150 at 15°. S. (alcohol) 2·7 at -16°; 7·3 at 12°. Obtained by treating mannite dichlorhydrin with sodium-amalgam (Siwoloboff, *A.* 233, 368). Prisms; v. e. sol. water and alcohol, insol. ether. Dextrorotatory. Sublimes at 14°, forming long needles. Does not yield mannite when heated with water. Air and platinum-black oxidise it, forming a syrupy liquid.

(*c*) *Isomannide* $C_6H_{10}O_4$ *i.e.*

O O

CH$_2$(OH).CH.CH.CH.CH.CH$_2$.OH? [87°]. (176° at 30 mm.). (274° at 760 mm.) $[\alpha]_D$ +91·4 in a 6 p.c. aqueous solution. Obtained by distilling mannite *in vacuo*; the product being fractionally distilled *in vacuo* (Fauconnier, *C. R.* 95, 991). Prepared by boiling mannite (200 g.) with HClAq (2,000 g.) for 24 hours; cooling, filtering, and distilling *in vacuo*. The distillate is allowed to stand for a fortnight, extracted with cold alcohol, the extract distilled *in vacuo*, and the fraction boiling at 176° recrystallised from alcohol (Fauconnier, *Bl.* [2] 41, 119). Large monoclinic, somewhat deliquescent, crystals. Boils at 274° with partial decomposition. V. e. sol. water, m. sol. alcohol, sl. sol. chloroform, insol. ether and benzene. Dextrorotatory. Not affected by heating with water at 150°. By heating with fuming HClAq in sealed tubes at 100° for 25 days it is converted into mannite dichlorhydrin $C_6H_8(OH)_4Cl_2$ [174°]. It is not acted upon by $POCl_3$, by bromine in the cold, or by sodium-amalgam.

Di-formyl derivative $C_6H_8O_2(OCHO)_2$. [115°]. (166° at 18 mm.). Small plates, sl. sol. cold water, v. sol. alcohol, sol. ether.

Acetyl derivative $C_6H_8O_2(OH)(OAc)$. (186° at 25 mm.). From isomannide and Ac_2O. Colourless oil; sol. ether.

Di-acetyt derivative $C_6H_8O_2(OAc)_2$. (198° at 28 mm.). From isomannide (1 pt.) by boiling with Ac_2O (3 pts.) for 8 hours. Viscid liquid, with bitter taste. Not altered by further treatment with Ac_2O.

Di-benzoyl derivative $C_6H_8O_2(OBz)_2$. [132°]. From mannite, alcohol, $ZnCl_2$, HCl, and BzCl (Meunier, *C. R.* 107, 346). Monoclinic or triclinic crystals; v. sl. sol. water and cold alcohol, sol. chloroform and benzene. Not decomposed by aqueous acids or alkalis.

Methyt derivative $C_6H_8O_2(OH)(OMe)$. [48°]. (174° at 24 mm.) From isomannide, KOH, MeI, and a little water at 150°. Crystals.

Ethyt derivative $C_6H_8O_2(OH)(OEt)$. (165° at 17 mm.). Formed by heating mannite, EtI, and conc. KOHAq in sealed tubes for 4 hours at 120°. Colourless mobile liquid; sol. water, alcohol, and ether.

Isomannide dichlorhydrin $C_6H_8O_2Cl_2$. [49°]. (143° at 43 mm.). From isomannide (1 pt.) by warming with PCl_5 (2 pts.). White needles or plates; v. sol. ether, m. sol. alcohol, insol. cold, sol. hot, water. Has a strong aromatic odour and a peppery taste. May be distilled with steam. It is very stable, not being attacked by alcoholic KOH at 150°, by PCl_5 at 125°, or by sodium-amalgam.

Anhydride of mannide $C_{12}H_{18}O_7$ *i.e.* $(C_6H_8O_2.OH)_2O$ (?). Deposited on standing from a sample of butyric acid (Geuther, *A.* 221, 59). Gummy.

Lævo-mannite $C_6H_{14}O_6$. [164°]. Formed by reducing lævo-mannose with sodium-amalgam. Globular groups of fine needles; v. sol. water, sl. sol. absolute alcohol, much more sol. methyl-alcohol. It tastes sweet, and does not reduce Fehling's solution. A solution of this mannite containing borax turns the ray of polarised light to the left. This substance is probably the one obtained by Kiliani (*B.* 20, 2714) by reduction of the double lactone of metasaccharic acid (Emil Fischer, *B.* 23, 375).

Inactive mannite. α-*Acrite*. [168°]. Formed by reducing inactive mannose with sodium-amalgam. Small prisms (from water), v. sol. water, m. sol. hot glacial acetic acid, sl. sol. methyl and ethyl alcohols. It is easily distinguished from ordinary mannite by its crystalline form and by its optical inactivity. A solution containing borax remains wholly inactive. This mannite is identical with (α)-acrite, a substance obtained by the action of sodium-amalgam on

(α)-acrose, a sugar obtained by the action of alkalis on acroleïn dibromide (Fischer, *B.* 22, 100). By oxidation with dilute HNO_3 inactive mannose is formed (Emil Fischer, *B.* 23, 383).

The mannites may be distinguished optically by means of their phenyl-hydrazides. ·1 g. of the phenyl-hydrazide dissolved in 1 c.c. of cold conc. HClAq and 5 c.c. of water gives in a tube 100 mm. long a rotation of $+1·2°$, $-1·2°$, and 0°, with the lævo-, dextro-, and inactive mannite respectively. In the course of 3 or 4 hours the rotation vanishes, the phenyl-hydrazide being decomposed by the HCl. When the di-phenyl-dihydrazide is used 1 g. is dissolved in warm HOAc, cooled, and examined in a 100 mm. tube. It gives a rotation of $+0·85°$, $-0·85°$, or 0° in the case of the lævo-, dextro-, and inactive compounds respectively. The dextro- and lævo-mannites themselves scarcely exhibit a rotation, but ·15 g. of the mannite dissolved in 5 c.c. water containing ·37 g. borax exhibits a rotation of $+0·85°$, $-0·85°$, or 0°, according as the mannite is dextro-, lævo-, or inactive (Fischer).

MANNITIC ACID $C_6H_{12}O_7$. Prepared by mixing mannite (2 g.) with platinum-black (4 g.), moistened with water, and exposing the mixture at 30° to 40° to the air for 3 weeks. The mass is then exhausted with water, the solution ppd. by lead subacetate, the pp. decomposed by H_2S, and the solution evaporated in the cold over H_2SO_4 (Gorup-Besanez, *A.* 118, 257). Gummy mass; sol. water and alcohol, nearly insol. ether. It is a strong acid, and dissolves zinc with evolution of hydrogen. It begins to decompose at 80°. It reduces silver nitrate solution and hot Fehling's solution. It is ppd. by baryta and by lime-water.—CaA″: amorphous powder, ppd. by adding alcohol to its aqueous solution.—CuA″: green amorphous mass left by evaporating its solution.—PbA″: granular.—Ag_2A'': curdy pp.

MANNITINE $C_6H_8N_2$. (170°). Prepared by distilling a mixture of mannite (1 mol.) and ammonium chloride (2 mols.). The distillate is mixed with KOHAq and shaken with ether (Scichilone a. Denaro, *G.* 12, 416; Étard, *C. R.* 92, 795). Brown oil, with strong odour; sol. alcohol and ether, m. sol. water. Gives an orange-yellow pp. with sodium phosphomolybdate, a reddish-yellow pp. with iodine in KIAq, a pink pp. with $HgCl_2$, and a black pp. with auric chloride. Hypodermically injected it produces diminution of the cardiac systole, and irregular respiration, followed by insensibility and death.

MANNITOSE $C_6H_{12}O_6$. Produced, together with mannitic acid, by the atmospheric oxidation of mannite in the presence of platinum-black (Gorup-Besanez, *A.* 118, 273). Optically inactive. Fermentable. Reacts like glucose with alkalis, Fehling's solution, basic bismuth nitrate, and Na_2CO_3; but it does not unite with NaCl. Its alcoholic solution gives with alcoholic potash a pp. of $(C_6H_{12}O_6)_2K_2O$. Mannitose is perhaps identical with lævulose (Dafert, *B.* 17, 228; 19, 911).

MANNONIC ACIDS $C_6H_{12}O_7$.

Inactive mannonic acid. *Lactone* $C_6H_{10}O_6$. [155°]. Formed from inactive mannose by oxidation with bromine (E. Fischer, *B.* 23, 376). Long glittering prisms, grouped in stars or needles (from alcohol); v. sol. hot water, sl. sol. hot alcohol. Has a sweet taste and does not reduce Fehling's solution. By means of the strychnine salt it can be split up into dextro-mannonic acid and arabinose-carboxylic acid, the strychnine salt of the latter being extremely sl. sol. alcohol. The morphine salts may also be employed, morphine dextro-mannonate crystallising out. *Penicillium glaucum* partly decomposes inactive mannonic acid, liberating some arabinose-carboxylic acid—$Ca(C_6H_{11}O_7)_2$. Groups of slender needles. Less soluble than calcium lævo-mannonate.

Phenyl hydrazide $C_{12}H_{18}N_2O_6$. [230°]. Colourless cubes, sl. sol. hot water, v. sl. sol. alcohol. Split up by hot baryta-water into phenyl-hydrazine and inactive mannonic acid.

Dextro-mannonic acid. Formed from gluconic acid by heating with twice its weight of quinoline for 40 minutes to 140° (Emil Fischer, *B.* 23, 801). Formed also as above and by oxidation of dextro-mannose by bromine. By heating dextro-mannonic acid with quinoline, gluconic acid is formed. For this purpose 20 g. of dextro-mannonic acid, 5 g. water, and 40 g. quinoline are heated to 140° for 40 minutes. The unchanged mannonic acid is separated by means of its brucine salt. Dextro-mannonic acid, like the other mannonic acids, when liberated from its salts condenses at once to the lactone $C_6H_{10}O_6$ [149°–153°]. Its rotation, $[\alpha]_D = 53·8$, is equal and opposite to that of the lactone of arabinose-carboxylic acid, which is therefore lævo-mannonic acid.

Salts.—$Ca(C_6H_{11}O_7)_2 2aq$.—$SrA'_2 3aq$.—BaA'_2 (dried at 100°).

Phenyl hydrazide $C_{12}H_{18}N_2O_6$. [216°]. Small colourless prisms, v. sol. hot water. Decomposed by hot baryta-water into dextro-mannonic acid and phenyl-hydrazine.

Lævo-mannonic acid. *Lactone* $C_6H_{10}O_6$. *Arabinose carboxylic acid.* [145°–150°]. $[\alpha]_D = -54·8$. Formed from arabinose (*v.* ARABIC ACID and SUGARS) by treatment with HCy and saponification of the product (Kiliani, *B.* 19, 3033). Formed also from inactive mannonic acid, as above.

MANNOSE $C_6H_{12}O_6$ *i.e.*
CHO.CH(OH).CH(OH).CH(OH).CH(OH).CH_2(OH).
Dextro-mannose. $[\alpha]_D = +13°$. Formed by heating 3 kilos of mannite with 20 litres of water and 10 litres of HNO_3 (S.G. 1·41) in the water-bath with shaking to 40°–45° until a test portion rendered neutral with soda gives a thick pale-yellow pp. of the hydrazide with phenyl-hydrazine acetate. The whole is then cooled with ice to about 25°, made feebly alkaline with crystallised Na_2CO_3, acidified with acetic acid, and treated with 1 kilo of phenylhydrazine dissolved in dilute acetic acid. The phenyl-hydrazide crystallised from hot water is converted into the sugar by solution in HCl (S.G. 1·19), allowing to stand, cooling, filtering, and neutralising the diluted filtrate with pure carbonate of lead. The whole is again filtered, made alkaline with $Ba(OH)_2$, and shaken with ether. The aqueous solution separated from ether contains the sugar, which remains as a syrup on evaporating, and is ppd. from absolute alcohol by ether (Emil Fischer a. Josef Hirschberger, *B.* 21, 1806; 22, 365). Mannose may

more easily be got from vegetable ivory nuts, *v.* SEMINOSE *infra.*

Properties.—Light-yellow syrup, with sweet taste. V. sol. water and alcohol. Reduces Fehling's solution; 1 c.c. corresponding to ·004307g. of mannose. Turned brown by heating with 20 p.c. HClAq; the solution then containing lævulic acid. Ferments easily with yeast, giving CO_2 and alcohol. The aqueous solution is dextrorotatory, but less so than glucose. Sodium-amalgam (2 p.c.) reduces mannose to mannite. Furfuraldehyde is formed by heating a dilute solution of mannose at 110° for four hours. AcCl forms a substance like acetochlorhydrose.

Phenyl hydrazide $C_{12}H_{18}N_2O_5$. [195°–200°]. S. 1 at 100°. Prepared as above. Slender prisms (from water). Sl. sol. alcohol and acetone. Its solution in dilute HClAq is lævorotatory. Concentrated mineral acids convert it into mannite and phenyl-hydrazine even in the cold. When it is heated with phenyl-hydrazine hydrochloride (3 pts.), NaOAc (4 pts.) and water (80 pts.) at 105° for 4 hours there is formed the 'osazone' of glucose $C_{18}H_{22}N_4O_4$, which crystallises from alcohol in slender yellow needles [206°].

Oxim $C_6H_{13}O_6N$. Crystalline; v. sol. hot water, insol. alcohol. When slowly heated it melts at 176°–180°; but when quickly heated, at 184° (Fischer a. Hirschberger, *B.* 22, 1155).

Inactive mannose. Formed by reducing the lactone of inactive mannonic acid with sodium-amalgam (E. Fischer, *B.* 23, 381). Colourless syrup; v. sol. water, sl. sol. absolute alcohol, m. sol. hot methyl alcohol. Resembles (dextro-) mannose except in being inactive. When subjected to fermentation lævo-mannose is left. Bromine oxidises it to inactive mannonic acid.

Phenyl hydrazide. [195°]. Decomposed on fusion. Sl. sol. water. Its solution in HCl is optically inactive. Cold conc. HCl splits it up into sugar and phenyl-hydrazine.

Di-phenyl hydrazide $C_{18}H_{22}N_4O_4$. [218°]. Formed by heating the inactive mannose with phenyl-hydrazine (2 mols.), the corresponding quantity of acetic acid and water. Fine yellow glittering needles; sl. sol. water, cold alcohol, and ether. Decomposes on fusion. At 45° conc. HCl forms the corresponding osone. The solution in 60 pts. glacial acetic acid is optically inactive. The properties of this di-phenyl-hydrazide are the same as those of (α)-acrosazone (the di-phenyl-hydrazide of (α)-acrose), and Emil Fischer (*B.* 23, 383) considers that they are identical.

Lævo-mannose. To prepare this body 1 pt. of the lactone of arabinose carboxylic acid is dissolved in 10 pts. water, acidified with H_2SO_4, and cooled to 0°. $2\frac{1}{2}$ p.c. sodium-amalgam is added in small portions. The liquid must remain acid. Colourless syrup; v. sol. water, sl. sol. absolute alcohol, m. sol. methyl-alcohol. The aqueous solution is slightly lævorotatory. It ferments little, if at all, with yeast.

Phenyl hydrazide $C_{12}H_{18}N_2O_5$. [195°]. Formed by adding phenyl-hydrazine acetate to a solution of the sugar. Slender, almost colourless crystals. It is more sol. water than the dextro-mannose phenyl-hydrazide. The hydrochloric acid solution is dextrorotatory. Cold HCl splits up the compound into phenyl-hydrazine and mannose.

Di-phenyl hydrazide. [205°]. Formed by heating the lævo-mannose phenyl-hydrazide with phenyl-hydrazine acetate and 30 pts. water to 100°. Fine yellow needles (from water). Decomposed on fusion. It is extremely like the di-phenyl-hydrazide of dextro-mannose, lævulose, and dextrose. It, however, turns the ray of polarised light strongly to the right (Emil Fischer, *B.* 23, 373).

Isomannitose, a sugar obtained, together with glucose, by boiling salep with acids, is probably identical with mannose (Tollens, *B.* 21, 2150). Its phenyl hydrazide $C_{12}H_{18}N_2O_5$ [188°] is sl. sol. alcohol.

Seminose, obtained by digesting with dilute H_2SO_4 the cellulose composing the thick-walled cells of the endosperm of vegetable ivory nuts, is identical with mannose (Reiss, *B.* 22, 609; Schultz, *B.* 22, 1192; Fischer a. Hirschberger, *B.* 22, 3218).

'Mannose carboxylic acid' $C_7H_{14}O_8$ *i.e.* $C_6H_{13}(CO_2H)O_6$. From mannose (50 g.) by dissolving in water (250 g.) and adding anhydrous HCy (18 c.c.) and a few drops of ammonia. After three days the mixture is heated to 50° for 4 hours. The product appears to contain the ammonium salt of the acid and its amorphous amide [183°], which may be ppd. by alcohol (Fischer a. Hirschberger, *B.* 22, 365). The acid changes to anhydride when set free from its salts. In preparing the lactone (*v. infra*) an acid [c. 169°], probably the free mannose carboxylic acid, is sometimes formed.

Salts.—BaA'_2. Obtained by boiling the ammonium salt with baryta. Colourless, semi-crystalline mass, m. sol. hot, v. sl. sol. cold, water, insol. alcohol. Boiling conc. HIAq reduces it slowly to *n*-heptoic acid.

Lactone $C_7H_{12}O_7$. [150°]. Obtained by decomposing a hot solution of the Ba salt with the theoretical quantity of H_2SO_4. Needles, v. sol. water, m. sol. alcohol, insol. ether.

Phenyl hydrazide $C_7H_{13}O_7N_2H_2Ph$. [220°–223°]. Formed by boiling the Ba salt with aqueous NaOH, and adding HOAc and phenyl hydrazine acetate (Fischer a. Passmore, *B.* 23, 2732). Very small prisms; sol. hot water. Decomposed on fusion.

MANTLE-MUCIN *v.* PROTEÏDS, *Appendix C.*

MARGARIC ACID $C_{17}H_{34}O_2$. (*Heptadecoic acid*). Mol. w. 270. [60°]. The name margaric acid was originally applied to an acid $C_{17}H_{34}O_2$ supposed to occur in the product of the saponification of solid natural fats; but this acid was shown by Heintz to be a mixture of palmitic acid $C_{16}H_{32}O_2$ and stearic acid $C_{18}H_{36}O_2$. An acid $C_{17}H_{34}O_2$ occurs, however, according to Ebert (*B.* 8, 775), in adipocere, a substance formed in dead tissues of animals. Formed by boiling its nitrile (cetyl cyanide) with alcoholic potash (Heintz, *P.* 102, 272). White crystals.—BaA'_2: white amorphous powder.—AgA': white amorphous powder.

Nitrile $C_{16}H_{33}CN$. [53°] (?) (Köhler, *J.* 1856, 579; *cf.* Becker, *A.* 102, 213). According to Heintz (*J.* 1857, 445), margaronitrile prepared from potassium cetyl sulphate and KCy is an oil.

Margaric acid $C_{16}H_{33}.CO_2H$. [60° uncor.]. (277° at 100 mm.). Prepared by the oxidation

of methyl-heptadecyl-ketone (Krafft, *B.* 12, 1672). Probably identical with the preceding acid.

MARJORAM OIL. S.G. $\frac{15}{}$ ·911 (Bruylants). The essential oil obtained by steam-distillation from the flowers of sweet marjoram (*Majorana hortensis* or *Origanum majorana*). Yellow oil which becomes brown on standing. It has a pungent smell, a hot peppery taste, and an acid reaction. According to Bruylants (*J. Ph.* [4] 30, 33; *cf.* Mulder, *A.* 31, 69) it begins to boil at 185° and the thermometer remains stationary at 215°–220°. Bruylants found it to consist of 5 p.c. of a dextrorotatory terpene, 85 p.c. of a mixture of dextrorotatory camphor and borneol, and 10 p.c. of resin. According to Kane (*A.* 32, 285) the essential oil of wild marjoram (*Origanum vulgare*) contains a terpene which boils at 161° and has S.G. ·867. According to Beilstein a. Wiegand (*B.* 15, 2855) oil of sweet marjoram contains a terpene $C_{10}H_{16}$ (178° i. V.). S.G. $\frac{18\cdot5}{}$ ·846, which absorbs HCl, forming liquid $C_{10}H_{16}HCl$. By distilling the oil of marjoram over sodium Beilstein a. Wiegand obtained liquid $C_{15}H_{26}O$ (200°–220°).

Cretan oil of marjoram from *Origanum hirtum* has S.G. $\frac{15}{}$ ·951, and 100 mm. produce a rotation of −0·4°. It contains 50 p.c. of carvacrol [2°] and dissolves in half its volume of 15 p.c. soda solution (Jahns, *Ar. Ph.* [3] 15, 1; 16, 277). The oil also contains a mixture of terpenes, and a phenol that is coloured violet by $FeCl_3$. Jahns found a little carvacrol in the oil from *Origanum vulgare.*

MARRUBIIN. [160°]. The bitter principle of white horehound (*Marrubium vulgare*) (Kromayer, *Ar. Ph.* [2] 108, 257; Harms, *J.* 1863, 593). Prepared by exhausting the dried herb with hot water, evaporating, and extracting with alcohol. Large tables (from ether) or needles (from alcohol). Almost insol. cold, sl. sol. hot, water. Not affected by alkalis. Metallic salts do not ppt. it. Not ppd. by tannin. Hot conc. HClAq does not affect it. Conc. H_2SO_4 gives a brownish-yellow solution. Cold HNO_3 has no action; hot HNO_3 forms a yellow solution.

MARSH GAS *v.* METHANE.

MARTYLAMINE *v.* *p*-AMIDO-DIPHENYL.

MASOPIN $C_{22}H_{36}O$. [155°]. Occurs in a resin used in Mexico for chewing; said to be the dried juice of a tree called Dschlite. The resin occurs in porous lumps, smelling like rotten cheese, but with little taste. The masopin is obtained by boiling the resin with water, and crystallising the residue from alcohol (Genth, *A.* 46, 124). White silky needles (from ether). After fusion, it melts a second time at 70°. On distillation it yields a terpene and a crystalline acid, of which the Ag salt contains 45·5 p.c. of silver.

MASTIC. A resin obtained by incisions in the bark of *Pistacia lentiscus*, a tree growing in Chios. Small round transparent grains with faint agreeable odour. Used for making varnishes and, from the earliest times, for chewing. Softens when masticated. S.G. 1·074. Aqueous alcohol dissolves the greater part $C_{10}H_{32}O_4$, leaving m a s t i c i n $C_{10}H_{0}O_2$ undissolved (Johnston, *P. T.* 1839, 132). Flückiger (*Ar. Ph.* 219, 170) found 2 p.c. of a dextrorotatory terpene in mastic.

MATEZITE $C_{10}H_{20}O_9$. [187°]. $[\alpha]_D = 64·7$. Occurs in Madagascar caoutchouc (mateza roritina) (Girard, *Bl.* [2] 21, 220; *C. R.* 110, 84). Identical with (*β*)-Pinite (Combes, *C. R.* 110, 46). Crystalline nodules, v. e. sol. water, m. sol. alcohol. Sublimes above 200°. Resembles dambonite but is dextrorotatory. Fuming HIAq splits it up on heating into MeI and m a t e z o - d a m b o s e $C_9H_{18}O_9$ [246°] $[\alpha]_D = 67·6$, which is dextrorotatory and more soluble in water than dambose. Matezodambose is identical with the (*β*)-inosite of Maquenne (*C. R.* 109, 812). It forms small tetrahedra when ppd. by adding alcohol to its aqueous solution.

MATICIN. A bitter substance which remains dissolved in the water in the retort in the preparation of the essential oil of matico by distilling the leaves of *Piper asperifolium* with steam. It is sol. water and alcohol, and insol. ether (Hodges, *P. M.* [3] 25, 204; *C. S. Mem.* 1, 123). Its solution is not ppd. by lead acetate.

MATICO-CAMPHOR $C_{12}H_{20}O$. [94°]. Occurs in the essential oil of matico-leaves (*Piper angustifolium*), from which it is obtained by distilling off the greater part and allowing the residue to crystallise (Kügler, *B.* 16, 2841). Hexagonal crystals. V. sol. alcohol, ether, benzene, petroleum-ether, &c. With HCl it gives a violet colour, passing into blue, and finally becoming green. H_2SO_4 colours it yellow, then red, and lastly violet. A mixture of H_2SO_4 and HNO_3 first produces a yellow, which then becomes violet, and finally a splendid blue.

MAUVANILINE $C_{19}H_{17}N_3$. A by-product in the preparation of rosaniline by the oxidation of crude aniline (De Laire, Girard a. Chapoteaut, *C. R.* 64, 416; *Bl.* [2] 7, 366); *cf.* Girard a. Pabst, *Bl.* [2] 34, 37). Light-brown crystals (containing $\frac{1}{2}$ aq, which is given off at 130° with decomposition). Insol. cold, v. sl. sol. hot, water, sol. alcohol, ether, and benzene. Its salts form lustrous bronze-green crystals, v. sl. sol. cold water, and dye silk and wool mallow-red. Tri-ethyl-mauvaniline $C_{19}H_{14}Et_3N_3$ dyes bluish-violet, while tri-phenyl-mauvaniline $C_{19}H_{14}Ph_3N_3$ is a blue dye.

MAUVEÏNE $C_{27}H_{24}N_4$. The first aniline dye introduced (Perkin, 1856). Obtained by adding a cold dilute solution of a salt of crude aniline to a cold dilute solution of $K_2Cr_2O_7$ and leaving the mixture to stand for 12 hours. The resulting black pp. is dried, extracted with benzene, dissolved in alcohol, and the filtrate evaporated. When aniline sulphate is used the product is $(C_{27}H_{25}N_4)_2SO_4$; aniline hydrochloride yields $C_{27}H_{25}N_4Cl$ (Perkin, *A.* 131, 200; *C. J.* 35, 717). On adding aqueous KOH to a solution of a salt of mauveïne the base separates as a violet-black crystalline substance. It dissolves in alcohol, forming a violet solution, which on addition of acids turns purple. Mauveïne is insol. benzene and ether. With dilute acids it forms purple solutions; with stronger acids, blue. Conc. H_2SO_4 forms a dirty-green solution. Dyes silk mauve. Used for postage stamps. Oxidised by PbO_2 and boiling HOAc it gives para-safranine $C_{20}H_{18}N_4$.

S a l t s.—B′HCl: tufts of small prisms with green metallic lustre. Insol. cold, sl. sol. hot, water, m. sol. alcohol, nearly insol. ether.—B′H_2Cl_2: blue, with coppery lustre. Unstable. Becomes B′HCl when dissolved in alcohol.—

$B'_2H_2PtCl_4$: green crystalline powder, v. sl. sol. alcohol.—$B'H_2PtCl_6$: blue.—$B'HAuCl_4$.—B'HBr.—B'HI: lustrous prisms.—$B'_2H_2SO_4$.—$B'H_2CO_3$: prisms, with green metallic lustre. On boiling its solution CO_2 is given off.

Ethyl-mauveïne $C_{27}H_{23}EtN_4$. Formed by heating mauveïne with EtI at 100°. Its colour is redder than that of mauveïne. During the manufacture crystals of $C_{27}H_{23}EtN_4HI_3$ sometimes appear.—$C_{27}H_{23}EtN_4$.HCl. Forms a reddish-purple solution in alcohol. — $(C_{27}H_{23}EtN_4HCl)_2PtCl_4$. Golden-green lustre.

Pseudo-mauveïne $C_{24}H_{20}N_4$ (Perkin, *C. J.* 35, 725). Present in commercial mauveïne. It is more soluble in alcohol than mauveïne. It is a strong base, and dyes silk almost exactly like mauveïne. Pure aniline gives pseudo-mauveïne on oxidation, hence it does not contain methyl. Mauveïne is probably derived from aniline and *p*-toluidine. The violet colouration given by bleaching-powder to a dilute solution of aniline is probably due to pseudo-mauveïne.—$C_{24}H_{20}N_4$HCl. Greenish-golden lustre.—$(B'HCl)_2PtCl_4$.

MAYER'S REAGENT *v.* Alkaloids, *Reaction* 3.

MAYNAS RESIN. *Calaba* or *Galba* of the Antilles (Lewy, *A. Ch.* [3] 10, 380). A resin extracted by incision from *Calophyllum calaba.* Alcohol extracts from it $C_{14}H_{18}O_4$, which separates on cooling in yellow monoclinic prisms. Maynas resin is insol. water, but v. sol. KOHAq and ammonia. It melts about 105°.

MECCA BALSAM. *Balm of Gilead.* The produce of *Balsamodendron gileadense*, a shrub growing in Arabia Felix. There appear to be several varieties of it. It contains a fragrant volatile oil, an acid resin sol. alcohol, and a resin, insoluble in alcohol (Bonastre, *A.* 3, 147; *cf.* Trommsdorff (*Trommsd. Neues Journal*, 16, 62).

MECONIC ACID $C_7H_4O_7$ 3aq, *i.e.* $C_5HO_2(OH)(CO_2H)_2$. Mol. w. 200. S. 25 at 100°. *Heat of neutralisation* (4 mols. NaOH) 37,382 (Gal a. Werner, *Bl.* [2] 47, 162). *Electrical conductivity*: Ostwald (*J. pr.* [2] 32, 368).

Occurrence.—In opium (Sertürner, *Am. S.* 55, 72; 57, 183; 64, 65; Robiquet, *A. Ch.* 5, 282; 51, 236; 53, 425; Liebig, *A.* 7, 37; 26, 113, 147).

Preparation.—Opium is exhausted with water at 38°; the extract is neutralised with $CaCO_3$, evaporated to a syrup, and mixed with a concentrated solution of $CaCl_2$, which ppts. calcium meconate. The pp. (1 pt.) is suspended in conc. HClAq (3 pts.) mixed with boiling water (20 pts.), and kept near 100° till dissolved. On cooling, acid calcium meconate separates in crystals. These (1 pt.) are again dissolved in a mixture of HClAq (3 pts.) and boiling water (20 pts.), and, on cooling, meconic acid separates (Gregory, *A.* 24, 43). It may be further purified by crystallising its ammonium salt from water (How, *A.* 83, 350).

Properties.—Micaceous scales or small trimetric prisms (containing 3aq) (Burghardt, *C. J.* 27, 937). It gives off its water of crystallisation at 100°, then becoming a white opaque mass. Has a sour taste and strongly reddens litmus. Sl. sol. cold water, v. sol. alcohol, sl. sol. ether. $FeCl_3$ colours its solutions blood-red. This colouration, like that with sulphocyanides, is much weakened by oxalic acid and by metaphosphoric acid (Dupré, *C. N.* 32, 15), but it is not destroyed by boiling or by dilute HClAq. Meconic acid may be regarded as a derivative of the hypothetical $CH{<}{\scriptstyle CH:CH \atop CH.CH_2}{>}O$.

Reactions.—1. *Heated* at 120° it gives off CO_2, and comenic acid $C_5H_2O_2(OH)(CO_2H)$ remains. At a higher temperature the comenic acid is further resolved, partly into CO_2 and pyromeconic acid $C_5H_3O_2(OH)$, and partly into water, acetic acid, and oily and carbonaceous products. 2. When boiled with *water* or with HClAq it gives CO_2 and comenic acid.—3. *Nitric acid* oxidises it, forming oxalic acid.—4. Boiling conc. KOHAq also yields oxalic acid.—5. Boiling aqueous *ammonia* forms comenamic acid $C_5H_3NO(OH)CO_2H$. Comenamic acid yields pyridine on dry distillation with zinc-dust (Lieben a. Haitinger, *B.* 16, 1263). The comenamic acid is di-oxy-picolinic acid, and comenic acid is probably an intermediate product in its formation.—6. *Bromine*, acting on its aqueous solution, forms a brominated comenic acid.—7. Aqueous HI gives comenic acid.—8. *Sodium-amalgam* reduces it to hydro-meconic acid.—9. Gives with alcohol and HCl a di-ethyl ether, $C_5HO_2(OH)(CO_2Et)_2$, whence a silver compound, $C_5HO_2(OAg)(CO_2Et)_2$, which gives with EtI a tri-ethyl derivative $C_5HO_2(OEt)(CO_2Et)_2$. [61°]. This gives no colour with $FeCl_3$ (Ost a. Mennel, *J. pr.* [2] 23, 439).—10. PCl_5 converts it into a liquid chloride, probably $C_5HCl_5(COCl)_2$, whence ice-water forms 'chloro-mecenic' acid, $C_5ClO(OH)(CO_2H)_2$ aq [165°], whereas warm water forms only oxalic acid (Hilsebein, *J. pr.* [2] 32, 136). Chloro-mecenic acid gives a green colour, with solution of ferric chloride. It forms an ether, $C_5ClO(OH)(CO_2H)(CO_2Et)$, [148°], which gives an acetyl derivative $C_5ClO(OAc)(CO_2H)(CO_2Et)$, [70°]. It also forms barium salts. Chloro-mecenic acid is decomposed by sublimation into carbonic acid and yellowish needles of *pyro-chloro-mecenic acid*, $C_5H_2ClO(OH)$, aq [174°]. The solution of this acid is turned dark-green by $FeCl_3$. Its alcoholic solution turns the skin red. It forms a crystalline calcium salt, $(C_5H_2ClO_2)_2Ca$. Chloro-mecenic acid dissolves in conc. NH_3, the solution turning successively red, violet, and blue, owing to the formation of two nitrogenous colouring matters, 'mecenic blue' and 'mecenic red.' Chloro-mecenic acid is reduced by treatment with sodium amalgam, forming *di-hydro-chloro-mecenic acid* $C_5H_2ClO(OH)(CO_2H)_2$, [145°]. Fuming HI at 100° reduces chloro-mecenic acid to an *oxy-pentane di-carboxylic acid*, $C_5H_{10}O(CO_2H)_2$. This body forms groups of needles [149°]. Its silver salt, Ag_2A'', is a crystalline powder, insol. water. Its barium salt, BaA'', forms white prisms. Its ether, Et_2A'', is an oil, boiling about (250°). Oxy-pentane di-carboxylic acid, when distilled with lime, yields amyl alcohol, (c. 130°) (Hilsebein, *J. pr.* [2] 32, 129-153).

Salts.—$(NH_4)H_2A'''$ aq: granular crystals, sl. sol. water.—$(NH_4)_2HA'''$ *x*aq: slender needles.—A barium salt is ppd. by adding $BaCl_2$ to a solution of an alkaline meconate, in white flakes, soluble in acetic acid.—$CaH_4A'''_2$ 2aq: ppd. by adding $CaCl_2$ to aqueous meconic acid.—CaHA''' aq: yellow gelatinous pp., formed by

adding $CaCl_2$ to a solution of ammonium meconate.—The cupric salts are green pps.—$Pb_3A'''_2$ 2aq: white flocks, ppd. by adding lead acetate to a solution of meconic acid (Stenhouse, *A.* 51, 231).—A sparingly soluble ferric salt may be obtained by the action of ferric sulphate on ammonium meconate (Stenhouse).—$Fe_2Ca_3A'''_4$ 5aq (Rennie, *C. N.* 42, 75).—Ag_2HA''': white pp. got by adding $AgNO_3$ to a solution of meconic acid.—Ag_3A''': yellow pp. from ammonium meconate and $AgNO_3$.—Aniline salt: $(C_6H_5NH_2)_2C_7H_4O_7$: crystalline (Korff, *A.* 138, 195).—Urea salt: $(CON_2H_4)_3C_7H_4O_7$ (Hlasiwetz, *J.* 1856, 699).—Narceïne salt [126°]: from narceïne (1 mol.) and meconic acid (1 mol.). Lemon-yellow crystals, sol. hot water (Merck, *C. C.* 1889, 384).—The acid morphine salt could not be obtained by Dott (*Ph.* [3] 17, 690). It will be observed that meconic acid has but little tendency to form tribasic salts, so that it might perhaps be more correctly regarded as a dibasic acid (*cf.* Dittmar a. Dewar, *Pr. E.* 1867; Dott, *Ph.* [3] 11, 576).

Ethyl derivative $C_5HO_2(CO_2H)_2(OEt)$. [200°]. Formed by boiling $C_5HO_2(CO_2Et)_2(OEt)$ for forty-eight hours with water, and evaporating the solution. Small prisms grouped in lumps. Decomposed by fusion. Gives no colour with $FeCl_3$. Gives, with most metallic salts, no pp. Lead acetate is an exception. Heated alone till it melts, CO_2 is given off, and the ethyl derivative of comenic acid formed. Its aqueous solution is converted by bromine into a brominated derivative of comenic ether.—PbA″ $1\frac{1}{2}$aq. Crystalline pp.

Mono-ethyl ether $C_5HO_2(CO_2Et)(CO_2H)(OH)$. [179°]. Prepared by dissolving meconic acid in alcohol, heating to 100°, and subjecting to a current of HCl till crystals begin to appear. The liquid on cooling deposits crystals of the mono-ethylic ether (E. Mennel, *J. pr.* [2] 26, 450). It gives a red colour with $FeCl_3$.—Silver salt $C_5HO_2(CO_2Et)(CO_2Ag)(OH)_2$aq.—Barium salts $BaC_9H_6O_7$ and $Ba(C_9H_7O_7)_2$.

Di-ethyl ether $C_5HO_2(CO_2Et)_2(OH)$. [112°]. Prepared by passing HCl into an alcoholic solution at 100° until the crystals (of mono-ethylic ether) which are first formed are dissolved up again. On pouring into water, plates of the di-ethylic ether separate (How, *A.* 83, 350; Mennel, *J. pr.* [2] 26, 453). Plates. From dilute solutions it crystallises with $\frac{1}{2}$aq as needles. Gives a red colour with $FeCl_3$. An amorphous pp. is formed by adding $AgNO_3$ and then *exactly* neutralising with NH_3.—$NH_4C_{11}H_{11}O_7$: needles (from alcohol), v. sol. water. Its solution is ppd. by various metallic salts.

Ethyl derivative of the diethyl ether $C_5HO_2(CO_2Et)_2(OEt)$. [61°]. From $C_5HO_2(CO_2Et)_2(OAg)$ and EtI. Gives no red colour with $FeCl_3$. Boiled with water it changes to the ethyl derivative of meconic acid (*q. v.*). Not acted upon by bromine.

Mono-amide $C_5HO_2(CONH_2)(CO_2H)(OH)$ aq. *Meconamic acid.* From the above by the action of aqueous NH_3 followed by HCl. Crystallises in hard lumps from water. Not decomposed by cold NaOH, converted by boiling NaOH into meconate. *Copper salt* $C_7H_3O_6Cu$ 2aq.

Basic ammonium salt of amide $C_5HO_2(CONH_2)(CO_2NH_4)(ONH_4)$. This yellow pp. is the first product of the action of NH_3 upon mono-ethylic meconate.

Di-amide $C_5HO_2(OH)(CONH_2)_2$. From the diethyl ether and boiling aqueous NH_3 (How). Powder, sl. sol. cold water.

Oxim $C_7H_4O_7NH$. Formed by treating meconic acid with hydroxylamine hydrochloride (Odernheimer, *B.* 17, 2081). Small colourless needles (containing H_2O). V. sol. water, sl. sol. alcohol, ether, and chloroform, insol. ligroïne. Decomposes suddenly at 190°. It gives a red colour with Fe_2Cl_6. It reduces Fehling's solution. By boiling with HCl hydroxylamine is split off.—A″Na_2: colourless crystals.—A″Ag_2 aq: white sparingly soluble pp.—A″Ba 10aq: sparingly soluble concentric needles.—A″Ca 2aq: sparingly soluble needles.

Hexahydride $C_7H_{10}O_7$. *Hydromeconic acid.* Obtained by reducing meconic acid suspended in water by adding sodium-amalgam (Korff, *A.* 138, 191). Separated by decomposing the lead salt by H_2S and evaporating the filtrate. Strongly acid syrup, v. sol. water, m. sol. alcohol, insol. ether. Ppd. as deliquescent flocks on adding ether to its alcoholic solution. Not affected by HI. Gives no colour with $FeCl_3$.—BaA″ 2aq: amorphous pp.; sol. water, insol. alcohol. — PbA″ $1\frac{1}{2}$aq: amorphous pp. — Ag_2A″ $\frac{1}{2}$aq: white granular pp.

Reference.—PYROMECONIC ACID and PYROMECAZONIC ACID.

MECONIDINE $C_{21}H_{23}NO_4$. [58°]. An alkaloid contained in the aqueous extract of opium (Hesse, *A.* 153, 47). The aqueous extract is ppd. by Na_2CO_3; the pp. dissolved in ether, the ethereal solution shaken with dilute acetic acid, and the acid solution poured into aqueous NaOH. After 24 hours the pp. of thebaïn and papaverine is removed by filtration, the filtrate neutralised by HCl, rendered alkaline by NH_3, and shaken with chloroform. The chloroform is then shaken with acetic acid; and the acid solution exactly neutralised by ammonia, which ppts. lanthopine. The filtrate is mixed with KOH and shaken with ether. Codanine and laudanine separate, and the mother-liquor is then shaken with dilute acetic acid, the solution saturated with NaCl, the ppd. meconidine hydrochloride decomposed by $NaHCO_3$ and the base extracted with ether and dried at 90°.

Properties. — Brownish-yellow transparent amorphous mass. Cannot be sublimed. Tasteless. Insol. water, v. sol. alcohol, ether, benzene, chloroform, and acetone. Its alcoholic solution turns red litmus blue. Sl. sol. NH_3Aq, v. sol. NaOHAq. Can be extracted by ether from its solution in ammonia but not from that in caustic soda. Its solution in dilute H_2SO_4 becomes rose-coloured in a few minutes, and purple-red on standing for some time, or immediately on boiling. Conc. H_2SO_4 gives an olive-green solution. Conc. HNO_3 colours it orange-red. The dilute solutions of the salts have an intensely bitter taste.—$B'_2H_2PtCl_6$: yellow amorphous pp. which soon turns reddish. The aurochloride is a dingy yellow amorphous pp.

MECONIN $C_{10}H_{10}O_4$, *i.e.* $C_6H_2(OMe)_2\langle{}^{CH_2}_{CO}\rangle O$. [1:6:3]? *Anhydride* of

Meconinic acid. Opianyl. Mol. w. 194. [99°] (M. a. F.); [102·5°] (Wegscheider, *M.* 3, 351; Prinz, *J. pr.* [2] 24, 371). S. ·4 in the cold; 5 at 100°. A neutral substance existing in opium (Dublanc, *A. Ch.* [2] 49, 17; Couerbe, *A. Ch.* 49, 11; 50, 337; 59, 148). It may also be extracted by ether from the root of *Hydrastis canadensis* (Freund, *B.* 22, 459).

Formation.—1. Together with cotarnine, opianic acid, and hemipic acid, by the action of warm dilute nitric acid on narcotine (Anderson, *Tr. E.* 20, 347; 21, 204).—2. From opianic acid by the action of sodium-amalgam, or of zinc and H_2SO_4 (Matthiessen a. Foster, *C. J.* 16, 349).—3. Together with hemipic acid by the action of caustic alkalis on opianic acid (M. a. F.).

Preparation.—1. A concentrated aqueous extract of opium is ppd. by dilute ammonia, and the filtrate evaporated to crystallisation. The crystals are extracted with alcohol, which after evaporation deposits crystals of meconin, which are recrystallised from water and ether successively (Couerbe).—2. The aqueous extract of opium is precipitated by chloride of calcium; the precipitated meconate of calcium is filtered; the filtrate evaporated to the crystallising point, and separated from the deposited hydrochloride of morphine; and the dark mother-liquor is diluted with water, filtered from the flocks which separate, and treated with ammonia, which precipitates narcotine, thebaïne, and a large quantity of resin. The filtrate is mixed with acetate of lead: the excess of lead is removed from the filtered liquid by dilute sulphuric acid; and the filtrate is neutralised with ammonia, and evaporated to the crystallising point at a moderate heat, whereupon narceïne separates out, and then sal-ammoniac by further concentration. The mother-liquor is repeatedly digested with ½ vol. ether at 26°, and the ether is distilled off from the extracts, a brown syrup then remaining. On treating this syrup with dilute hydrochloric acid, papaverine dissolves, and meconin remains in the form of a dark-grey crystalline powder, which, to free it from resin and purify it completely, must be several times crystallised from boiling water, with addition of animal charcoal (Anderson).

Properties.—Colourless hexagonal prisms. Appears tasteless at first, but afterwards acrid. May be sublimed. Sl. sol. cold water, m. sol. alcohol and ether. Sol. KOHAq, nearly insol. NH_3Aq. Inactive. Its aqueous solution ppts. lead subacetate but not lead acetate. Dilute H_2SO_4 forms a colourless solution which becomes dark green when evaporated (Couerbe). Conc. H_2SO_4 forms a colourless solution which becomes purple on heating.

Reactions.—1. Conc. HClAq at 100° gives MeCl and methyl-normeconin $C_9H_8O_4$ (M. a. F.). HI acts in like manner.—2. *Baryta-water* dissolves meconin forming 'barium meconinate' $(C_6H_2(OMe)_2(CH_2OH).CO_2)_2Ba$. This salt crystallises in needles, but the free acid splits up at once into water and its anhydride meconin (Hessert, *B.* 11, 240; Prinz, *J. pr.* [2] 24, 373). 3. *Potash-fusion* forms methyl-normeconin $C_9H_8O_4$ [125°] and, finally, protocatechuic acid. 4. Oxidised by MnO_2 and dilute H_2SO_4 to opianic acid.—5. $KMnO_4$ oxidises it to hemipic acid [180°].

Chloro-meconin $C_{10}H_9ClO_4$. [175°]. Obtained by passing chlorine into a cold saturated aqueous solution of meconin (Anderson, *A.* 98, 47). Colourless needles. May be sublimed. Sl. sol. cold water, v. sol. alcohol and ether. Hot H_2SO_4 gives a greenish-blue colour.

Bromo-meconin $C_{10}H_9BrO_4$. [167°] (Anderson); [177°] (Salomon, *B.* 20, 888). From meconin and bromine-water. Colourless needles, sl. sol. water.

Iodo-meconin $C_{10}H_9IO_4$. [112°]. From meconin and chloride of iodine (A.). Needles, nearly insol. water, m. sol. alcohol and ether.

Nitro-meconin $C_{10}H_9(NO_2)O_4$. [158°]. From meconin and HNO_3. White needles (from alcohol).

Amido-meconin $C_{10}H_9(NH_2)O_4$. [171°]. Obtained by reducing nitro-meconin with iron and acetic acid (S.). M. sol. hot benzene.

Methyl-normeconin $C_9H_8O_4$ *i.e.*

$C_6H_2(OH)(OMe)<{CH_2 \atop CO}>O$. [125°]. Obtained by heating meconin with conc. HClAq (Matthiessen a. Foster); by heating meconin with KCy at 180° (Bowman, *B.* 20, 890); or by potash-fusion from meconin or narcotine (Beckett a. Wright, *J.* 1876, 810). Monoclinic prisms; v. sol. hot water and alcohol, sl. sol. ether. $FeCl_3$ colours it blue. It reduces silver salts in the cold. Potash-fusion converts it into protocatechuic acid.—CaA'_2.—BaA'_2.

Meconin-acetic acid $C_{12}H_{12}O_6$ *i.e.*

$C_6H_2(OMe)_2<{CO \atop CH.CH_2.CO_2H}>O$. [167°]. Obtained by heating opianic acid with a mixture of malonic acid, acetic acid, and sodium acetate for 10 hours at 100° (Liebermann a. Kleemann, *B.* 19, 2290). Glistening needles. By boiling with baryta-water it is converted into opianyl-acetic acid $C_6H_2(OMe)_2(CO_2H).CH(OH).CH_2.CO_2H$. By heating with HI it is dimethylated, giving

$C_6H_2(OH)_2<{CO \atop CH.CH_2.CO_2H}>O$ [228°], of which the ethyl ether melts at 131°.

Salts.—A'Ag: white slightly soluble crystals. —A'_2Ca: needles, sl. sol. water.—A'_2Cu^x: blue crystalline pp.

Methyl ether A'Me: [124°]; glistening plates.

Ethyl ether A'Et: [83°]; plates, sol. alcohol, ether, and hot water.

Nitro-meconin acetic acid

$C_6H(NO_2)(OMe)_2<{CO \atop CH.CH_2.CO_2H}>O$. [176°]. Nearly colourless crystals. Obtained by nitration of meconin-acetic acid. It dissolves in cold H_2SO_4 with a yellow colour, which becomes red on warming from formation of an indigo derivative. By tin and HCl it is reduced to the lactone of (*Py.* 1:3)-di-oxy-(*B.* 2:3)-di-methoxy-di-hydro-quinoline-(*B.* 1)-carboxylic acid

$$\begin{array}{l} CO\text{———}O \\ / \qquad\quad CH.CH_2 \\ C_6H(OMe)_2< \quad\;\; | \\ \qquad\qquad\quad NH.CO \end{array}$$ [256°].

Salts.—A'_2Ca: yellow needles.—$A'Ag^x$: curdy pp.—A'_2Cu^x: green pp.

Ethyl ether A'Et: [129°]; glistening needles; insol. water, sol. alcohol and benzene (Liebermann a. Kleemann, *B.* 19, 2295).

ψ-Meconin $C_6H_2(OMe)_2<^{CH_2}_{CO}>O$ $\left[1:6:\frac{2}{3}\right]$? *Di-methyl derivative* of *di-oxy-phthalide.* [124°]. When hemipimide, the imide of hemipic acid $C_6H_2(OMe)_2<^{CO}_{CO}>NH$, is heated with tin and hydrochloric acid it is reduced to hemipimidine $C_6H_2(OMe)_2<^{CH_2}_{CO}>NH$ [181°], which yields a nitroso- derivative $C_6H_2(OMe)_2<^{CH_2}_{CO}>N.NO$ [156°], which on treatment with dilute NaOH in the cold yields pseudo-meconin (Salomon, *B.* 20, 883). Obtained also by boiling hemipimide with zinc-dust and acetic acid. Long colourless needles (from water). Sl. sol. cold water, sol. benzene, alcohol, and ether. Unlike meconin it is not affected by boiling with dilute H_2SO_4 and MnO_2. Dilute HNO_3 at 150° forms nitro-hemipic acid and nitro-ψ-meconin, whereas meconin yields only nitro-meconin. Fusion with KOH or KCy does not affect ψ-meconin.

Bromo-ψ-meconin $C_{10}H_9BrO_4$. [142°]. From ψ-meconin and bromine. White flocculent pp., sol. benzene, insol. petroleum.

Nitro-ψ-meconin $C_{10}H_9(NO_2)O_4$. [166°]. From ψ-meconin and fuming HNO_3. Yellow needles, which yield oxalic acid on further treatment with nitric acid.

Amido-ψ-meconin $C_{10}H_9(NH_2)O_4$. [165°]. Obtained by reducing the preceding. More basic than amido-meconin.

MECONOISIN $C_8H_{10}O_2$. [88°]. S. 3·7. Occurs in opium, and found in the mother-liquor after separation of meconin. When this is allowed to stand, crystals are deposited, which are washed with alcohol and recrystallised from water (T. a. H. Smith, *Ph.* [3] 8, 981). Large, leaf-shaped crystals; v. e. sol. hot water. It gives a green colour when heated with dilute H_2SO_4.

MEDULLIC ACID $C_{21}H_{42}O_2$. [72·5°]. A fatty acid said to be produced, together with stearic and palmitic acids, by the saponification of beef-marrow (Eylerts, *Ar. Ph.* [2] 104, 129).

MELAM *v.* CYANIC ACIDS.

MELAMINE *v. Cyanuramide* in the article CYANIC ACIDS.

MELAMPYRITE *v.* DULCITE.

MELANILINE *v.* DI-PHENYL-GUANIDINE.

MELANIN. C 60; H 4·8; N 10·8; ash 2·2. A black pigment covering the choroid membrane of the eye (Scherer, *A.* 40, 63). Insol. water, alcohol, and ether.

Phymatorhusin. C 55·7; H 6·0; N 12·3; S 8 to 9; Fe ·07 to ·2. A pigment occurring in melanotic urine and tumours. It is obtained by ppg. with baryta, dissolving in Na_2CO_3, and ppg. with dilute H_2SO_4 (Berdez a. Nencki, *J. Th.* 1886, 477; Mörner, *H.* 11, 81). It is a brownish-black amorphous powder, insol. water, alcohol, ether, chloroform, and dilute mineral acids; v. e. sol. ammonia, aqueous NaOH, Na_2HPO_4, and Na_2CO_3. Ppd. from its solution in NaOH by baryta, $MgSO_4$, and $BaCl_2$. With potash-fusion it gives skatole, volatile fatty acids, nitriles, KCy, and K_2S. Hot H_2SO_4 forms pyridine. Phymatorhusin is accompanied by another black substance, which differs from it in being soluble in 50–75 p.c. acetic acid. It contains 5·9 p.c. of sulphur and ·2 p.c. Fe.

Hippomelanin. C 53·5–55·6; H 2·7–3·9; N 10·5–10·9; S 2·8–3·0. Occurs in melanotic tumours of horses. May be obtained by diluting the emulsion of a melanotic spleen with water and adding $CaCl_2$ and Na_2HPO_4. The pp. is washed at 40°, and then treated with a digestive fluid until the solution ceases to give a reaction for peptones. The residue is washed with aqueous soda, alcohol and ether (Miura, *C. C.* 1887, 250). Brownish-black powder; insol. water, alcohol, and ether. Dissolves on warming in dilute acids and alkalis. Potash-fusion gives KCy, succinic acid, formic acid, and hippomelanic acid. Hippomelanic acid is a black amorphous body, sol. ammonia, and reppd. by HCl. It contains less S and more C than the melanin (Nencki a. Sieber, *C. C.* 1888, 587). The **black pigment** in dark hair and in bird's feathers after purifying by alcoholic NH_3 and dilute H_2SO_4 may be represented by the formula $C_{18}H_{16}N_2O_8$ (Hodgkinson a. Sorby, *J.* 1876, 936). Black powder. Not affected by dilute acids and alkalis.

Sepiaic acid. C 56·3; H 3·6; N 12·3; S ·5; O 27·2. Obtained by digesting the pigment from the ink-bag of *sepia* with 15 pts. of 10 p.c. potash. Sol. alkalis; ppd. from ammoniacal solution by ammonia-zinc chloride or copper sulphate (Nencki a. Sieber).

MELANTHIN $C_{20}H_{33}O_7$. [205°]. Occurs in the seeds of *Nigella sativa* (Greenish, *Ph.* [3] 10, 909, 1013). Prepared by extracting the seeds with alcohol, evaporating the extract, dissolving the pp. in alcohol, and fractionally ppg. with water. Minute grey crystals (from alcohol). Insol. water, benzene, CS_2, and light petroleum; v. sol. alcohol, sol. alkalis, sl. sol. chloroform. Conc. H_2SO_4 gives a red colouration. H_2SO_4 and sugar give a violet-blue colour. Boiling dilute HCl splits it up into a sugar and m e l a n t h i g e n i n $C_{14}H_{23}O_2$, which forms minute crystals, sl. sol. water.

MELANURENIC ACID *v.* AMMELIDE.

MELEM *v.* CYANIC ACIDS.

MELENE $C_{30}H_{60}$. [62°]. (370°–380°). S.G. ·89. V.D. 10–11·8. S. (alcohol) ·13 in the cold; 3·6 at 78°. An olefine (?) produced by the dry distillation of bees'-wax (Ettling, *A.* 2, 252; Lewy, *A. Ch.* [3] 5, 395; Brodie, *A.* 71, 156).—White nacreous plates (from ether). Insol. water, sl. sol. cold alcohol, v. sol. ether. Not attacked by cold H_2SO_4; slightly attacked by boiling HNO_3. Attacked by chlorine.

MELEZITOSE $C_{12}H_{22}O_{11}$. [148°]. $[\alpha]_D = 94°$ (B.); 88·5° (V.). A sugar discovered by Bonastre in the manna of Briançon which exudes from the young branches of 'mélèzo' (*Pinus Larix*) (Berthelot, *A. Ch.* [3] 55, 282). It occurs also in 'taranjobine' or Turkestan manna (Villiers, *Bl.* [2] 27, 98; Alekhine, *Bl.* [2] 46, 824). Obtained by extracting the Briançon manna with boiling alcohol, and evaporating. After a few weeks melezitose separates; it is then recrystallised from alcohol. Monoclinic crystals containing aq (V.), or anhydrous crystals (A.). About as sweet as glucose. Dextrorotatory. V. sol. water, nearly insol. cold, sl. sol. boiling, alcohol, insol. ether. Its aqueous solution is ppd. by ammoniacal lead acetate. Boiling dilute H_2SO_4 forms glucose. It is turned brown by alkalis.

It does not reduce Fehling's solution. Does not ferment with yeast. It forms a compound with phenyl hydrazine. It gives an octo-acetyl derivative.

MELIDO-ACETIC ACID $C_5H_8N_6O_2$ *i.e.* $(CN)_3N_3H_5CH_2.CO_2H$. Formed by treating cyanamide with chloro-acetic ether and NaOEt (Drechsel, *J. pr.* [2] 11, 332). Amorphous mass, but obtained in a crystalline state by ppg. its ammonium salt with HCl. Decomposed by heat without previous fusion. Insol. alcohol and ether, v. sl. sol. cold water. Sol. aqueous HClAq, baryta, and KOHAq, but insol. NH_3Aq.—HA'HCl: needles, sl. sol. cold water.—$HA'HNO_3Aq$.—$AgA'HNO_3Aq$.—$(HA')_2H_2SO_4$ 4aq.

MELILOTIC ACID *v.* Oxy-phenyl-propionic acid.

MELILOTOL $C_{18}H_{16}O_5$ (?). An oil found, together with coumarin, in the yellow melilot (*Melilotus officinalis*). Extracted by distilling the plant, when in flower, with steam, and extracting the distillate with ether (Phipson, *C. N.* 32, 25; *C. R.* 86, 830). Liquid, v. sl. sol. water, alcohol, and ether. Has an agreeable odour. When boiled with conc. KOHAq it yields oxy-phenyl-propionic (melilotic) acid $C_9H_{10}O_3$. Melilotol is perhaps identical with the lactone of melilotic acid $C_6H_4\left\langle\begin{matrix}CH_2.CH_2\\ \quad\ |\\ O\ .\ CO\end{matrix}\right.$.

MELINOIN - TRI - SULPHONIC ACID $C_{34}H_{17}O_3(SO_3H)_3$.

Formation.—1. By warming a mixture of *p*-oxy-benzoic-aldehyde, (β)-naphthol, and H_2SO_4. 2. From benzoic-aldehyde, (β)-naphthol, and H_2SO_4.—3. By heating Baeyer's condensation product $C_{34}H_{26}O_3$ (from benzoic-aldehyde and (β)-naphthol) with H_2SO_4 (Trzcinski, *B.* 16, 2835; 17, 500).—Yellow crystalline powder. Insol. absolute alcohol, tolerably sol. water, the dilute solution being of a rose-red colour with a green fluorescence. It dissolves in strong H_2SO_4 or HNO_3 with a splendid green fluorescence, and is not attacked even on boiling. It forms unstable compounds with HCl and H_2SO_4, although it is itself a strong acid.

Salts.—$A'''K_3$: easily soluble fine colourless needles.—A'''_2Ca_3 aq: colourless soluble crystals.—A'''_2Ba_3: sparingly soluble white amorphous pp. or microscopic needles.

MELISSIC ACID $C_{30}H_{60}O_2$ *i.e.* $C_{29}H_{59}CO_2H$, or $C_{31}H_{62}O_2$ *i.e.* $C_{30}H_{61}.CO_2H$. [90°]. Occurs in bees'-wax (Nafzger, *A.* 224, 225). Formed by heating the myricyl alcohol of bees'-wax with soda-lime at 270°-300° in absence of air (Brodie, *A.* 71, 156; Von Pieverling, *A.* 183, 344; Stürcke, *A.* 223, 295; Schwalb, *A.* 235, 106). Silky scales, composed of minute needles. Sol. alcohol, light petroleum, chloroform, and CS_2, sl. sol. ether. According to Schalfeeff (*B.* 12, 697) melissic acid is a mixture of acids.

Salts.—PbA'_2. [119°]. Insol. alcohol and ether, sl. sol. boiling toluene, chloroform, and glacial acetic acid.—MgA'_2.—CuA'_2.—AgA': [95°]; amorphous pp.

Methyl ether MeA'. [71°]. Needles (from ligroïn).

Ethyl ether EtA'. [70°] (Schwalb); [73°] (P.). Needles (from alcohol). Split up on heating into ethylene and the free acid.

Isoamyl ether $C_5H_{11}A'$. [69°].

MELISSYL ALCOHOL *v.* Myricyl alcohol.

MELITOSE *v.* Raffinose and Sugars.

MELLITIC ACID $C_{12}H_6O_{12}$ *i.e.* $C_6(CO_2H)_6$. *Mellic acid. Benzene hexa-carboxylic acid.* Mol. w. 342. H.C.v. 790,800. H.C.p. 788,200. H.F. 546,800 (Stohmann, Kleber, a. Langbein, *J. pr.* [2] 40, 141). *Heat of neutralisation*: 84,034 (Gal a. Werner, *Bl.* [2] 47, 162).

Occurrence.—As aluminium mellitate in honey-stone or mellite (Klaproth, *A. D.* 1799; Baeyer, *A. Suppl.* 6, 1).

Formation.—1. By the oxidation of hexa-methyl-benzene by cold alkaline $KMnO_4$ (Friedel a. Krafts, *A. Ch.* [6] 1, 470).—2. By the oxidation of charcoal by $KMnO_4$ (Schulze, *B.* 4, 802, 806).—3. By the electrolysis of acidified water or of KOH using a positive electrode of gas carbon (Bartoli a. Papasogli, *G.* 11, 468; *C. C.* 1881, 327).—4. In very small quantity by oxidising coal, animal charcoal, or lampblack by alkaline NaOCl (Bartoli a. Papasogli, *G.* 15, 446).

Preparation.—Powdered honey-stone is boiled with ammonium carbonate, ammonia is added, and the filtrate evaporated to crystallisation. The ammonium mellitate is recrystallised with addition of a little ammonia, dissolved in water, ppd. by lead acetate, and the pp. decomposed by H_2S (Wöhler, *A.* 37, 263; Schwarz, *A.* 66, 47; Claus, *B.* 10, 559).

Properties.—Stellate groups of delicate silky needles (from alcohol); v. sol. water and alcohol. Decomposed by heat into CO_2 and pyromellitic acid $C_{10}H_6O_8$ (Erdmann, *J. pr.* 52, 432), which solidifies in the neck of the retort as a radio-crystalline mass. When strongly heated with glycerin it yields CO_2 and trimesic acid $C_9H_6O_6$. When heated to redness with soda-lime it yields benzene (Baeyer, *A. Suppl.* 7, 5). Not decomposed by boiling HNO_3, sulphuric acid, HIAq, chlorine, or bromine. When its aqueous solution is electrolysed, CO_2, hydrogen, CO, and oxygen are given off (Bunge, *J. R.* 12, 421).

Salts.—$(NH_4)_6C_{12}O_{12}$ 3aq: trimetric crystals (Schwarz, *A.* 66, 47). Decomposed at 150° with formation of paramide and ammonium euchroate.—$(NH_4)_2H_4C_{12}O_{12}$ 4aq: trimetric prisms. From ammonio-cupric mellitate and H_2S.—K_6A^{vi} 9aq: trimetric crystals.—$K_4H_2A^{vi}$ 8aq.—$K_3H_3A^{vi}$ 6aq: large prisms, more soluble in water than the normal potassium salt.—$(K_3H_3A^{vi})_4(KNO_3)_3$ 9aq (?).—Na_6A^{vi} 12aq: needles (from a hot conc. solution).—Na_6A^{vi} 18aq: large striated triclinic crystals.—Ba_3A^{vi} 3aq: white gelatinous pp., changing to scales.—Mg_3A^{vi} 18aq: crystalline mass.—$Mg_2(NH_4)_2A^{vi}$ 15aq: large glassy prisms.—Zn_3A^{vi} 15aq.—Zn_3A^{vi} 9aq.—Mn_3A^{vi} 18aq: minute needles, more sol. cold than hot water. S. (hot water) ·125.—Co_3A^{vi} 18aq: minute prisms (from boiling water).—Ni_3A^{vi} 24aq: v. sl. sol. water.—Al_2A^{vi} 18aq. *Mellite.* S.G. 1·6. S.H. ·336 (Bartoli, *G.* 14, 105). Occurs in lignite at Asten in Thuringia, Bilin in Bohemia, and near Walchau in Moravia. Massive nodules. Dimetric crystals: $a:c = 1:\cdot745$.—$Fe_3A^{vi}Fe_3O_3$ 9aq: minute lemon-yellow crystals, v. sl. sol. water.—Cu_3A^{vi} 12aq. From boiling mellitic acid and cupric acetate. Amorphous pp., becoming crystalline.—$Cu_2H_2A^{vi}$ 12aq.—$Cu_2(NH_4)_2A^{vi}$ 12aq: from cupric sulphate and ammonium mellitate.—Hg_3A^{vi} 6aq (dried at 100°): granular mass.—

Hg_6A^{vi} 6aq (dried at 100°): granular pp.—Pb_3A^{vi} (dried at 180°): bulky white pp.—$Pd_3A^{vi}(NH_3)_{12}$ 6aq: colourless trimetric crystals (Karmrodt, *A.* 81, 164).—Ag_6A^{vi}: white crystalline powder (Wöhler, *A.* 30, 1).

Methyl ether Me_6A^{vi}. [187°]. From silver mellitate and MeI (Kraut, *J.* 1862, 281; *A.* 177, 273). Plates. H.C. 1,825,600. H.F. 487,400 (Stohmann, *J. pr.* [2] 40, 353).

Ethyl ether Et_6A^{vi}. [73°].

Isoamyl ether $(C_5H_{11})_6A^{vi}$. Oil.

Chloride $C_6(COCl)_6$. [190°] (Claus, *B.* 10, 561). Formed, together with an oxychloride $C_{12}O_8Cl_2$, from PCl_5 and mellitic acid. Hard vitreous prisms (from ether). Sublimes in laminæ at 240°. Slowly decomposed by water into HCl and mellitic acid.

Tri-imide $C_{12}H_3N_3O_6$ *i.e.*

$C_6\left\{<^{CO}_{CO}>NH\right\}_3$. *Paramide.* Formed, together with euchroic acid, by heating ammonium mellitate at 160° as long as NH_3 escapes. Water extracts ammonium euchroate from the residue leaving paramide undissolved (Wöhler, *A.* 37, 268; Schwarz, *A.* 66, 52). White amorphous powder, insol. water and alcohol. Sol. H_2SO_4 but reppd. by water. Boiling with water slowly converts it into $(NH_4)_3H_3C_{12}O_{12}$. Alkalis convert it first into euchroïc and then into mellitic acid. $AgNO_3$ forms in its ammoniacal solution a gelatinous pp. which gives off NH_3 when heated, leaving $Ag_3N_3C_{12}O_6$. An ammoniacal solution of paramide dropped into HClAq gives a white crystalline pp. called 'paramic acid' $C_{12}H_5N_3O_7$ (?) or

$\begin{matrix}CO_2H\\CO(NH_2)\end{matrix}>C_6\left\{<^{CO}_{CO}>NH\right\}_2$.

Tri-phenyl-tri-imide

$C_6\left\{<^{CO}_{CO}>NPh\right\}_3$. Formed by heating mellitic acid or ammonium mellitate (1 mol.) with aniline (6 mols.) at 160° for 7 hours (Hötte, *J. pr.* [2] 32, 238). White amorphous mass.

Di-imide $C_{12}H_4N_2O_8$ *i.e.*

$(CO_2H)_2C_6\left\{<^{CO}_{CO}>NH\right\}_2$. *Euchroïc acid.* Prepared by heating ammonium mellitate at 160° for several hours, dissolving in water, and adding HCl to the hot solution. The crystals which separate on cooling are recrystallised from water (Wöhler, *P.* 52, 610; Schwarz, *A.* 66, 49). Small prisms (containing 2aq); sl. sol. cold water. Strongly acid. Melts about 280°. Euchroïc acid is not decomposed by boiling water or HClAq. When a solution of euchroïc acid is treated with zinc the metal becomes covered with a dark-blue deposit of 'euchrone.' This deposit detaches itself when the zinc is immersed in dilute HClAq. After drying, euchrone is a black mass which becomes colourless when heated in air, being re-oxidised to euchroïc acid. Euchrone forms a deep-purple solution in NH_3Aq or KOHAq, but the solution is quickly decolourised by the air. When a solution of euchroïc acid is electrolysed, the negative platinum becomes coated with the blue deposit.

Salts.—$(NH_4)_2C_{12}H_2N_2O_8$: white crusts.—An acid ammonium salt separates from hot solutions in yellowish crystals.—BaA″aq: pale-yellow powder.—PbA″aq.—PbA″4aq.—Ag_2A'': sulphur-yellow powder.

Hexahydride $C_6H_6(CO_2H)_6$. *Hydromellitic acid.* Formed by treating an ammoniacal solution of mellitic acid with sodium-amalgam; neutralising with acetic acid; ppg. by lead acetate; and decomposing the pp. with H_2S. (Baeyer, *A. Suppl.* 7, 15). Formed also in the electrolysis of aqueous KOH with a positive electrode of carbon (Bartoli a. Papasogli, *C. C.* 1881, 327). Hygroscopic syrup; v. e. sol. water. By heating with H_2SO_4 (5 pts.) there is formed, together with CO_2 and SO_2, trimesic acid $C_6H_3(CO_2H)_3$, prehnitic acid $C_6H_2(CO_2H)_4$, mellophanic acid $C_6H_2(CO_2H)_4$, and prehnomalic acid $C_{10}H_8O_9$.

Salts.—The alkaline salts are gummy, v. e. sol. water.—The calcium salt is more soluble in hot than in cold water.—Pb_3A^{vi} (dried at 150°). Amorphous pp.—Ag_6A^{vi}: amorphous pp.

Isohexahydride $C_6H_6(CO_2H)_6$. *Isohydromellitic acid.* Formed by heating the preceding hexahydride with conc. HClAq for 3 hours at 180° (Baeyer). Prisms (from water). V. sol. water, but ppd. on additiou of HCl. Not affected by heating with fuming HClAq at 300°. Decomposed in the same manner as its isomeride when heated with H_2SO_4. Chromic acid mixture oxidises it to acetic acid and CO_2.—Pb_3A^{vi}.

Methyl ether of the *Isohexahydride* $Me_6C_{12}H_6O_{12}$. [125°]. Needles, v. e. sol. alcohol.

References. — HEMI-MELLITIC ACID; PYRO-MELLITIC ACID.

TRIMELLITIC ACID $C_9H_6O_6$ *i.e.* $C_6H_3(CO_2H)_3$ [1:2:4]. *Benzene tricarboxylic acid.* Mol. w. 210. [218°].

Formation.—1. Together with isophthalic acid and pyromellitic anhydride by heating the tetrahydride of pyromellitic acid $C_6H_6(CO_2H)_4$ with 5 pts. of H_2SO_4 (Baeyer, *A. Suppl.* 7, 40).—2. By oxidising the acid $C_6H_3Me(CO_2H)_2$, prepared from ψ-cumene, by $KMnO_4$ (Krinos, *B.* 10, 1491).—3. By oxidising alizarin carboxylic acid with dilute HNO_3 (Hammerschlag, *B.* 11, 88).—4. By oxidising the acid $C_6H_3Me(C_4H_9)CO_2H$ with dilute nitric acid (S.G. 1·12) at 240° (Effront, *B.* 17, 2338).—5. By the action of cuprous cyanide upon the diazo- compound from amido-terephthalic acid, and saponification of the product with aqueous KOH (Ahrens, *B.* 19, 1634).—6. By heating mono-potassic (β)-sulpho-phthalate with sodium formate, isophthalic acid being also formed (Graebe a. Rée, *C. J.* 49, 532).

Preparation.—100 g. pulverised colophony and 2 litres of nitric acid (1 vol. commercial acid to 2 vols. water) are introduced into a retort with its beak directed upwards, and the liquid is heated to boiling, whereupon the colophony melts, and is quickly attacked, with copious evolution of red vapours, and converted iuto an orange-yellow viscid mass. After the boiling has been continued for 6 or 8 hours, fresh resin and strong nitric acid are added alternately, till about 1 kg. resin has been introduced, the contents of the retort being kept in constant ebullitiou; this process takes about a fortnight. The resulting wine-yellow liquid, which on addition of water should merely show turbidity, and not yield any lumpy precipitate, is then distilled off till the remaining liquid begins to froth; and

this liquid, while still hot, is poured into a tenfold volume of cold water, decanted after twenty-four hours from the varnish-like resin which separates, and evaporated to a syrupy consistence. The whole then solidifies after a while to a thick crystalline pulp, which may be freed from the syrupy mother-liquor by means of an aspirator and porous carthenware plates, and afterwards boiled with water. The extract on cooling deposits isophthalic acid in slender needles, and on further concentration, first a little more of the same acid and then trimellitic acid, which may be purified by solution in alcohol and crystallisation from water. 30 g. of trimellitic acid may be thus obtained from 50 g. of resin (Schreder, *A.* 172, 93).

Properties.—Rosettes of small needles; m. sol. water and ether. When heated above its melting-point the anhydride distils over, condensing in concentrically arranged groups of needles. On fusion with NaOH it gives benzene and diphenyl (Barth a. Schreder, *B.* 12, 1257). It also yields benzene when distilled with lime.

Salts.—$Ba_3A'''_2$ 4aq (when air-dried). Gives off 3aq at 160°. Sl. sol. water.—$Ba_3A'''_2$ 3aq (when dried over H_2SO_4).—Ag_3A''': white pp., not much affected by light: sl. sol. water.

Anhydride $C_6H_3(CO_2H)\langle{}^{CO}_{CO}\rangle O$. [158°]. Formed by heating the acid (Baeyer, *A.* 166, 340). Crystalline mass, sl. sol. cold, v. sol. hot, water.

Reference.—Sulpho-trimellitic acid.

MELLITYL ALCOHOL *v.* Penta-methyl benzyl alcohol.

MELLOGEN $C_{11}H_2O_4$. On the electrolysis of water by a battery of 1,200 Daniell's cells, the anode being gas-carbon, the liquid becomes of an inky colour, and there is deposited in the voltameter a black residue. This is washed with water until the filtrate is quite colourless; from the washings the mellogen is ppd. with a small quantity of dilute hydrochloric acid (Bartoli a. Papasogli, *G.* 11, 468; 12, 117; 13, 37; 15, 464; *C. R.* 94, 1339; *A. Ch.* [6] 7, 364). A black solid, of conchoidal fracture, sol. water and alkalis, insol. alcohols and hydrocarbon, and in most mineral acids and salts. It is not readily combustible, and is converted by oxidising agents, *e.g.* NaOCl, into mellitic and pyromellitic acid and their hydrides. At ordinary temperatures it has the composition $2C_{11}H_2O_4 + 3H_2O$; at 100° it may be represented by $2C_{11}H_2O_4.H_2O$. The aqueous solution of mellogen is dark-coloured, and is ppd. by acids and by many salts. With baryta mellogen gives an insoluble pp. Nitric acid (S.G. 1·36) oxidises mellogen forming an amorphous compound $C_{11}H_6O_3$, sol. water, alcohol, and ether: a soluble acid $C_{11}H_6O_7$ 2½aq, forming the salts $Ba_3(C_{11}H_3O_7)_2$ and $Ag_3C_{11}H_3O_7$; and a black compound resembling mellogen.

MELLONE *v.* Cyanic acids.

MELLOPHANIC ACID $C_{10}H_6O_8$ *i.e.* $C_6H_2(CO_2H)_4$ [1:2:3:5]. *Benzene i-tetra-carboxylic acid.* [238°]. Obtained, together with prehnitic acid $C_6H_2(CO_2H)_4$ [1:2:3:4], by heating the hydride of pyromellitic acid $C_6H_6(CO_2H)_4$ [1:2:4:5] with H_2SO_4 (Baeyer, *A.* 166, 327). Formed also by the oxidation of iso-durene $C_6H_2Me_4$ (Jacobson, *B.* 17, 2516). Small four-sided prisms; v. sol. water, but ppd. by HCl from a conc. solution. Converted into an anhydride on fusion. Calcium acetate gives in hot solutions of the acid a pp. which re-dissolves on cooling. Baryta-water gives a pp. which becomes crystalline on heating. Lead acetate gives a flocculent pp., insol. acetic acid. Sodium-amalgam forms a hydride of mellophanic acid.

Anhydride [238°]. Formed by fusing the acid. Insol. ether.

MELOLONTHIN $C_5H_{12}N_2SO_3$. Found, together with leucine and hypoxanthine, in cockchafers (*Melolontha vulgaris*). The insects are extracted with water, the extract boiled, ppd. with lead subacetate, and the filtrate freed from lead by H_2S and evaporated. The crystals are freed from leucine by treatment with alcohol (Schreiner, *B.* 4, 763). 30lbs. of cockchafers yield 1·5 g. melolonthin. Silky needles (from water); sl. sol. cold, m. sol. hot, water; v. sl. sol. dilute alcohol and ether; v. sol. acids and alkalis. Does not act on light.

MELMESIDINE *v.* Di-mesityl-guanidine.

MENAPHTHYLAMINE $C_{11}H_{11}N$ *i.e.* $C_{10}H_7.CH_2NH_2$. (292°). Formed by treating the amide of (α)-thionaphthoic acid $C_{10}H_7.CS.NH_2$ with zinc and HCl (Hofmann, *B.* 1, 100). Alkaline liquid, readily absorbing CO_2 from the air.—B'HCl: long, sparingly soluble crystals.—$B'_2H_2PtCl_6$: yellow crystalline pp.

MENISPERMINE $C_{18}H_{24}N_2O_2$ (?). [120°]. Occurs in the seeds of *Menispermum cocculus* (Pelletier a. Caventou, *A. Ch.* [2] 54, 178). To extract the menispermine, the alcoholic extract of the seeds is first treated with cold water, then exhausted with hot acidulated water; the brown solution is ppd. by an alkali; and the pp. is exhausted with very weak acetic acid, which leaves a brown-black mass undissolved. Or the seeds may be made up into a heap, and exhausted with alcohol of specific gravity 0·833; the alcohol distilled off; the residue boiled with water; and the liquid filtered at the boiling heat; it then, on cooling, deposits crystals of picrotoxine, especially if a small quantity of acid has been added. The part insol. boiling water is then treated with acidulated water, and ppd. by an alkali; a granular pp. is thereby formed, from which alcohol extracts a peculiar yellow substance; and the residue is finally dissolved in ether, which deposits menispermine in the crystalline form. The ether leaves undissolved a viscous substance, which may be dissolved in absolute alcohol: and the solution, evaporated at 45°, ultimately yields crystals of paramenispermine.

Properties.—Prisms; insol. water, sol. alcohol and ether. Is not poisonous. Its sulphate forms prismatic needles, sol. water.

Paramenispermine [250°]. Isomeric with menispermine. Insol. water, sl. sol. ether, v. sol. boiling alcohol. Dissolves in dilute acids.

MENTHENE $C_{10}H_{18}$. Mol. w. 138. (167·4° cor.) (Atkinson a. Yoshida, *C. J.* 41, 53); (163°) (Oppenheim, *C. J.* 15, 29). V.D. 4·94 (calc. 4·78). S.G. $\frac{15}{15}$ ·814; $\frac{0}{4}$ ·8226; $\frac{20}{4}$ ·8073 (A. a. Y.). C.E. (0°–10°) ·000994; (0°–60°) ·00100. $[\alpha]_j = +13{\cdot}25$ (A. a. Y.). R_∞ 74·0. *Specific refractive energy*, ·548. *Specific dispersive energy*, ·0313 (Gladstone, *C. J.* 49, 622). Obtained by distilling menthol (1 pt.) with $ZnCl_2$ (2 pts.), or with P_2O_5 (Walter, *A.* 32, 288). Formed also by the action

of conc. H_2SO_4 on menthol (Beckmann, *A.* 250, 358).

Properties.—Colourless oil, smelling like cymene; m. sol. ether and alcohol, v. sol. benzene, turpentine, and petroleum. Dextrorotatory.

Reactions.—1. Combines with fuming HCl, forming a yellow oil $C_{10}H_{19}Cl$. Combines also with HI, forming $C_{10}H_{19}I$, identical with the product obtained by heating terpilene dihydro-di-iodide $C_{10}H_{16}2HI$ with HI (Bouchardat a. Lafont, *C. R.* 107, 916).—2. Combines with *bromine*, forming $C_{10}H_{18}Br_4$, which is split up by heat into HBr and cymene (Beckett a. Wright, *C. J.* 29, 1). 3. Fuming *nitric acid* oxidises it to glutaric acid.

MENTHOL $C_{10}H_{20}O$ *i.e.*

$$C_3H_7.CH\!<\!\begin{array}{l}CH_2—CH_2\\CH(OH).CH_2\end{array}\!>\!CH.CH_3 \text{ or}$$

$$C_3H_7.CH\!<\!\begin{array}{l}CH_2.CH_2\\CH_2.CH(OH)\end{array}\!>\!CH.CH_3\ (?).$$ *Methyl-propyl-phenol hexahydride.* Mol. w. 156. [42°]. (212°). V.D. 5·62 (calc. 5·41). S.G. $\frac{15}{15}$ ·890. $[\alpha]_j = -59·3$ (Moriya); $[\alpha]_D = -59·6$ (Oppenheim); $= -49·4$ in a 5 p.c. alcoholic solution at 22° (Arth, *A. Ch.* [6] 7, 438). $R_\infty = 77·4$ in a 21 p.c. benzene solution (Kanonnikoff, *J. pr.* [2] 31, 348). H.C. 1,509,100 (Louguinine, *A. Ch.* [5] 23, 387). Deposited in crystals when the essential oil of peppermint is kept for a long time or cooled to a low temperature (Dumas, *A.* 6, 252; Blanchet a. Sell, *A.* 6, 293; Walter, *A.* 32, 288; Kane, *P. M.* 16, 418; Laurent, *Rev. Scient.* 14, 341; Oppenheim, *C. J.* 15, 24). Menthol is imported from Japan in the solid state as 'peppermint camphor' (Moriya, *C. J.* 39, 77). White crystals, smelling of peppermint; sl. sol. water, v. e. sol. alcohol, ether, CS_2, HOAc, and fixed and volatile oils. Insol. aqueous alkalis. From alcoholic NaOH it crystallises in long needles. Sodium dissolves in it with evolution of hydrogen. Conc. acids dissolve menthol, but it is reppd. on dilution with water. Menthol has the refractive and dispersive energy of a saturated compound (Gladstone, *C. J.* 49, 621). The rate of etherification of menthol by acetic acid is that of a secondary alcohol (Menschutkin, *J. R.* 13, 569).

Reactions.—1. With $K_2Cr_2O_7$ and H_2SO_4 in sealed tubes at 120° gives an inactive oil 'menthone' (205°), $C_{10}H_{18}O$, S.G. $\frac{15}{15}$ ·9032, sol. alcohol, ether, and chloroform.—2. Fuming HNO_3 forms an explosive oil, S.G. $\frac{15}{15}$ 1·061, which may be reduced to a yellow oil $C_{10}H_{19}NH_2$ (185°–190°). 3. Excess of fuming HNO_3 forms an acid, probably glutaric (*q.v.*).—4. *Bromine* in acetic acid forms $C_{10}H_{19}Br$. Unstable oil.—5. Conc. HClAq at 100° slowly forms menthyl chloride. PCl_5 forms the same body.—6. $ZnCl_2$ or P_2O_5 dehydrate menthol, producing menthene.—7. $KMnO_4$ in acid solution forms (β)-pimelic acid $C_7H_{12}O_4$ [87°], of which the amide [191°] crystallises from water in prisms (Arth, *A. Ch.* [6] 7, 440; *C. R.* 107, 107). Formic, propionic, butyric, and oxymenthylic acids are formed at the same time. The oxymenthylic acid $C_{10}H_{18}O_3$ boils at 174° under 15 mm. pressure.—8. Boiled with HI (S.G. 1·7) for 3 days it forms a mixture of hydrocarbons chiefly consisting of $C_{10}H_{16}$ (168·6°) V.D. 67·25, $[\alpha]_j = +5·2$. S.G. $\frac{0}{4}$ ·8254; $\frac{20}{4}$ ·8111; C.E. (0°–10°) ·000929; (0°–60°) ·000694. R_∞ 73·28. Colourless oil; v. sol. petroleum or benzene, less so in alcohol or ether. Odour resembles cymene (Atkinson a. Yoshida, *C. J.* 41, 54).—9. Menthol does not react with hydroxylamine (Nägeli, *B.* 16, 499).—10. On heating with sodium and ether on the water-bath, and, after cooling, adding CS_2 there is formed menthyl-xanthogenic acid $C_{10}H_9O.CS.SH$, a liquid which undergoes spontaneous decomposition, but forms a yellow crystalline copper salt CuA'_2 (Bamberger a. Lodter, *B.* 23, 213).

Acetyl derivative $C_{10}H_{19}OAc$. *Menthyl acetate.* (223°). $[\alpha] = -114°$. From menthol and HOAc at 120° (Oppenheim, *C. J.* 15, 26). Liquid. Not decomposed by cold alkalis, but saponified by alcoholic NaOH at 120°.

Butyryl derivative $C_{10}H_{19}O.CO.C_3H_7$. *Menthyl butyrate.* Obtained by heating menthol with butyric acid at 200° for 30 hours (Oppenheim). (230°–240°). $[\alpha] = -89°$.

Benzoyl derivative $C_{10}H_{19}OBz$. [54°]. (230°). $[\alpha]_D = -91°$. In a one p.c. benzene solution, trimetric crystals partially decomposed on distillation into menthene and benzoic acid (Arth, *A. Ch.* [6] 7, 479).

Carbamyl derivative $C_{11}H_{21}NO_2$ *i.e.* $C_{10}H_{19}O.CO.NH_2$. *Menthyl carbamate.* [165°]. $[\alpha]_D = -85°$ in a ·58 p.c. chloroform solution at 21°. Formed by passing dry cyanogen into a solution of sodium-menthol in dry toluene. The product is washed with water and the toluene distilled off. The crystalline mass is then recrystallised from alcohol, from which the carbamyl derivative separates in slender prismatic needles (Arth, *C. R.* 94, 872; 98, 521; *A. Ch.* [6] 7, 433). Needles; m. sol. alcohol and benzene. Sublimes at 100°. Decomposes at about 200°, yielding cyanuric acid. Alcoholic KOH forms menthol and potassium cyanate. Ac_2O at 130° forms $C_{10}H_{19}OAc$. Benzoic aldehyde and HCl form $(C_{10}H_{19}OCO.NH)_2CHPh$ [143°].

Carbonyl derivative $(C_{10}H_{19}O)_2CO$. *Menthyl carbonate.* [105°]. Obtained in the preparation of the carbamyl derivative by evaporating the alcoholic mother-liquor and boiling the residue with water as long as menthol and ammonia come off. On cooling, the carbonyl derivative is deposited as a crystalline mass, sol. boiling alcohol (Arth). Plates (from alcohol) or prisms (from toluene); v. sl. sol. alcohol, v. sol. ether and benzene. Alcoholic KOH at 100° saponifies it.

Phenyl-carbamyl derivative $C_{10}H_{19}O.CO.NHPh$. *Menthyl phenyl-urethane. Menthyl phenyl-carbamate.* [111°]. From menthol and phenyl cyanate (Leuckart, *B.* 20, 115). Silky needles (from hot alcohol).

Succinoxyl derivative $C_{10}H_{19}O.CO.CH_2.CH_2.CO_2H$. [62°]. $[\alpha]_D = -59·6°$ in a 1·4 p.c. benzene solution. Formed by heating menthene (1 mol.) with succinic anhydride (1 mol.) at 110° (Arth). Acicular crystals; v. e. sol. alcohol, v. sl. sol. hot water. Its Na and K salts are very deliquescent; the Ca and Ba salts are white pps.—$AgC_{14}H_{23}O_4$: small needles (from hot water).

Succinyl derivative $(C_{10}H_{19})_2C_4H_4O_4$. [62°]. (220°). $[\alpha]_D = -81·5°$ in a 1·9 p.c. benzene solution. From menthol (1 mol.) and succinic acid (2 mols.) at 150°. Trimetric crystals (from alcohol). Decomposes on distillation into succinic acid and menthene.

Phthaloxyl derivative $C_{18}H_{24}O_4$ *i.e.* $C_{10}H_{19}.O.CO.C_6H_4.CO_2H$. [110°]. $[\alpha]_D = -105·6°$ in a 1·6 p.c. benzene solution. Formed by heating menthol (1 mol.) with phthalic anhydride (1 mol.) at 110° (Arth). Minute needles; insol. cold water, v. sol. alcohol and ether. Gives white pps. with Ba and Ca salts.—$Mg(C_{18}H_{23}O_4)$: laminæ; almost insol. cold water.

Phthalyl derivative $C_{28}H_{42}O_4$ *i.e.* $(C_{10}H_{19})_2C_8H_4O_2$. [133°]. $[\alpha]_D = -94·7°$ in a 2 p.c. benzene solution at 20°. From phthalic anhydride (1 mol.) and menthene (2 mols.) at 140°. Trimetric crystals (from ether); sl. sol. boiling alcohol.

Menthyl chloride $C_{10}H_{19}Cl$. (c. 204°). Obtained by treating menthol with PCl_5 (Walter, *A.* 32, 292) or with conc. HClAq for a week at 100° (Oppenheim). The same body appears to be formed by heating menthene with fuming HClAq at 120° (Arth, *C. R.* 97, 323). Light oil; sl. sol. water, m. sol. alcohol. Not attacked by alcoholic KOH. With sodium menthol it gives menthene and menthol.

Menthyl bromide $C_{10}H_{19}Br$. From menthol and bromide of phosphorus. Non-volatile liquid. Gives with bromine $C_{10}H_{14}Br_6$.

Menthyl iodide $C_{10}H_{19}I$. From menthol and conc. HIAq. Liquid; decomposed by alcoholic K_2S into menthene and HI.

Tetra-menthyl-silicate $Si(OC_{10}H_{19})_4$. [82°]. (350°) at 155 mm. Formed by the action of $SiCl_4$ upon menthol; the yield is 75 p.c. of the theoretical (Hertkorn, *B.* 18, 1695). Colourless prisms; v. sol. ether, benzene, ligroïn, chloroform, CS_2, and warm alcohol; sl. sol. cold alcohol.

Oxymenthylic acid $C_{10}H_{18}O_3$. (175°) at 15 mm. (280°). A product of the oxidation of menthol by $KMnO_4$ (Arth, *A. Ch.* [6] 7, 448). Colourless liquid, partially decomposed on boiling at 280°; v. sl. sol. water, v. sol. alcohol and ether. The salts of alkalis and alkaline earths are very soluble. A solution of the sodium salt is ppd. by salts of Pb, Fe''', Cu, and Pt. It forms no acetyl derivative.—AgA'.—NaA': white deliquescent crystals.

Methyl ether MeA'. (137°) at 17 mm. Liquid.

Ethyl ether EtA'. (145°) at 18 mm. Thick liquid.

MENTHONE $C_{10}H_{18}O$. (206·3° cor.). $[\alpha]_j = +21°$. S.G. $\frac{0}{4}$ ·9126; $\frac{20}{4}$ ·8972. C.E. (0°–10°) ·000862; (0°–100°) ·000923. R_∞ 75·3. From menthol (30 g.), $K_2Cr_2O_7$ (10 g.), and H_2SO_4 (10 g.) at 135°. The light oil is subjected several times to the action of the same oxidising mixture (Atkinson a. Yoshida, *C. J.* 41, 49). Colourless oil, miscible with alcohol, chloroform, benzene, and CS_2. Smells like diluted peppermint. Does not combine with $NaHSO_3$. If a solution in petroleum is treated with Na and CO_2 successively and then shaken with water crystals of menthol are got [42°]; but having $[\alpha]_j = -39°$ not $-59°$.

Lævo-menthone $C_{10}H_{18}O$ *i.e.* $CHPr{<}^{CH_2.CH_2}_{CH_2.CO}{>}CHMe$(?) (207°). S.G. $\frac{20}{20}$ ·8960. $[\alpha]_D = -28·2°$. Menthone is a mixture of two isomerides—one dextro-, the other lævorotatory. By using very little acid the lævomenthone may be obtained free from dextromenthone and menthol. The best proportions are 60 g. $K_2Cr_2O_7$, 50 g. H_2SO_4, 300 g. water, and 45 g. menthol, the mixture being kept at 30° to 55° (Beckmann, *A.* 250, 325). The menthone is extracted with ether, washed with dilute alkalis, and distilled with steam.

Properties.—Mobile liquid, smelling faintly of peppermint; sl. sol. water, miscible with alcohol, ether, and petroleum-ether. The molecular weight determined by Raoult's method agrees with the formula. The molecular refraction $\left(\frac{n^2-1}{n^2+2}\right)\frac{P}{d}$ is 46·3. Lævo-menthone is converted into a mixture of dextro- and lævomenthone by acids, bases, water, heat, or even on keeping.

Oxim $C_{10}H_{18}NOH$. Mol. w. 169. [58°]. $[\alpha]_D = -42·5°$. Crystalline; sol. dilute alcohol, ether, and petroleum-ether. Raoult's method gives, when acetic acid is used, the mol. w. 169, but when benzene is used it gives 251. With HCl the oxim forms a compound $(C_{10}C_{18}NOH)HCl$ [119°], a white crystalline powder.—$^{\times}C_{10}H_{18}NONa$.

Dextro-menthone $C_{10}H_{18}O$. Mol. w. 154. (208°). S.G. $\frac{20}{20}$ ·900. $[\alpha]_D = +28·14°$. Obtained by freezing a mixture of H_2SO_4 (10 pts.) and water (1 pt.), adding menthene, (2 pts.), and shaking. The temperature is slowly raised to 30°, the product poured into ice, and the menthone extracted by ether (Beckmann, *A.* 250, 334). Colourless mobile oil; sl. sol. water, miscible with alcohol, ether, and petroleum-ether. The mol. w. determined by Raoult's method is 150. The action of acids, bases, water, heat, and time convert dextro-menthone into a mixture of dextro- and lævo-menthone.

Oxim $C_{10}H_{18}NOH$. Thick oil, slightly lævorotatory. The mol. w. determined by Raoult's method is 165 when acetic acid is used, and 228 when benzene is employed as solvent. — $(C_{10}H_{18}NOH)HCl$. [c. 97°]. Deliquescent. — $^{\times}C_{10}H_{18}NONa$.

MENYANTHIN $C_{30}H_{46}O_{14}$. [60°–115°]. A bitter glucoside found in buckbean (*menyanthes trifoliata*) (Brandes; Kromayer, *Ar. Ph.* [2] 108, 257; 124, 37; *Fr.* 1, 15). Prepared by treating the aqueous extract with animal charcoal at 65°, and subsequently extracting the charcoal with alcohol. Amorphous yellowish mass; sl. sol. cold water, v. sol. hot water and alcohol, insol. ether. Dissolves in aqueous alkalis. Its solutions are not ppd. by metallic salts. It is ppd. by tannin. When distilled with dilute H_2SO_4 it gives off volatile menyanthol, while glucose $C_6H_{12}O_6$ 6aq remains behind.

Menyanthol C_8H_8O is an oil smelling like benzoic aldehyde. It reduces ammoniacal $AgNO_3$. By exposure to the air, or by potash-fusion, it is converted into a crystalline sublimable acid.

Menyanthin. This name has also been applied to inulin when prepared from buckbean.

MERCAPTALS. Compounds of the form $RCH(SR')_2$. They may be viewed as thio-acetals or as the sulphur-compounds corresponding to the alkyl derivatives of ortho-aldehydes. *V.* THIO-ALDEHYDES.

MERCAPTAN C_2H_6S *i.e.* C_2H_5SH. *Ethyl mercaptan. Thio-alcohol.* Mol. w. 62. (36·5°). S.G. $\frac{20}{4}$ ·8391. V.D. 2·11 (calc. 2·15). S.V. 76 (Lossen, *A.* 254, 71). H.F.p. 14,430. H.F.v.

13,271 (Thomsen). R_∞ 18·62 (Nasini, *G.* 13, 301).

Formation.—1. By distilling calcium ethyl sulphate $CaEt_2(SO_4)_2$ with a solution of barium sulphydrate (Zeise, *P.* 31, 369).—2. A mixture of alcohol and H_2SO_4 is neutralised with KOH, decanted from ppd. K_2SO_4, mixed with excess of KOH, saturated with H_2S, and distilled (Wöhler).—3. A solution of KOH (S.G. 1·3) is saturated with H_2S, mixed with an equal volume of a conc. solution of $KEtSO_4$, and distilled from a water-bath (Liebig, *A.* 11, 14; 23, 34). The product is freed from Et_2S by fractional distillation (Claesson, *J. pr.* [2] 15, 193).—4. From KSH and EtCl (Regnault, *A. Ch.* [2] 71, 390).—5. From KSH and EtI (Baudrimont, *C. R.* 54, 616).—6. By reducing with HI at 160° the solid thio-aldehyde obtained by passing H_2S into a mixture of aldehyde solution and iodine (Böttinger, *B.* 11, 2203).—7. Together with $HEtSO_4$ and ether, by heating alcohol saturated with SO_2 in sealed tubes (Endemann, *A.* 140, 336; Pagliani, *B.* 11, 155).

Preparation.—A cold mixture of alcohol (1 litre) and H_2SO_4 (500 c.c.) is diluted with ice and then added to a solution of crystallised sodium carbonate (4 kilos). The product is concentrated until Na_2SO_4 separates. The mother-liquor is further concentrated, and mixed with KOH (800 g.) dissolved in water (1,500 c.c.) previously saturated with H_2S. The whole is heated on a water-bath, and the gases are passed first through a strong solution of caustic potash (50 g.) and then into a solution of KOH (350 g.) in water (700 g.). The small amount of H_2S contained in the latter solution is ppd. by lead acetate, and the mercaptan liberated by HCl. It is dried with K_2CO_3 and distilled (Klason, *B.* 20, 3407).

Properties.—Colourless, very mobile, liquid, having a peculiarly persistent alliaceous odour. V. sl. sol. water, miscible with alcohol and ether. Very inflammable, and burns with a blue flame. A drop of it when briskly agitated on the end of a glass rod becomes solid, possibly through formation of a hydrate. Neutral to litmus. An alcoholic solution forms a yellow pp. with lead salts, and white pps. with cupric acetate, mercuric salts, and trichloride of gold. The alcoholic solution is turned blue by $FeCl_3$ (Rathke, *A.* 161, 148). Mercaptan is a reducing agent: thus it converts nitro-benzene into azo-benzene. Mercaptan decomposes salts of phenyl with formation of sodium phenylate and a thio-ether (R. Seiffert, *J. pr.* [2] 31, 462). But with phenyl salicylate it acts thus: $C_6H_4(OH)CO_2Ph + NaSEt = C_6H_4(ONa)CO_2Ph + HSEt$. A trace of isatin dissolved in sulphuric acid gives, with a trace of mercaptan, a fine green colouration (Berthelot, *C. R.* 108, 350).

Reactions. 1. Boiling *nitric acid* (S.G. 1·4) becomes red, deposits an oil, and ultimately forms ethane sulphonic acid. Weaker nitric acid (S.G. 1·23) forms $EtSO_2SEt$.—2. *Potassium* forms hydrogen and KSEt.—3. P_2S_5 forms Et_3PS_4 and Et_2HPS_4 (Carius, *A.* 112, 190).—4. *Bromine* forms EtBr and S_2Br_2 (Friedel a. Ladenburg, *A.* 145, 189).—5. Heated in sealed tubes with *diazo-compounds* (diazo-salicylic acid, diazo-phenol chloride) it forms di-ethyl disulphide, the diazo- compound being reduced exactly as when boiled with alcohol (R. Schmitt a. O. Mittenzwey, *J. pr.* 126, 192): $C_6H_4(OH).N:NCl + 2EtSH = Et_2S_2 + N_2 + C_6H_5.OH + HCl$.—6. PCl_3 at 100° forms thiophosphorous ether $P(SEt)_3$, a fetid oil, resolved by distillation into phosphorus and Et_2S_2.—7. CCl_4, acting on NaSEt, forms $C(SEt)_4$ a light oil, S.G. 1·01, decomposed on distillation. C_2Cl_6 with NaSEt gives $C_2(SEt)_6$, a heavy fetid oil, solidifying at very low temperatures. C_2Cl_4 heated with NaSEt at 100° gives $C_2(SEt)_4$, crystallising in rhombohedra [54°].—8. S_2Cl_2 forms HCl and Et_2S_4, which is resolved by distillation into Et_2S_2 and S_2.—9. $TiCl_4$ gives $EtSHTiCl_4$ and $(EtSH)_2TiCl_4$ (Demarçay, *Bl.* [2] 20, 132).—10. Reacts with ketones forming 'mercaptoles' or thioketates. Thus HCl passed into a mixture of acetone and mercaptan forms $(CH_3)_2C(SEt)_2$ (Baumann, *B.* 18, 887).—11. Mercaptan suspended in ice-water and mixed with diazobenzene sulphonic acid and soda gives explosive yellow needles of $SO_3Na.C_6H_4.N_2SEt$. When the alcoholic solution of this salt is boiled $SO_3Na.C_6H_4.SEt$ and nitrogen are formed (Stadler, *B.* 17, 2075).

Salts.—All metallic mercaptides are decomposed by HCl.—×KSEt. From mercaptan and K. Dull white granular mass, v. sol. water, sl. sol. alcohol. Its aqueous solution gives a yellow pp. with lead salts.—NaSEt. From mercaptan and Na or NaOEt. Crystalline mass, v. sol. water and alcohol. Its aqueous solution is alkaline in reaction, and gives off all its mercaptan on boiling. In dry air it oxidises to $C_2H_5SO_3Na$. When oxygen is passed through its alcoholic solution Et_2S is formed.—$Zn(SEt)_2$: white, indistinctly crystalline pp. obtained by adding mercaptan to aqueous zinc acetate. Sol. NH_3Aq and reppd. on neutralisation.—$Cd(SEt)_2$.—$Co(SEt)_2$: gummy pp. Unlike the other mercaptides it is not attacked by fuming HNO_3.—$Ni(SEt)_2$: chocolate brown powder, not decomposed by water.—×$Fe(SEt)_2$: from $FeCl_3$, mercaptan, and ammonia. Black slimy mass, resolved by heating into mercaptan and ferrous hydrate.—$EtSFe(NO)_2$ [78°]. From $KSFe(NO)_2$ and EtI (Pavel, *B.* 15, 2607).—TlSEt: yellow curdy pp., sl. sol. water.—$Cu(SEt)_2$. Obtained by adding mercaptan to a solution of $CuSO_4$ mixed with NaOAc. Pale-yellow amorphous powder (Klason, *B.* 20, 3407).—$Hg(SEt)_2$. [77°]. S. 7 in 85 p.c. alcohol. Formed on shaking HgO with mercaptan or with an alcoholic solution of mercaptan, the action being attended with great evolution of heat. It is from this body that mercaptan derives its name (*corpus mercurio aptum*). White unctuous scales. When its alcoholic solution is heated to 190° it is decomposed into mercury and Et_2S_2 (Otto, *B.* 13, 1289; 15, 125). The same decomposition appears to occur when it is heated in the dry state. It is not decomposed by aqueous KOH, but aqueous K_2S forms some HgS and KSEt. H_2S forms HgS and mercaptan. Nitric acid oxidises it to $(C_2H_5SO_3)_2HgHgO$. When melted with lead the products are mercury, PbS, and Et_2S. Mercury mercaptide forms with iodoform needles of $((EtS)_2Hg)_2CHI_3$ [85·5°] (Jackson a. Oppenheim, *B.* 8, 1033).—EtSHgCl. White bulky pp. obtained on mixing an alcoholic solution of mercaptan with $HgCl_2$. Changes after some time to crystalline laminæ. Sl. sol. water and ether,

m. sol. boiling alcohol (Debus, *A.* 72, 18).—$Pb(SEt)_2$. Yellow pp., got by mixing alcoholic solutions of lead acetate and mercaptan. Decomposed by heating with alcohol at 190° into PbS and Et_2S.—$Bi(SEt)_3$. [79°]. Obtained by mixing a solution of a salt of bismuth with mercaptan. Long flexible yellow needles, m. sol. alcohol and ether. Oxidises in the air. Resolved by heat into BiS and Et_2S.—$Sn(SEt)_4$. Formed by mixing solutions of mercaptan and $SnCl_4$ in CS_2, and evaporating the solvent. Also from mercaptan and a conc. aqueous solution of $SnCl_4$. Oil, remaining liquid at −40°. May be distilled *in vacuo*, but when heated under atmospheric pressure it decomposes yielding Et_2S_2 and metallic tin.—$Sn(SEt)_2$: yellow pp. which quickly oxidises in air.—$EtSSbCl_2$. Oil, formed by evaporating a mixture of mercaptan and $SbCl_3$. Decomposed by water with liberation of mercaptan.—$As(SEt)_3$. Obtained by adding NaSEt to an ethereal solution of $AsCl_3$. Oil, with unpleasant odour. Decomposed on distillation into arsenic and Et_2S_2.—$ClAs(SEt)_2$. From $AsCl_3$ and mercaptan in the cold.—EtSAu. White gelatinous pp. obtained on mixing dilute alcoholic solutions of auric chloride and mercaptan.—$Pt(SEt)_2$: light yellow pp.—$Rh_2(SEt)_6$: yellow pp.

Hydrate EtSH $18H_2O$. Solidifies as a crystalline mass when moist vapour of mercaptan is passed through a condenser cooled below 8° (H. Müller, *Ar. Ph.* [2] 150, 147). Mass of small needles, insol. water and mercaptan. A compound containing 1·6 p.c. carbon, crystallising in prisms, is obtained by pouring mercaptan into a solution of H_2S at 0°. It perhaps contains H_2S as well as water. It melts and decomposes above 3° (Blaikie, *Pr. E.* 10, 87).

MERCAPTANS. (*Sulphydrates.*) Compounds of the formula RSH where R is a hydrocarbon radicle. They may be viewed as acid ethers of sulphydric acid or as alcohols in which O has been displaced by S. Just as H_2S is more acid than H_2O, the mercaptans are more acid than the alcohols. Thus they readily form salts by reacting with metallic oxides, and they derive their name from the ease with which they form mercuric salts. The salts of mercaptans may be called mercaptides. The mercaptans boil at a lower temperature than the corresponding alcohols, just as H_2S has a lower boiling-point than H_2O. The mercaptans have an unpleasant odour. They are very readily oxidised, forming disulphides R_2S_2, and finally sulphonic acids RSO_3H. The oxidation to sulphonic acids is best effected by nitric acid, and the chlorides of the sulphonic acids RSO_2Cl when reduced by tin and HCl yield the mercaptans again (Vogt, *A.* 119, 152). By heating mercaptans with H_2SO_4 disulphides R_2S_2 are formed (Erlenmeyer a. Lisenko, *J.* 1861, 590).

Preparation.—1. Fatty, but not aromatic, mercaptans are formed by heating a solution of KSH with alkyl chlorides or iodides or with potassium alkyl sulphates.—2. By heating alcohols or phenols with P_2S_5 (Kekulé, *A.* 90, 311; *Z.* 1867, 193). The yield is small.—3. By reducing chlorides of sulphonic acids with zinc or tin and dilute H_2SO_4 or HCl. This process is very convenient for the preparation of aromatic mercaptans. The product is distilled with steam.—4. Aromatic mercaptans may be prepared by treating diazo- compounds with K_2S (Klason, *B.* 20, 350).—5. Aromatic mercaptans may be obtained by reducing the corresponding disulphides with zinc and H_2SO_4.—6. Aromatic mercaptans can be formed, together with the corresponding sulphides, by the action of aluminium chloride on a mixture of hydrocarbon and sulphur at 80° (Friedel a. Crafts, *Bl.* [2] 31, 464).—7. When three atoms of hydrogen in the benzene nucleus have been displaced by chlorous radicles, and two of these are NO_2 and a halogen in ortho-position to each other, alcoholic KSH displaces the halogen by SH (Beilstein a. Kurbatoff, *A.* 197, 75).—8. By treating aromatic diazo- compounds with sodium thiosulphate and reducing the resulting aromatic thiosulphates with zinc and H_2SO_4 (Leuckart, *G. P.* 1887, 45,120).

Properties.—Oils or crystalline solids with unpleasant odour. Insol. water. The salts of the heavy metals are sparingly soluble in water. The mercuric salts can usually be recrystallised from alcohol. When a small quantity of a 1 p.c. solution of isatin in H_2SO_4 is mixed with a few c.c. of the strong acid and a small quantity of a fatty mercaptan, a green colouration is produced. Aldehydes and the higher alcohols interfere with the isatin reactions, and in this case the liquid may be shaken with a solution of KOH and then mixed with a little sodium nitroprusside, when a reddish-violet colouration is produced (Denigès, *C. R.* 108, 350). The alkyl sulphides do not give this reaction. When sulphides are present they should first be ppd. by an alkaline solution of PbO.

Reactions.—1. The ammoniacal solutions of aromatic mercaptans oxidise in the air with formation of disulphides.—2. When HCl is passed into a mixture of a ketone and a mercaptan condensation takes place and a thioketate or ' mercaptole ' is formed, *e.g.*:

$$(CH_3)_2CO + 2HSEt = (CH_3)_2C(SEt)_2 + H_2O$$

(Baumann, *B.* 18, 887).—3. The alkoyl derivatives of aromatic o-amido-mercaptans readily split off H_2O, forming anhydro- compounds, *e.g.*:

$$C_6H_4{<}^{NH.CO.CH_3}_{SH} = H_2O + C_6H_4{<}^{N}_{S}{\gg}C.CH_3.$$

These anhydro- compounds may even be formed by boiling the alkoyl derivatives of aromatic amines with sulphur. They are also formed by the oxidation (by K_3FeCy_6) of the thio-alkoyl derivatives of aromatic amines. They are volatile liquids which exhibit feeble basic characters, and regenerate the amido-mercaptans when fused with potash (Hofmann, *B.* 13, 8, 1223; Jacobsen, *B.* 19, 1069). When o-amido-mercaptans are diazotised they produce characteristic stable compounds of the form $C_6H_4{<}^{N}_{S}{\gg}N$.

MERCAPTURIC ACIDS. Acids obtained by placing chloro- or bromo- benzene in food eaten by dogs. *V.* Bromo-phenyl- and Chloro-phenyl-mercapturic acids.

MERCURAMMONIUM COMPOUNDS. (*Ammonio-mercury compounds. Ammoniacal mercury bases. Mercuramines.*) By the reactions of ammonia, or ammonium salts, on compounds of Hg, compounds are obtained, many of which may be represented by the empirical formulæ $xHgX.yNH_3$ and $xHgX_2.yNH_3$ where X = acidic radicle; some of the compounds, however, con-

tain N and H in the ratio $N:H_2$; and some are composed of N, Hg, and acidic radicles only. The mercurammonium compounds, as a class, do not react as loose compounds of Hg salts with NH_3, but rather as compounds of Hg, N, H, and acidic radicles.

The mercurammonium compounds were regarded by Kane as compounds of NH_2Hg. Thus, the compound $HgO.NH_3$ was formulated as $NH_2Hg.OH$, and the compound $HgSO_4.2NH_3$ as $NH_2Hg.O.SO_2ONH_4$ (*A. Ch.* [2] 72, 215). Hirzel (*A.* 84, 258) represented the mercurammonium compounds as compounds of *mercuric nitride*, N_2Hg_3. Gerhardt suggested that these compounds are derived from NH_3 by replacing H by Hg; and after the ammonium hypothesis had been somewhat developed, Hofmann attempted to derive the compounds in question from different hypothetical mercurammoniums, *i.e.* compounds formed by replacing the H of NH_4 more or less completely by Hg (*v. Handwörterbuch der Chemie* [2nd ed.] 2, 751; *cf.* Schmieder, *J. pr.* 75, 147; Nessler, *J.* 1856. 409). On this view, the compounds $HgCl_2.2NH_3$ and $HgSO_4.2NH_3$ are represented as $Hg{<}^{NH_3Cl}_{NH_3Cl}$ and $Hg{<}^{NH_3}_{NH_3}{>}SO_4$, derived from $^{NH_4Cl}_{NH_4Cl}$ and $^{NH_4}_{NH_4}{>}SO_4$. The mercurammonium compounds may be divided, on this view, into classes according to the hypothetical Hg derivative of ammonium from which they are supposed to be derived. Thus we have the following: N_2H_6Hg = *mercurammonium*, $N_2H_6Hg_2$ = *mercurosammonium*, $N_2H_4Hg_2$ = *dimercurammonium*, $N_2H_4Hg_4$ = *dimercurosammonium*; the mercurammonium compounds are those containing divalent Hg, and the compounds of monovalent Hg are called mercurosammonium derivatives. The compound $2HgO.NH_3$, obtained by the reaction of HgO with NH_3Aq, is represented on the ammonium hypothesis as hydrated *mercurammonium hydroxide*, $NHg_2OH.H_2O$.

A division is sometimes made between those mercurammonium compounds which contain N and H in the ratio $N:H_3$, and those which contain these elements in the ratio $N:H_2$; the latter are called *mercuramide compounds.*

Although some compounds readily give off NH_3 when heated, and others only when heated with alkali, yet it seems simpler to name all the compounds under consideration in accordance with the ammonium hypothesis. In this article the mercurammonium compounds are divided into two classes, mercurous and mercuric; the former being called mercuro- and the latter mercuri- compounds; the name given to each compound is intended to indicate the number of NH_4 groups from which the compound is derived, and the number of Hg atoms (mercuro- or mercuri-) in the formula. Several compounds are known whose reactions seem well expressed by supposing them to contain the group Hg.O.Hg; such compounds are called mercuroxy-ammonium derivatives in this article.

The following table presents the classification and nomenclature adopted in the present article:—

Class I. Mercurous compounds.
- Series (i.) *Mercuro-ammonium compounds*; *e.g.* $(NH_3Hg)Cl$.
- ,, (ii.) *Dimercuro-ammonium compounds*; *e.g.* $(NH_2Hg_2)Cl$.

Class II. Mercuric compounds.
- Series (i.) *Mercuri-ammonium compounds*; *e.g.* $(NH_2Hg)Cl$.
- ,, (ii.) *Dimercuri-ammonium compounds*; *e.g.* $(NHg_2)_2O$.
- ,, (iii.) *Mercuri-diammonium compounds*; *e.g.* $(N_2H_6Hg)I_2$.
- ,, (iv.) *Dimercuri-diammonium compounds*; *e.g.* $(N_2H_4Hg_2)SO_4.H_2O$.
- ,, (v.) *Trimercuri-diammonium compounds*; *e.g.* $(N_2H_2Hg_3)SO_4.2H_2O$.

Class III. Mercuroxy-ammonium compounds; *e.g.* $(NH_2Hg_2O)OH$; $(NH_2Hg_2O)_2SO_4$.

Dimercuro-ammonium chloride $(NH_2Hg_2)Cl$ is sometimes called *mercuro-chloramide* or *amido-mercurous chloride*; to express this view of its constitution the formula is written $Hg_2(NH_2)Cl$. So also mercuro-ammonium chloride $(NH_3Hg)Cl$ is sometimes called *ammonio-mercurous chloride*, and the formula is written, empirically, $HgCl.NH_3$; the formula of this compound is frequently doubled, and the name *mercurosammonium chloride*—$(N_2H_6Hg_2)Cl_2$—is given to it. The salts called in this article mercuroxy-ammonium compounds may be regarded as hydrated *dimercuri-ammonium* salts; thus, the chloride $(NH_2Hg_2O)Cl$ may be written $(NHg_2)Cl.H_2O$, and the carbonate $(NH_2Hg_2O)_2CO_3$ may be written $(NHg_2)_2CO_3.2H_2O$.

Class I. Mercurous compounds. $NH_{4-x}Hg_xX$.

The experiments of Barfoed (*J. pr.* [2] 39, 201) make it probable that the so-called mercuro-ammonium compounds are really mixtures of mercuri- compounds and Hg. B. asserts that exactly half the Hg in the black pps. formed by NH_3Aq in solutions of mercurous salts exists uncombined, that nearly the whole of this Hg disappears as vapour when the pps. are freely exposed to air, and that the light-coloured compounds remaining are the same as those produced by adding NH_3Aq to mercuric salts. To the pp. produced from $HgNO_3$ Barfoed gives the composition $3Hg + 2(HgNH_2.NO_3)HgO$; that produced from Hg_2SO_4 is $4Hg + (NH_2Hg)_2SO_4.2HgO$; that from HgCl is $Hg + NH_2HgCl$; and that from $Hg_2C_2O_4$ is $4Hg + (NH_2Hg)_2C_2O_4.2HgO$.

Series (i.) *Mercuro-ammonium compounds*; NH_3HgX.

Mercuro-ammonium chloride, $(NH_3Hg)Cl$. (*Ammonio-mercurous chloride* ($HgCl.NH_3$). *Mercuros-ammonium chloride* ($N_2H_6Hg_2.Cl_2$).) A black powder, obtained by saturating HgCl, prepared by ppn., with NH_3 gas; on gently warming all NH_3 is given off (H. Rose, *P.* 20, 158). The dissociation of this compound has been studied by Isambert (*C. R.* 66, 1259; *v.* Dissociation, vol. ii. p. 397). According to Barfoed (*J. pr.* [2] 39, 201) the compound formulated as above is really a mixture of Hg, mercuri-ammonium chloride (NH_2HgCl), and NH_4Cl.

Series (ii.) *Dimercuro-ammonium compounds*; NH_2Hg_2X.

Dimercuro-ammonium chloride, $(NH_2Hg_2)Cl$. (*Mercurochloramide* or *amido-mercurous chloride* $(Hg_2NH_2.Cl)$. *Tetramercuro - diammonium chloride* $(N_2H_4Hg_4.Cl_2)$.) A black solid, obtained by digesting HgCl with NH_3Aq ($2HgCl + 2NH_3Aq = NH_2Hg_2Cl + NH_4ClAq$). Becomes dark-grey when dried; heated, gives off NH_3 and N, and at a higher temperature yields a sublimate of HgCl and Hg; treated with HCl gas, gives HgCl and NH_4Cl (Kane, *A. Ch.* [2] 72, 215; Ullgren, *P.* 42, 395). According to Barfoed (*J. pr.* [2] 39, 201) the black solid obtained as described is a mixture of Hg and NH_2HgCl.

Mercuro-ammonium nitrates. Various compounds of the form $xHg_2O.yN_2O_5.zNH_3$ have been described by Kane (*l.c.*) and Mitscherlich (*P.* 9, 387; 16, 41); but Barfoed's experiments make it very probable that these bodies are mixtures of Hg and mercuri-ammonium salts (*v. supra*).

Class II. Mercuric compounds. $N_xH_{4x-\frac{y}{2}}Hg_yX$.

Series (i.) *Mercuri-ammonium compounds*; NH_2HgX. Obtained by interaction of excess of NH_3Aq with mercuric salts in solution.

Mercuri-ammonium chloride, $(NH_2Hg)Cl$. (*Mercuri-chloramide*, or *amido-mercuric chloride* $(Hg.NH_2.Cl)$. *Dimercuri-diammonium chloride* $(N_2H_4Hg_2.Cl_2)$. *Infusible white precipitate.*) According to Rammelsberg (*J. pr.* [2] 38, 558) this salt is a double compound of dimercuri-ammonium chloride—NHg_2Cl—and NH_4Cl; R. assigns to it the formula $NHg_2Cl.NH_4Cl$ (*v. infra*).

When excess of NH_3Aq is added to $HgCl_2Aq$, or when $HgCl_2Aq$ is dropped into NH_3Aq, a white pp. is obtained; this pp. was long considered identical with that obtained by adding Na_2CO_3Aq to $HgCl_2Aq$ mixed with NH_4ClAq, and known in pharmacy as *Mercurius precipitatus albus*. Wöhler (*P.* 26, 203) found that the pp. formed by NH_3Aq was volatilised without fusion when heated in a Pt dish, but that the pp. formed by Na_2CO_3Aq melted before it volatilised. The pp. by NH_3Aq was then called *infusible white precipitate*, and to that produced by Na_2CO_3Aq the name *fusible white precipitate* was given.

Preparation.—$HgCl_2Aq$ is added to excess of cold NH_3Aq, the pp. is collected at once, rapidly washed with a little cold water, and dried at 110° (André, *C. R.* 108, 233, 290). André (*l.c.*) has examined the compounds obtained by the interaction of NH_3Aq with $HgCl_2Aq$, varying the relative masses of the reacting bodies and the time of contact. Using equal volumes of $HgCl_2Aq$, containing 33·875 g. $HgCl_2$ per litre, and NH_3Aq containing 4·25 g. NH_3 per litre, the pp. after drying at 110° was not quite pure NH_2HgCl, but contained a little mercuroxy-ammonium chloride $(NH_2.Hg_2O)Cl$. The quantity of $(NH_2.Hg_2O)Cl$ increased by allowing the reacting bodies to remain in contact, and also by increasing the quantity of NH_3Aq; when the NH_3 and $HgCl_2$ were present in the ratio $6NH_3:HgCl_2$, the pp. contained equal molecular proportions of NH_2HgCl and $(NH_2.Hg_2O)Cl$, and by further increasing the NH_3, only $(NH_2.Hg_2O)Cl$ was obtained. André found that NH_4Cl tends to change $(NH_2.Hg_2O)Cl$ into NH_2HgCl; by adding 1 vol. $HgCl_2Aq$ to 5 vols. NH_3Aq (strength as given above), decanting after 24 hours, and agitating the pp. for 2 days with 2 vols. NH_4ClAq (containing 13·4 g. per litre), pure NH_2HgCl was obtained. André has also examined the pps. obtained by adding NH_3Aq, and also NH_4ClAq, to $HgCl_2Aq$ in presence of KOH (*C. R.* 108, 1108, 1164). The pps. are compounds of NH_2HgCl, NHg_2Cl, and $(NH_2.Hg_2O)Cl$ in varying proportions.

Properties.—A white solid, which volatilises completely, when strongly heated, without melting. Readily sol. in HClAq; not blackened by NH_3Aq; dissolved by acids, also by hot solutions of NH_4 salts.

Reactions.—1. When *heated*, in an open vessel, does not melt but yields a sublimate of HgCl and a mixture of 1 vol. N and 2 vols. NH_3 ($6NH_2HgCl = 6HgCl + 4NH_3 + N_2$; Kane, *A. Ch.* [2] 72, 215). When slowly heated in a retort to c. 340°, $HgCl_2$ and NH_3 are given off, and a red crystalline compound, $2NHg_2Cl.HgCl_2$, remains.—2. Decomposed by *water*, slowly by cold, more rapidly by hot, eventually with formation of yellow mercuroxy-ammonium chloride, $(NH_2.Hg_2O)Cl$, and NH_4Cl ($2NH_2HgCl + H_2O + Aq = (NH_2.Hg_2O)Cl + NH_4ClAq$).—3. *Potash* or *soda* separates $(NH_2.Hg_2O)Cl$ and evolves NH_3. Only half the N of the original NH_2HgCl is evolved as NH_3 (Kane, *l.c.*); but by boiling for some days with KOHAq, renewed from time to time, all the N is removed as NH_3, and HgO remains (Schmieder, *J. pr.* 75, 147). The fact that only half the N is readily evolved as NH_3, by the action of alkalis on NH_2HgCl, has induced Rammelsberg (*J. pr.* [2] 38, 558) to regard this body as a compound of dimercuri-ammonium chloride and NH_4Cl, and to give it the formula $NHg_2Cl.NH_4Cl$. But it is to be remembered, as pointed out by Kane, that water readily separates NH_2HgCl into $(NH_2.Hg_2O)Cl$ and NH_4Cl; hence the NH_3 obtained by the action of aqueous alkali is probably due to the direct decomposition of NH_4Cl by the alkali.—4. Boiled with *very dilute sulphuric acid* till dissolved, the compound $HgCl_2.2NH_4Cl.2HgSO_4$ forms on cooling (Kosman, *A. Ch.* [3] 27, 238).—5. Heated in dry *hydrogen chloride*, $HgCl_2$ and NH_4Cl are produced (Ullgren, *A.* 26, 203).—6. Heated with solutions of *sodium chloride*, *potassium iodide*, *barium sulphide*, &c., NH_3 is evolved and $HgCl_2$, HgI_2, HgS, &c., formed; *e.g.* $NH_2HgCl + 2KIAq + H_2O = HgI_2 + KClAq + KOHAq + NH_3$ (Kane, *l.c.*; Rammelsberg, *P.* 48, 182).—7. Boiled with *ammonium chloride* solution, mercuri-diammonium chloride $N_2H_6Hg.Cl_2$ (*fusible white precipitate*) is produced.—8. Decomposed by heating with *sulphur*, with formation of a yellow sublimate of a chlorosulphide of N.—9. Rubbed with *iodine* and a little alcohol, HgI_2 is formed and then an explosion occurs, probably from production and decomposition of N iodide (Rice, *Ph.* [3] 6, 765; *cf.* Schwarzenbach, *B.* 8, 1231; Flückiger, *B.* 8, 619).—10. *Bromine* and *chlorine* cause evolution of N and formation of $HgBr_2$ or $HgCl_2$ (Schwarzenbach, *B.* 8, 1231).—11. Decomposed by *alcoholic iodides*, *e.g.* EtI (*v.* Sonnenschein, *A.* 101, 20).—12. For reaction with *amylic mercaptan* *v.* Wagner, *J. pr.* 53, 378.

Combinations.—1. Forms various compounds with NHg_2Cl and $(NH_2.Hg_2O)Cl$; obtained by adding NH_3Aq or NH_4ClAq to solutions of $HgCl_2Aq$ containing KOH (André, *C. R.* 108, 1108, 1164).—2. Combines with $HgCl_2$ to form

$NH_2HgCl.HgCl_2$; produced by slowly heating to c. 340° in a retort (Millon, *A. Ch.* [3] 18, 392).

Mercuri-ammonium bromide, $(NH_2Hg)Br$. (*Mercuri-bromamide*, or *amido-mercuric bromide* ($Hg.NH_2.Br$). *Dimercuri-diammonium bromide* ($N_2H_4Hg_2.Br_2$).) A yellow powder, obtained by ppg. $HgBr_2Aq$ with excess of NH_3Aq (*cf. Mercuri-ammonium chloride, supra*). Insol. water or alcohol, slowly changed by cold water, more quickly by hot water, to NHg_2Br (Pesci, *G.* 19, 509). E. sol. NH_3Aq. Heated gives N, NH_3, and HgBr; when very slowly heated to c. 340° gives NH_3, $HgBr_2.NH_3$, and $NHg_2Br.HgBr_2$ (Mitscherlich, *J. pr.* 19, 455).

Series (ii.) *Dimercuri-ammonium compounds*; $NHg_2.X$. According to Pesci (*G.* 19, 509) many and probably all the dimercuri-ammonium salts, when digested with NH_4Cl, NH_4Br, or NH_4I solution, evolve NH_3 in the proportion of $4NH_3$ for each NHg_2 group in the dimercuri-ammonium salt. This reaction may be applied to estimate dimercuri-ammonium salts, by conducting the digestion in a closed vessel containing a dish with a measured quantity of normal oxalic acid.

Dimercuri-ammonium hydroxide, $NHg_2.OH$. (*Mercurammonium hydroxide*). Prepared by saturating yellow HgO with NH_3 under increased pressure, finely powdering, and again saturating with NH_3; or by shaking HgO with alcoholic NH_3 for some hours and drying at ordinary temp. in NH_3 gas; the product, which is $NHg_2OH.H_2O$, is then heated in dry NH_3 to 80°–85°. The operation should be conducted in the dark (Weyl, *P.* 121, 601; 131, 539). A brown powder; explodes when strongly heated; decomposed by water, with evolution of NH_3; absorbs CO_2 from air, evolving NH_3 at the same time; dissolves in warm HClAq or HNO_3Aq with formation of salts of Hg and NH_4.

Heated to 100° in absence of air, gives *dimercuri-ammonium oxide* $(NHg_2)_2O$. A dark-brown powder which explodes when heated, struck, or rubbed in a mortar; readily combines with water to form $NHg_2.OH.H_2O$; soluble in HClAq and HNO_3Aq; reacts with HCl gas to form $HgCl_2$ and NH_4Cl. This oxide is also formed by the action of liquid NH_3 on HgO.

The hydrate of dimercuri-ammonium hydroxide $NHg_2OH.H_2O$, is a yellow powder, obtained as described above. It appears to be isomeric with mercuroxy-ammonium hydroxide $(NH_2.Hg_2O)OH$ (p. 211).

Dimercuri-ammonium chloride, $NHg_2.Cl$. (*Mercurammonium chloride.*) Obtained by treating the hydroxide (*v. supra*) with alcoholic solution of HCl; also by treating the oxychloride formed by fusing together HgO and $HgCl_2$ in the ratio $3HgO:HgCl_2$, with liquid NH_3, and removing excess of NH_3 by warming in a stream of dry air at 150°. Forms a yellow powder; decomposed suddenly at 300° to HgCl, Hg, and N (Weyl, *P.* 121, 601; 131, 539). Not acted on by boiling water; decomposed by hot KOHAq with production of NH_3 and HgO; slowly dissolved by cold HClAq.

Forms a double compound with mercuric chloride $2NHg_2Cl.HgCl_2$ (*dimercuri-ammonium-mercuric chloride*). A red crystalline solid, resembling HgO, produced by very slowly heating mercuri-ammonium chloride, $NH_2Hg.Cl$, in a retort until HgCl begins to sublime. This compound reacts with hot HClAq to form NH_4Cl and $HgCl_2$; it is said to be unchanged by conc. HNO_3Aq, dilute H_2SO_4Aq, H_2O, or boiling alkali solutions (Mitscherlich, *J. pr.* 19, 453). Heated to 360° it separates into N, HgCl, and Hg.

Dimercuri-ammonium bromide, $NHg_2.Br$. (*Mercurammonium bromide.*) Obtained by ppg. $HgBr_2Aq$ by excess of NH_3Aq and digesting the pp. (NH_2HgBr) with water; better, by adding excess of NH_4 carbonate to $HgBr_2Aq$, washing the pp. of $4NHg_2Br.5NH_4Br$ with NH_4 carbonate, warming with KOHAq, and washing with cold water (Pesci, *G.* 19, 509). Also obtained, according to Pesci, by the action of dilute HBrAq on Millon's base $(NH_2.Hg_2O)OH$. A yellow powder, insol. water, sol. HClAq, insol. HNO_3Aq; decomposed by heat, without melting, yielding NH_3 and a sublimate which contains Hg (Pesci, *l.c.*). Digested for a short time with boiling NH_4BrAq, and filtered, small crystals of $NHg_2Br.3NH_4Br$ are obtained. This compound seems similar to *fusible white precipitate*; it is described on p. 210 as *mercuri-diammonium bromide.* The double compound $4NHg_2Br.5NH_4Br$ is obtained, in clear microscopic needles, by adding excess of NH_4 carbonate to $HgBr_2Aq$ (Pesci, *l.c.*).

Dimercuri-ammonium iodide, NHg_2I, is obtained by the action of liquid NH_3 on the oxy-iodide formed by fusing together HgO and HgI_2 in the ratio $3HgO:HgI_2$ (Weyl, *P.* 121, 601; 131, 539).

Dimercuri-ammonium selenate, $(NHg_2)_2SeO_4.2H_2O$. A white pp. which darkens in light and is decomposed by heat; obtained by dissolving the basic selenate $HgSeO_4.2HgO$ in conc. NH_3Aq, and ppg. by much water (Cameron a. Davy, *C. N.* 44, 63).

Series (iii.) *Mercuri-diammonium compounds*; $N_2H_6HgX_2$.

Mercuri-diammonium chloride, $N_2H_6Hg.Cl_2$. (*Mercurammonium chloride. Fusible white precipitate. Ammonio-mercuric chloride*, $HgCl_2.2NH_3$.) Rammelsberg (*J. pr.* [2] 38, 558) regards this salt as a double compound of dimercuri-ammonium chloride—NHg_2Cl—and NH_4Cl. He formulates it as $NHg_2Cl.3NH_4Cl$ (*v. infra*).

When an alkali carbonate is added to $HgCl_2Aq$ containing NH_4Cl, a white pp. is obtained; this pp. was called in pharmacy *mercurius precipitatus albus*, and for long was supposed to be the same as that formed by adding NH_3Aq to $HgCl_2Aq$. Wöhler (*P.* 26, 203) found that the pp. formed by alkali carbonate, in presence of sal-ammoniac, melted when heated, before volatilising, but that the pp. formed by ammonia volatilised without melting. The former pp. was then called *fusible white precipitate*, to distinguish it from the latter to which the name *infusible white precipitate* was given.

The researches of Krug (*Ar. Ph.* 42, 1) have shown that pure mercuri-diammonium chloride cannot be obtained by addition of alkali carbonate to $HgCl_2Aq$ containing NH_4Cl at the ordinary temperature; the pp. consists of a mixture of mercuri-ammonium chloride (*infusible white precipitate*, $NH_2Hg.Cl$) and mercuri-diam-

monium chloride (*fusible white precipitate*, $N_2H_6Hg.Cl_2$); the longer the pp. remains in contact with the supernatant liquor, and the higher the temperature, the greater is the amount of *fusible white precipitate* formed. Krug found that almost pure NH_2HgCl (*infusible white precipitate*) was obtained by adding Na_2CO_3Aq to $HgCl_2Aq$ mixed with NH_4Cl at 0°, and filtering at once (about $4Na_2CO_3:3HgCl_2:9NH_4Cl$). The first pp. formed by the alkali carbonate therefore probably always consists mostly of mercuri-ammonium chloride, $NH_2Hg.Cl$, but this is acted on by the NH_4Cl present, and thus more or less $N_2H_6Hg.Cl_2$ is produced; CO_2 is also given off from the alkali carbonate used, and this CO_2, according to Krug's experiments, seems to change some of the NH_2HgCl to $HgCl_2.xHgO$ (with simultaneous formation of NH_4Cl and NH_4HCO_3), which oxychloride then probably reacts with NH_4Cl to produce $N_2H_6Hg.Cl_2$.

Preparation.—$HgCl_2Aq$ is dropped into boiling NH_4ClAq containing NH_3, as long as the pp. which forms is redissolved, and the liquid is allowed to cool. The compound crystallises out in garnet-red dodecahedra. Melts at c. 300° with decomposition.

Properties and Reactions.—Small red dodecahedra; also formed by ppn. with Na_2CO_3 as a white powder. Gently *heated*, gives off half its NH_3, leaving $HgCl_2.NH_3$ (*v. infra*); melts at c. 300°, evolving N and NH_3 and yielding a sublimate which reacts with water to form NH_4Cl, $HgCl_2$, and $HgCl$. *Boiling water* reacts to form mercuroxy-ammonium chloride, $(NH_2.Hg_2O)Cl$, and NH_4Cl. *Alkalis* evolve NH_3. According to Rammelsberg (*J. pr.* [2] 38, 558) three-fourths of the N of mercuri-diammonium chloride is evolved by the action of hot alkali solution; hence R. assigns to this compound the formula $NHg_2Cl.3NH_4Cl$; but as the action of boiling water on $N_2H_6Hg.Cl_2$ is to produce $(NH_2.Hg_2O)Cl$ and NH_4Cl in the ratio $(NH_2.Hg_2O)Cl:3NH_4Cl$, it is easy to account for the action of boiling alkali without supposing fusible white precipitate to be a double compound of NHg_2Cl with NH_4Cl. *Iodine* reacts energetically; according to Flückiger (*B.* 8, 1619) the reaction is expressed thus $6(N_2H_6Hg.Cl_2) + 2I_2 = N_2 + 6NH_4Cl + 4NH_3 + 2HgCl_2 + 2HgI_2 + 2HgCl$. *Liquid ammonia* dissolves $N_2H_6HgCl_2$; after prolonged action, and evaporation of the excess of NH_3, a white crystalline mass remains which has the same composition as the original, according to Weyl (*P.* 1, 547).

Combination.—The compound $HgCl_2.NH_3$ may be regarded as a compound of $N_2H_6Hg.Cl_2$ with $HgCl_2$ $[N_2H_6Hg.Cl_2.HgCl_2 = 2(HgCl_2.NH_3)]$. This compound is formed by heating $HgCl_2$ in dry NH_3, or by distilling HgO with NH_4Cl; it melts when heated and distils without much change; it is decomposed by water, forming $NH_2Hg.Cl$ and $HgCl_2.NH_4Cl$ (Kane, *A. Ch.* [2] 72, 215).

Mercuri-diammonium bromide, $N_2H_6Hg.Br_2$. Small microscopic, rhombohedral, transparent crystals; obtained by adding excess of NH_4 carbonate to $HgBr_2Aq$, boiling the pp. of $4NHg_2Br.5NH_4Br$ for a short time with NH_4BrAq, filtering, and allowing to cool (Pesci, *G.* 19, 509). Also formed by treating dimercuri-ammonium bromide (NHg.Br) with boiling NH_4BrAq; by the action of NH_3Aq on solution $HgBr_2.NH_4Br$; also by adding alcoholic NH_3 to $HgBr_2$ dissolved in alcohol (P., *l.c.*). Melts at c. 180° with evolution of NH_3: more strongly heated, yields two distinct sublimates. Easily sol. HClAq; H_2SO_4Aq forms $HgBr_2$; alkalis produce NHg_2Br (P., *l.c.*). Forms a compound with $HgBr_2$, viz. $N_2H_6Hg.Br_2.HgBr_2(=HgBr_2.NH_3)$ similar to the chloro- compound already described (H. Rose, *P.* 20, 160).

Mercuri-diammonium sulphate, $N_2H_6Hg.SO_4.H_2O$. Lustrous, orthorhombic, crystals. Obtained by adding, little by little, yellow HgO to pure, saturated, cold $(NH_4)_2SO_4Aq$, each portion of HgO being allowed to dissolve before another portion is added, the liquid being kept cold; addition of HgO is continued till the liquid begins to grow turbid, the clear liquid is decanted and allowed to evaporate in the air or *in vacuo*. This compound is decomposed by the smallest quantity of water with production of a compound of mercuroxy-ammonium sulphate and mercuri-ammonium sulphate,

$$3(NH_2.Hg_2O)_2SO_4.(NH_2Hg)_2SO_4;$$

boiling water removes more H_2SO_4, finally forming $(NH_2.Hg_2O)_2SO_4$ (*v. Mercuroxy-ammonium sulphate*, p. 211; *cf.* Millon, *A. Ch.* [3] 18, 410; Schmieder, *J. pr.* 75, 147). It is e. sol. in $(NH_4)_2SO_4Aq$, NH_4ClAq, HClAq, dilute H_2SO_4Aq, and HNO_3Aq; insol. conc. HNO_3Aq. Boiled with conc. H_2SO_4 it gives $(NH_4)_2SO_4$ and $HgSO_4$; decomposed by KOHAq, forming a basic compound; with boiling conc. KOHAq, NH_3 is evolved and HgO formed. Heated to 115° water is evolved, and at a higher temperature complete decomposition results.

Mercuri-diammonium iodide $N_2H_6Hg.I_2$; *Mercuri-diammonium fluoride* $N_2H_6Hg.F_2$; and the double compound $N_2H_6Hg.I_2.HgI_2$, have been described (*v.* H. Rose, *P.* 20, 160; Nessler, *C. C.* 1856. 530; Finkener, *P.* 110, 147; Rammelsberg, *P.* 48, 170; Caillot a. Carriol, *J. Ph.* 9, 381).

Series (iv.) *Dimercuri-diammonium compounds*; $N_2H_4Hg_2X_2$.

Dimercuri-diammonium sulphate, $N_2H_4Hg_2.SO_4.H_2O.(=SO_3.2HgO.2NH_3)$. Obtained, according to Millon (*A. Ch.* [3] 18, 410), by saturating 70 c.c. cold conc. NH_3Aq with $HgSO_4$, allowing to stand in an atmosphere of NH_3 over CaO for some months, powdering the crystals which separate, and drying over CaO.

Series (v.) *Trimercuri-diammonium compounds*; $N_2H_2Hg_3X_2$.

Trimercuri-diammonium sulphate, $N_2H_2Hg_3.SO_4.2H_2O$ $(=SO_3.3HgO.2NH_3)$. Prepared similarly to preceding salt, but using 90 c.c. NH_3Aq (Millon, *l.c.*).

Class III. MERCUROXY-AMMONIUM COMPOUNDS $(NH_2.Hg_2O)X$.

The name *mercuroxy-* is here given to the group Hg_2O, which is supposed to act as a dyad radicle in these compounds. The salts of this series may be regarded as *hydrated tetramercuri-diammonium compounds*; thus the carbonate $(NH_2.Hg_2O)_2CO_3$ may be written $N_2Hg_4.CO_3.2H_2O$, and the chloride $(NH_2.Hg_2O)Cl$ may be written $N_2Hg_4.Cl_2.2H_2O$. Some of the salts of this series may also be regarded as hydrated *dimercuri-*

ammonium compounds; thus the chloride $(NH_2.Hg_2O)Cl$ loses water at 200°, and is therefore regarded by Rammelsberg as $NHg_2Cl.H_2O$.

Mercuroxy-ammonium hydroxide, $(NH_2.Hg_2O)OH$. (*Millon's base.*) This is the final product of the reaction of NH_3Aq on HgO; the hydroxide contains H_2O. Millon gave the formula $NH_2.Hg_2O.OH.H_2O$; Gerresheim, the formula $2(NH_2.Hg_2O.OH).H_2O$ (*A.* 195, 373); and Rammelsberg, more recently (*J. pr.* [2] 38, 558), assigns the composition $3(NH_2.Hg_2O.OH).2H_2O$. The empirical formula for the base is $2HgO.NH_3xH_2O$.

Preparation.—Yellow HgO is agitated with NH_3Aq, quite free from carbonate, so long as any change occurs; if red HgO is used the change is not completed for some days. The yellow-brown product is washed with cold water, crystallised from hot water, and dried (Millon, *A. Ch.* [3] 18, 392).

Properties.—Yellow, microscopic crystals, probably rhombic. Appears to be isomeric with hydrated dimercuri-ammonium hydroxide $NHg_2OH.H_2O$ (p. 209). Insol. alcohol or ether; somewhat sol. water. S. ·007 at 17°, ·06 at 80°. Acts as a very strong base; decomposes NH_4 salts energetically with evolution of NH_3, and rapidly combines with CO_2 when exposed to air. Several salts may be obtained by dissolving the base in excess of acetic acid, and ppg. by alkali permanganate, chromate, &c. Over H_2SO_4 loses H_2O and becomes brown; heated to 130° further loses $\frac{1}{2}H_2O$, leaving *mercuroxy-ammonium oxide* $(NH_2.Hg_2O)_2O$.

Reactions.—1. The hydrated base is very slowly decomposed by boiling *alkali* solution; the dehydrated base is only decomposed by molten alkali.—2. Decomposes *ammonium salts* rapidly, with evolution of NH_3.—3. Combines so rapidly with *carbon dioxide* that it is almost impossible to obtain the base quite free from carbonate. — 4. With acids forms salts $(NH_2.Hg_2O)X$ ($X = NO_3, \frac{1}{2}SO_4$, &c.) (*v.* Rammelsberg, *J. pr.* [2] 38, 558).—5. Decomposed by *heat* with more or less explosion (Millon, *l.c.*; *cf.* Hirzel, *J.* 1852. 419; 1853. 381).—6. Many *salts*, *e.g.* sulphates and chlorides, are decomposed by shaking with Millon's base, with complete removal of the acid of the salt used (*v.* Gerresheim, *A.* 195, 373).—7. Heated with *ethylic iodide* to 100° yields crystals of $2NEt_4I.3HgI_2$; ethylic bromide reacts similarly.—8. A thiocarbonate of the base is obtained by heating with *carbon disulphide* (Gerresheim, *l.c.*).

Mercuroxy-ammonium chloride, $(NH_2.Hg_2O)Cl$. (*Hydrated tetramercurammonium chloride* $N_2Hg_4.Cl_2.2H_2O$. *Hydrated dimercuri-ammonium chloride* $NHg_2Cl.H_2O$.) This compound is formed by the reaction of boiling water with either fusible white pp. $N_2H_6Hg.Cl_2$, or infusible white pp. $NH_2Hg.Cl$. It is also produced by passing dry NH_3 over the oxychloride $3HgO.HgCl_2$ at 150° (Ullgren, *P.* 42, 395). A heavy, yellow powder; v. sl. sol. water; e. sol. HClAq and HNO_3Aq (Kane, *P.* 42, 367). Decomposed by heat, giving NH_3, N, H_2O, HgCl, and Hg. Decomposed by excess of solutions of KCl, NaCl, and KI, with evolution of NH_3. Loses water at 200°, and is therefore regarded by Rammelsberg as $NHg_2Cl.H_2O$ (*J. pr.* [2] 38, 558).

Mercuroxy-ammonium chloride combines with NH_2HgCl and NHg_2Cl to form various double compounds, *e.g.*

$$3(NH_2.Hg_2O)Cl.NH_2HgCl$$
$$\text{and } (NH_2.Hg_2O)Cl.NHg_2Cl;$$

these compounds were obtained by André by ppg. $HgCl_2Aq$ with NH_3Aq, some of them requiring the presence of KOH for their production (*C. R.* 108, 233, 290, 1108, 1164).

Mercuroxy-ammonium iodide, $(NH_2.Hg_2O)I$. (*Hydrated tetramercurammonium iodide* $N_2Hg_4.I_2.2H_2O$. *Hydrated dimercuri-ammonium iodide* $NHg_2I.H_2O$.) This compound is formed by adding NH_3Aq to *Nessler's reagent* (alkaline solution of HgI_2 in KIAq); the composition of the pp. thus produced is often represented as $Hg.NH_2.I + HgO$, or as $Hg.NHg.I + H_2O$. The compound is best prepared by dissolving $HgI_2.2KI$ in KOHAq, adding NH_4Aq, washing thoroughly with cold water, and drying at 100°

$$(2K_2HgI_4Aq + 3KOHAq + NH_3Aq$$
$$= (NH_2.Hg_2O)I + 7KIAq + 2H_2O;$$

v. Rammelsberg, *P.* 48, 170). $(NH_2.Hg_2O)I$ is also formed by heating $3HgO.HgI_2$ to 180° in NH_3 (Rammelsberg); and by boiling HgI_2 with excess of conc. NH_3Aq.

Mercuroxy-ammonium iodide is a brown powder with a purple-red tint. Begins to give off water at 128°; heated more highly, out of contact with air, it melts to a dark-brown liquid, and then decomposes violently, giving H_2O, Hg, HgI_2, NH_3 and N. Sol. warm KIAq, with formation of K_2HgI_4 and KOH and evolution of NH_3. Sol. warm HClAq; HgI_2 and HgICl are deposited on cooling (Rammelsberg). Decomposed by hot BaSAq, with evolution of all N as NH_3. Heated in HCl gas, gives a sublimate of $HgCl_2$, NH_4Cl, NH_4I, and $(NH_4)_2HgI_4$.

Mercuroxy-ammonium nitrates. Several nitrates, and some double nitrates, of the mercuroxy-ammonium compounds seem to exist.

The salt often called *Soubeiran's ammoniacal salt* is probably the *normal nitrate* $(NH_2.Hg_2O)NO_3$ (Soubeiran, *J. Ph.* 12, 465). This compound is obtained by ppg. dilute $Hg(NO_3)_2Aq$, containing only a little free acid, with very dilute NH_3Aq, boiling with water till the pp. becomes compact and curdy, washing, and drying.

The loose flocculent pp. produced by adding very dilute NH_3Aq to dilute $Hg(NO_3)_2Aq$, sometimes known as *Mitscherlich's ammoniacal salt*, is probably a *double compound of mercuroxy-ammonium nitrate and mercuri-ammonium nitrate*, $(NH_2.Hg_2O)NO_3.(NH_2Hg)NO_3.H_2O$.

Other compounds are obtained by boiling Mitscherlich's salt with excess of NH_3Aq with addition of NH_4NO_3Aq, and by dissolving Soubeiran's salt in hot conc. NH_4NO_3Aq; the salts thus formed are probably *double compounds of mercuroxy-ammonium nitrate and ammonium nitrate*, but their exact composition and constitution are not yet decided (*v.* Mitscherlich, *P.* 9, 387; 16, 41; Millon, *A. Ch.* [3] 18, 392; Kane, *A. Ch.* [2] 72, 215; Nessler, *J.* 1856. 409).

Mercuroxy-ammonium sulphate, $(NH_2.Hg_2O)_2SO_4$. (*Hydrated tetramercurammonium sulphate*, $N_2Hg_4.SO_4.2H_2O$. *Hydrated dimercuri-ammonium sulphate*,

$(NHg_2)_2SO_4.2H_2O$. *Ammoniacal turpethum*). Obtained by saturating conc. NH_3Aq with $HgSO_4$, and allowing to evaporate in air, or over H_2SO_4; also by digesting the basic sulphate $HgSO_4.HgO$ (*mineral turpethum*) with NH_3Aq; also by digesting HgO with hot $(NH_4)_2SO_4Aq$ (Millon, *A. Ch.* [3] 18, 392; Ullgren, *P.* 42, 395; Hirzel, *J.* 1852. 419; 1853. 381). Schmieder (*J. pr.* 75, 147) obtained the salt by repeatedly treating mercuri-diammonium sulphate, $N_2H_6Hg.SO_4.H_2O$ (*v.* p. 210), with boiling water, till the filtrate was free from sulphates. Forms a heavy yellow-white powder; sl. sol. water; easily sol. HClAq or HNO_3Aq. Decomposed by heat to H_2O, N, NH_3, and Hg_2SO_4. Treated with KOHAq, gives NH_3 and a *basic salt* $(NH_2.Hg_2O)_2SO_4.HgO$ (perhaps $NH_2.Hg_2O.NH_2.Hg_3O_2.SO_4$); and on further treatment with KOHAq yields NH_3, HgO, and K_2SO_4.

Besides the mercuroxy-ammonium salts described above, the following have been prepared:—

Mercuroxy-ammonium bromate $(NH_2.Hg_2O)BrO_3$ (Rammelsberg, *P.* 55, 82).

Mercuroxy-ammonium carbonate $(NH_2.Hg_2O)_2CO_3$ (Millon, *A. Ch.* [3] 18, 392; Hirzel, *J.* 1852. 419; 1853. 381).

Mercuroxy-ammonium chromate $(NH_2.Hg_2O)_2CrO_4$; and a *double basic salt* $(NH_2.Hg_2O)_2CrO_4.3HgCrO_4.HgO$ (Hirzel, *l.c.*).

Acid mercuroxy-ammonium fluoride $(NH_2.Hg_2O)F.HF$ (Finkener, *P.* 110, 632).

Mercuroxy-ammonium-ammonium iodate $(NH_2.Hg_2O)IO_3.2NH_4IO_3$ (Millon, *A. Ch.* [3] 18, 410).

Mercuroxy-ammonium-mercuric phosphate $(NH_2.Hg_2O).Hg.PO_4$ (Hirzel, *J.* 1852. 419; 1853. 381).

Mercuroxy-ammonium-mercuric sulphite $(NH_2.Hg_2O)_2SO_3.HgSO_3$ (Hirzel, *l.c.*).

M. M. P. M.

MERCURIALINE. The volatile base obtained by distilling the seeds of *Mercurialis annua* or *M. perennis* with lime and water, and formerly called 'mercurialine,' is identical with methylamine (E. Schmidt, *B.* 10, 2226; *A.* 193, 73; *cf.* Reichardt, *J. pr.* 104, 301).

MERCURY. (*Quicksilver.*) Hg. At. w. 199·8. Mol. w. 199·8. [−38·5°] (Regnault, *Acad.* 26, 525). [−38·85°] (Mallet, *P. M.* [5] 4, 145). (357·25° at 760 mm.) (Regnault, *l. c.*; for table of B.P. of Hg at pressures from 123 to 798 mm. *v.* Ramsay a. Young, *C. J.* 47, 656). S.G. $\frac{0°}{4°}$ 13·5958 to 13·596 (Regnault); $\frac{20°}{4°}$ 13·546 (Volkmann, *W.* 13, 209; a very full table of S.G. and volume of Hg from 0° to 360° is given). S.G. solid Hg, $\frac{-38·85°}{4°}$ = 14·1932 (Mallet, *P. M.* [5] 4, 145). V.D. 99·3 at 440° to 1565° (V. Meyer, *B.* 12, 1426). S.H. ·03312 from 20° to 50°, ·03278 from 25° to 142° (Winkelmann, *P.* 159, 152; *v.* also Pettersson, *B.* 12, 1718). $\frac{S.H.p.}{S.H.v.}$ 275° to 356° = 1·666 (Kundt a. Warburg, *P.* 157, 353; experimentally determined). C.E. ·00018153 from 0° to 100° (Regnault, *Acad.* 21, 271; *v.* also Wüllner, *P.* 153, 440). T.C. (Ag = 100) 5·3 (Calvert a. Johnson, *P. M.* [4] 16, 381; *cf.* Weber, *W.* 10, 490). E.C. c. 1·96 (Cu = 100). For electrical resistance of Hg *v.* Kohlrausch, *W.* 35, 700; (*cf.* Grunmach, *W.* 37, 508). For table of vapour-pressures of Hg from 135° to 520° *v.* Ramsay a. Young, *C. J.* 49, 37. Heat required to change 200 grm. Hg at 358° to gas = 12,400 gram-calories; heat required to melt 200 grm. solid Hg = 564 (Person, *A. Ch.* [3] 24, 257; *ibid.* 21, 295). Chief lines in emission-spectrum 6151, 5460·5, 4358 (Thalén, 1868; for table of lines of high refrangibility *v.* Hartley a. Adeney, *T.* 1884. 136). S.V.S. c. 14. Crystallises in regular octahedra.

Occurrence.—Small quantities of Hg are found as globules disseminated through ores of Hg, or in the rocks in which these ores occur. The chief ore of Hg is *cinnabar*, HgS, found in limited quantities in Illyria, Spain, Bohemia, Peru, China, California, the Ural, and one or two other localities. An amalgam of Hg and Ag is sometimes found native; iodide, chloride, and minute quantities of selenide, of Hg are also known to occur.

Preparation.—1. By distilling cinnabar in a regulated supply of air, condensing the Hg in a suitable apparatus, and allowing the SO_2 to escape.—2. By heating cinnabar with lime; CaS and $CaSO_4$ are formed, and the Hg distils and is condensed.—3. By heating cinnabar with iron (smithy-scales), Hg, FeS, and SO_2 are produced; the Hg is condensed in long chambers, or by downward distillation in a trough filled with water.

To purify Hg from dust, &c., it may be filtered through a paper cone having a minute hole at the apex, or pressed through leather. Traces of metals in solution may be removed by leaving the Hg in contact with cold conc. H_2SO_4 for some weeks, with frequent agitation, and then digesting with very dilute HNO_3Aq, or with $HgNO_3Aq$ (Branchi, *R. P.* 6, 77; Wittstein, *R. P.* 65, 362). Karsten and Ulex (*A.* 60, 210) recommend to rub the Hg in a basin for ten minutes, with 1-60th of its weight of $FeCl_3Aq$, S.G. 1·48 diluted with an equal weight of water, to pour off the liquid, which contains the foreign metals and some $HgCl_2$, to wash with water, and then to dry the Hg by heating it. L. Meyer (*B.* 12, 437) has described a convenient apparatus for purifying Hg by bringing a fine stream of it into contact with $FeCl_3Aq$. Brühl (*B.* 12, 204) shakes Hg with an equal volume of chromate solution, made by dissolving 5 grams $K_2Cr_2O_7$ in 1 litre water, and adding a few c.c. of H_2SO_4; the shaking is continued until the red $HgCrO_4$ at first produced has disappeared, and the liquid is coloured green by $Cr_2(SO_4)_3$; the fine greyish powder which is formed, and which consists of oxides of foreign metals, is washed away by a rapid stream of water. The process is repeated, and the Hg is then shaken with pure water until no more greyish powder is formed. About half p.c. of Hg is lost. Crafts (*Bl.* [2] 49, 856) removes Pb, Zn, Sn, and most other metallic impurities from Hg by placing the Hg in a slightly inclined glass tube, and aspirating a gentle current of air through the apparatus for about forty-eight hours. The oxides of the foreign metals collect at the top. Ag cannot be be removed by this method.

Pure Hg may be obtained by distilling equal parts of cinnabar and burnt lime or Fe filings. Also by boiling pure $HgCl_2Aq$ with pure Fe.

Also by heating HgO in a retort, and digesting the residual Hg, which contains a little HgO, with dilute HNO_3Aq or H_2SO_4. Millon (*B. J.* 27, 110) prepares HgO (from which to make Hg) by shaking Hg for some time with dilute HNO_3Aq to remove foreign metals, washing, dissolving in such a quantity of HNO_3Aq that 1-10th of the Hg remains undissolved, evaporating to dryness, and heating.

After purifying Hg by one of the foregoing methods it is advisable to distil it. A very convenient apparatus for distilling Hg under reduced pressure is described by Wright (*Am. S.* [3] 22, 479; *v.* also Weber, *Carl. Rep.* 15, 52; Weinhold, *Carl. Rep.* 15, 1).

Properties.—A very lustrous metal, white, with the slightest tinge of blue. Exists as a very mobile liquid at ordinary temperatures, and does not solidify above $-38 \cdot 5°$. Hg boils at c. 360°, but it is very easy volatilised; even at $-13°$ sufficient Hg is vaporised to produce a daguerreotype by twenty-four hours' exposure (Regnault, *C. R.* 73, 1462). According to Merget (*C. R.* 73, 1386) solid Hg at $-44°$ is very slowly vaporised. Solid Hg is a tin-white, ductile mass of octahedral and needle-shaped crystals. It may be cut with a knife. Hg is a very coherent liquid. By trituration with sugar, grease, sulphur, chalk, &c., or by agitation with ether, turpentine, and some other liquids, Hg appears as a grey powder, which consists of minute globules of Hg separated by the foreign matter present (*extinction* or *deadening of mercury*). Finely-divided Hg is also obtained by mixing about equal parts of $SnCl_2$, dissolved in HClAq, and $HgCl_2$ dissolved in hot water ($SnCl_2Aq + HgCl_2Aq = SnCl_4Aq + Hg$). In this state of fine division, Hg is slowly oxidised by contact with air. Pure Hg adheres very slightly to glass. When foreign metals are present the Hg leaves a blackish film on glass. A globule of pure Hg should roll down a slightly inclined surface without losing its round form, and without leaving any streak behind it. When shaken in a bottle with dry air it should not form any black powder.

Pure Hg is not oxidised by exposure to air at ordinary temperatures; when heated to near its B.P., HgO is slowly formed. [Berthelot (*C. R.* 91, 871) asserts that pure Hg is very slightly oxidised in air]. Hg obtained in a state of fine division by trituration, *e.g.* with chalk, is slowly oxidised at the ordinary temperature. Ozone oxidises Hg at ordinary temperatures (Volta, *G.* 9, 521; *cf. Reactions*, No. 2). Hg combines directly with O, S, and the halogens; it alloys with most of the metals, in some cases forming definite compounds (*v. Mercury, amalgams of*). Hg reacts with hot conc. H_2SO_4 to produce $HgSO_4$ and SO_2; with HNO_3Aq it produces $HgNO_3$, $Hg(NO_3)_2$, or a basic nitrate, according to the temperature and the quantity of acid. HClAq does not react with Hg.

The atomic weight of Hg has been determined (1) by analysing HgO (Sefström, *S.* 22, 328; Turner, *A.* 13, 18; Erdmann a. Marchand, *J. pr.* 31, 395); (2) by determining Cl in HgCl and $HgCl_2$ (Turner, *l.c.*; Svanberg, *J. pr.* 45, 468; Millon, *A. Ch.* [3] 18, 345); (3) by estimating Hg in HgS (Erdmann a. Marchand, *J. pr.* 31, 400); (4) by determining S.H. of Hg.

Hg is distinctly a metallic element. It forms salts by replacing the H of most acids. These salts belong to two series, HgX and HgX_2, where $X = NO_3$, ClO_3, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c. Both series are well represented by definite and stable salts. HgO dissolves in molten KOH, and crystals of $K_2O.HgO$ are obtained on cooling. The compound $Na_2O.HgO$ is said also to exist. HgS dissolves in NaHSAq and conc. KHSAq. The compound $K_2S.HgS.5H_2O$ has been isolated. The existence of these compounds shows that HgO and HgS are slightly acidic towards K_2O and KHS.

The molecular weight of Hg has been directly determined; the molecule is monatomic. The atom of Hg is divalent in the gaseous molecules $HgCl_2$, $HgBr_2$, and HgI_2. The molecular formula of calomel is probably HgCl; if this is so, the atom of Hg is monovalent in this molecule.

Hg is related to Mg and Zn, and more distantly to Be, Ca, Sr, and Ba (*v.* MAGNESIUM GROUP OF ELEMENTS, p. 165; and *cf.* CLASSIFICATION, vol. ii. pp. 204, 207).

Reactions.—1. Heated in *air* or *oxygen*, to near its B.P., Hg slowly forms HgO.—2. *Ozone* produces some Hg_2O at ordinary temperatures; perfectly dry ozone does not react with dry Hg (Shenstone a. Cundall, *C. J.* 51, 619).—3. Hg is oxidised by agitation with solution of *potassium permanganate*; Hg_2O is formed if the solution is cold, and HgO if hot (Kirchmann, *Ar. Ph.* [2] 150, 203).—4. Hg does not react with *hydrochloric acid.*—5. *Sulphuric acid*, when hot and conc., forms $HgSO_4$, or Hg_2SO_4 if there be an excess of Hg and the acid is not very hot, and SO_2; dilute H_2SO_4Aq scarcely acts on Hg.—6. *Nitric acid*, cold and dilute, forms $HgNO_3$; with hot HNO_3Aq and excess of Hg, basic mercurous nitrates, $xHg_2O.yN_2O_5$, are formed; excess of hot HNO_3Aq produces $Hg(NO_3)_2$.—7. Warm conc. *hydrobromic* and *hydriodic acids* produce $HgBr_2$ and HgI_2, respectively (*cf.* Berthelot, *A. Ch.* [5] 16, 433).—8. *Hydrogen sulphide*, or *alkaline polysulphides*, produce HgS.—9. With *nitrogen tetroxide*, forms $HgNO_3$ and NO (Ramsay, *B.* 18, 3154).

Combinations. — 1. Hg combines with the *halogens*, forming HgX or HgX_2 according to the relative quantities of the reacting bodies.—2. With *oxygen*, Hg forms Hg_2O and HgO.—3. With *sulphur* and *selenion*, HgS and HgSe are produced.—4. Hg probably combines with *phosphorus*, but no definite compound has been isolated with certainty.

Detection and Estimation.—Solid Hg compounds are decomposed by drying, mixing well with dry Na_2CO_3, and heating strongly in a small tube closed at one end; Hg is volatilised, and condenses on the cold part of the tube in minute globules. Mercurous salts in solution give a white pp. (HgCl) with HClAq, or a soluble chloride; this pp. is blackened by NH_3Aq with formation of NH_2Hg_2Cl. Mercurous salts are oxidised to mercuric salts by boiling with HNO_3Aq. Mercuric salts are not ppd. by HClAq. H_2SAq, or a soluble sulphide, ppts. black HgS; addition of a small quantity of the reagent causes the formation of a compound of HgS with the original salt present; this pp. is white, yellow, or brown, according to the quantity of reagent used.

Hg is sometimes estimated by heating its dry compounds with powdered CaO, condensing the Hg under water, transferring to a weighed crucible, drying by blotting paper and then over H_2SO_4; the metal is sometimes ppd. by $SnCl_2$ or H_3PO_3Aq at c. 60°, dried, and weighed. Hg is also estimated as HgCl, by adding HClAq, then nearly neutralising with KOHAq, adding K or Na formate, digesting for some days at 60°–70° (Hg is ppd. at boiling temperature), collecting the HgCl on a weighed filter, washing, drying at a low temperature and weighing. Hg is also determined as HgS, by ppn. from $HgCl_2Aq$ by H_2S, and collection on a weighed filter. If the pp. is formed from solutions containing HNO_3Aq or $FeCl_3Aq$ &c., free S is ppd. with the HgS; the pp. may then be heated with CaO and the Hg collected, or heated in Cl, the $HgCl_2$ passed into water, and Hg ppd. by $SnCl_2$. Hg may also be determined by depositing it by electrolysis on a weighed Pt dish. A mercurous salt, in presence of mercuric, may be estimated by ppg. by HClAq, from a cold very dilute solution, not more than a very small quantity of HNO_3 being present.

There are several methods for the volumetric determination of Hg; that described by Hannay, which is based on the fact that the turbidity produced in mercuric salt solutions by a few drops of NH_3Aq is removed by a definite quantity of KCNAq, is said to give satisfactory results. (For details of the methods *v. Manuals of Analysis.*)

Mercury, alloys of; *v.* next line.

Mercury, amalgams of. The alloys of Hg are usually called *amalgams*; the word is supposed to be an alchemist's anagram of μάλαγμα = a soft mass. Amalgams are known of most of those metals which have been fairly well studied. Amalgams are formed by mixing the other metal with Hg, by ppg. the other metal on Hg (or Hg on the other metal), and by placing the other metal in contact with Hg and a dilute acid. Many amalgams are definite compounds, others seem to be merely solutions of metals in Hg, and others are probably solutions of definite compounds in excess of Hg. Amalgams of Bi, Pb, Sn, and Zn, for instance, retain Hg at 360° (B.P. of Hg), but not at 410°. Crystalline amalgams of K and Na, K_2Hg and Na_3Hg, are obtained by heating solutions of K and Na in Hg to 440°.

The best-known amalgams are those of Al, Ba, Bi, Cd, Cs, Ca, Cr, Co, Cu, Au, Fe, Pb, Mg, Mn, Ni, Os, Pd, Pt, K, Ag, Na, Sr, Tl, Sn, and Zn. For brief accounts of these amalgams, with the exception of those of Cu which are described below, *v.* the various metals, ALUMINIUM, BARIUM, &c.; the articles, AMALGAMS, vol. i. p. 149, and ALLOYS, vol. i. p. 132, should be consulted. An interesting paper on *Amalgams*, by Dudley, will be found in *Proc. Amer. Ass. for Advancement of Science*, 1890. 145.

COPPER AMALGAMS (should have been described under COPPER, ALLOYS OF, vol. ii. p. 254). Amalgams of Cu are formed by placing Cu foil in $HgNO_3Aq$, by triturating 3 parts Hg with a mixture of 1 part very finely divided Cu and a few drops of $HgNO_3Aq$, by triturating Hg with NaCl and verdigris, by making Hg the negative electrode during electrolysis of $CuSO_4Aq$, by immersing Na-amalgam, or Zn-amalgam, in $CuSO_4Aq$, and in some other ways. By dissolving Cu in Hg, and removing excess of Hg by pressure, Joule obtained an amalgam having the composition CuHg (*Chem. Gazette*, 1850. 339). By heating amalgams rich in Hg, De Souza obtained $Cu_{16}Hg$ at c. 410°, and $Cu_{14}Hg$ at c. 360° (*B.* 9, 1050). By ppg. Cu from $CuSO_4Aq$ by Fe, washing well, moistening with $HgNO_3Aq$, and rubbing with Hg, amalgams are obtained which harden after a time. The amalgam with from 25 to 33 p.c. Cu, may be obtained soft and plastic by heating nearly to 360°, and kneading for some time in a warm mortar; this amalgam slowly hardens without either contracting or expanding; it is used for stopping teeth (*v.* Von Gersheim, *A.* 70, 344).

Mercury, ammonio-compounds of; *v.* MERCURAMMONIUM COMPOUNDS, p. 206.

Mercury, antimonates of; *v.* vol. i. pp. 285–6.

Mercury, antimonide of. A substance of the nature of an amalgam is formed by triturating together Sb and Hg; little is known of its composition and properties; it is very easily decomposed.

Mercury, arsenates of; *v.* vol. i. p. 309.

Mercury, arsenide of. Bergmann obtained what he thought was a compound of 1 pt. As with 5 pts. Hg by heating Hg and As together.

Mercury, arsenites of; *v.* vol. i. p. 306.

Mercury, bromides of. Two bromides of Hg are known, HgBr and $HgBr_2$. Mercuric bromide has been vaporised; its mol. w. is 359·3 = $HgBr_2$. Mercurous bromide has also been vaporised; the results indicate the mol. w. 279·55 = HgBr; but it is not certain whether partial dissociation into $HgBr_2$ and Hg occurred during vaporisation (*v. infra*; also *Mercurous chloride*, p. 215). Both HgBr and $HgBr_2$ form double compounds with the bromides of metals more positive than Hg.

MERCUROUS BROMIDE. HgBr. (*Mercury proto-* or *mono-bromide.*) Mol. w. 279·55 (?). H.F. [Hg,Br] = 25,475 (Thomsen, *Z. P. C.* 2, 21).

Preparation.—1. By subliming an intimate mixture of 80 pts. Br and 200 pts. Hg.—2. By adding KBrAq to $HgNO_3Aq$.—3. By heating saturated $HgNO_3Aq$, as free as possible from HgO and slightly acidified with HNO_3Aq, with Br, decanting, and allowing to cool in the dark (Stroman, *B.* 20, 2818).—4. By adding alcoholic solution of Br to cold conc. $HgNO_3Aq$ (Stroman, *l.c.*).

Properties and *Reactions.*—As prepared by method 3 (*supra*), forms small, white, nacreous, tetragonal, scales; prepared by method 2, appears as yellow, crystalline, spangles (Stroman, *l.c.*). S.G. 7·307 (Karsten, *S.* 65, 394). Sublimes at 340°–350°. Melts c. 405° (?) (Carnelley, *C. J.* 33, 277). V.D. 146·3 according to Mitscherlich (*P.* 29, 193). Tasteless and odourless. Insol. in water. Hot conc. H_2SO_4 dissolves HgBr with evolution of SO_2; dissolves slowly in hot HNO_3Aq S.G. 1·42; decomposed by hot HClAq dil. or conc.; decomposed by NH_3Aq or KOHAq, forming NH_4Br or KBr, and leaving a black residue which contains Hg (Stroman, *l.c.*). Slowly decomposed by boiling KBrAq, giving $HgBr_2$ and Hg. Soluble in some NH_4 salt solutions.

Combinations.—Two compounds with *strontium chloride* are described by Löwig (*P.* 14, 485). By dissolving HgBr in boiling $SrBr_2Aq$, allowing

to cool, pouring off from separated HgBr, and evaporating, crystals of $6HgBr.SrBr_2$ separate; by dissolving these crystals in water, filtering from HgBr which separates, and evaporating, a very soluble crystalline compound $2HgBr.SrBr_2$ is obtained.

Mercuric bromide. $HgBr_2$ (*Dibromide of Mercury*). Mol. w. 359·3. H.F. $[Hg,Br^2] = 41,880$ (Thomsen, *Z. P. C.* 2, 21).

Preparation. — 1. By dissolving HgO in HBrAq, and crystallising.—2. By bringing Hg into slight excess of Br, warming to remove uncombined Br, and subliming.—3. By heating an intimate mixture of $HgSO_4$ with rather more than its own weight of KBr; the $HgBr_2$ which sublimes is said to contain HgBr.—4. By adding KBrAq to $Hg(NO_3)_2Aq$, evaporating as long as $HgBr_2$ crystallises out, and crystallising from alcohol.—5. By agitating Hg with water, adding Br as long as its colour is removed, boiling, filtering, allowing to crystallise, and drying at c. 150°.—6. By adding excess of Br to a slightly acid solution (S.G. 1·197) of $Hg(NO_3)_2$; HBrOAq is formed in the reaction (Sievers, *B.* 21, 647).

Properties.—White rhombic prisms, isomorphous with $HgCl_2$; $a:b:c = ·6817:1:·9975$ (Hjordthal, *Z. K.* 3, 362). S.G. 5·9202 (Karsten, *S.* 65, 394), 5·7298 at 16°, 5·7461 at 18° (Clarke's *Specific Gravity Tables*, new ed. 32). V.D. 175·5, Mitscherlich (*P.* 29, 193). Melts at 244° (Carnelley a. Williams, *C. J.* 37, 127). Can be sublimed unchanged. S. 1·06 at 9°, 20–25 at 100° (Lassaigne). Very sol. in alcohol and ether. $HgBr_2Aq$ reddens litmus.

Reactions. — 1. Heated with *phosphorus*, *arsenic* or *antimony*, forms bromide of P, As, or Sb.—2. Decomposed, yielding HgBr, by *sunlight*, or contact with *copper* or *mercury*, or by mixing with *cuprous bromide* dissolved in HBrAq.—3 $HgBr_2Aq$ with *ammonia* gives a white pp. of $HgBrNH_2$ (Mitscherlich, *J. pr.* 19, 455).—4. With *sodium hypochlorite*, $HgBr_2Aq$ gives oxychlorides $xHgO.yHgCl_2$ (Rammelsberg). — 5. With *hypochlorous acid*, $HgCl_2$ and $Hg(BrO_3)_2$ are formed (Balard).—6. Decomposed by *nitric* or *sulphuric acid*, giving off Br.—7. Oxybromides, $xHgO.yHgBr_2$, are obtained by boiling $HgBr_2Aq$ with *mercuric oxide*.—8. Mixed with *mercuric iodide* and crystallised from ether or acetone, HgIBr is obtained; this compound is also formed by the action of an *alkyl iodide*, *e.g.* EtI, on $HgBr_2$ dissolved in acetone (Oppenheim, *B.* 2, 571) (*v. Mercury, iodobromide of*, p. 221).

Combinations.—1. With *hydrobromic acid* to form *bromomercuric acid* $HHgBr_3$ (*v. infra*).—2. Combines with many *bromides of more positive metals* than Hg, to form salts regarded by Von Bonsdorff as *bromomercurates* (*P.* 19, 339). These salts are obtained by evaporating solutions of the component bromides; the more important are $HgBr_2.KBr$ and $HgBr_2.2KBr$; $HgBr_2.MgBr_2$ and $2HgBr_2.MgBr_2$; $HgBr_2.SrBr_2$ and $2HgBr_2.SrBr_2$ (Löwig, *P.* 14, 485). Salts containing NaBr, $CaBr_2$, $BaBr_2$, and $ZnBr_2$ were also obtained by Von Bonsdorff (*l.c.*). *Bromomercuric acid*, $HHgBr_3$, was obtained by Neumann (*M.* 10, 236), in long transparent needles, by slightly warming excess of $HgBr_2$ with HBrAq, filtering through asbestos, and cooling to between 0° and −4°. This acid is readily decomposed by moisture or heat. Solution of $HgBr_2$ in HBrAq reacts with alkalis to give $HgBr_2.2MX$ (M = alkali metal); the heat produced is c. 27,200 for 2MOH; the solution of $HgBr_2$ in HBrAq probably contains the acid H_2HgBr_4.—3. With *mercuric cyanide and potassium cyanide*, forms lustrous tablets of $HgBr_2.HgCy_2.2KCy.4H_2O$ (Geuther, *A.* 29, 325). With *mercuric cyanide and zinc cyanide*, forms transparent prisms of $HgBr_2.HgCy_2.ZnCy_2.8H_2O$ (Varet, *C. R.* 109, 809).—4. Heated with *mercuric sulphide*, forms $HgBr_2.2HgS$ (Schneider, *P.* 115, 167); this salt is also obtained by boiling $HgBr_2Aq$ with freshly ppd. HgS (H. Rose, *P.* 13, 59) (*v. Mercuric sulphide, Combinations*, No. 4, p. 225).

Mercury, bromiodide of; *v. Mercury, iodobromide of*, p. 221.

Mercury, bromosulphide of; *v. Mercuric sulphide, Combinations*, No. 4, p. 225.

Mercury, chlorides of. Two chlorides are known, HgCl and $HgCl_2$. The molecular weight of the latter has been determined from the V.D. of the compound. The numbers obtained for the V.D. of the former agreed with the formula HgCl; but it was shown that the vapour produced by heating mercurous chloride contained Hg and $HgCl_2$, hence the V.D. could not decide between the possible formulæ HgCl and Hg_2Cl_2. More recently it has been found that the V.D. calculated from observations of V.D. of mercurous chloride vaporised into an atmosphere of $HgCl_2$ agrees with that required by HgCl (*v. infra*).

Mercurous chloride. HgCl. (*Protochloride of mercury. Calomel*). Mol. w. very probably 235·17. Sublimes at 400°–500° without melting. S.G. 6·993 (Karsten, *S.* 65, 394), to 7·176 (Hassenfratz, *A. Ch.* 28, 3). V.D. 118·6 at 440° (Deville a. Troost, *C. R.* 45, 821); 120·8 (Mitscherlich, *P.* 29, 193). V.D. calculated for HgCl = 117·58. Odling showed that gold-leaf is amalgamated when exposed to calomel vapour at c. 400°; hence he concluded that the vapour contained Hg, and that therefore the observed V.D. did not prove the formula HgCl (*J.* 1864. 280). Debray found that only a limited portion of the calomel vaporised at 440° is decomposed with separation of Hg (*C. R.* 83, 330); hence it appears impossible that calomel should have the molecular formula Hg_2Cl_2, else the observed V.D. at c. 440° would be considerably greater than 120 (calc. for $Hg_2Cl_2 = 235·16$). In 1881, Fileti showed that when a mixture of mercurous and mercuric chlorides is heated to c. 400° in a Pt tube, containing a tube of silver-gilt traversed by a stream of cold water, not a trace of Hg is deposited on the gilt tube. He then determined the V.D. of a mixture of mercurous and mercuric chlorides, and calculated the V.D. of the mercurous chloride in the mixed vapours; the results were 115·9 and 120·1; hence the molecular formula of calomel is most probably HgCl (*G.* 1881. 341). S.H. at 7°–99°, ·05205 (Regnault, *A. Ch.* [3] 1, 129). Crystallises in tetragonal forms, $a:c = 1:1·7414$. H.F. [Hg,Cl] = 32,600 (Thomsen, *Z. P. C.* 2, 21). For T. C. *v.* Von Lang, *P.* 135, 29; for heat of vaporisation, *v.* Marignac, *C. R.* 67, 877.

Occurrence.—As *horn-quicksilver*; in tetragonal crystals. S.G. 6·482.

Formation.—1. By passing Cl over excess of Hg; action proceeds slowly at ordinary temperatures, rapidly at near B.P. of Hg.—2. By reducing $HgCl_2Aq$, saturated at 50°, by SO_2 (Wöhler, *A.* 90, 124; Sartorius, *A.* 96, 325).—3. By reducing $HgCl_2Aq$ by oxalic acid in sunshine (Eder, *B.* 13, 166).—4. By shaking Hg with $FeCl_3Aq$. 5. By ppg. a mercurous salt by HClAq.—6. By heating $HgCl_2$ with Hg.—7. By heating $HgSO_4$ with Hg and NaCl.—8. By triturating Hg with NaCl, $Fe_2(SO_4)_3$, and a little water, till the metal has lost its fluidity, and subliming ($Fe_2(SO_4)_3 + 6NaCl + 2Hg = 3Na_2SO_4 + 2FeCl_2 + 2HgCl$).

Preparation.—1. An intimate mixture of 4 pts. $HgCl_2$ with 3 pts. Hg is made by moistening with alcohol and triturating until the Hg loses its fluidity; the mixture is gently heated for a few hours, again pulverised, and then slowly sublimed in a flask or retort, not more than a quarter filled with the mixture and placed on a thin layer of sand.—2. 4 pts. Hg, 9 pts. dry $HgSO_4$, and 3 pts. water are very intimately mixed, a quantity of NaCl equal to the weight of the Hg and $HgSO_4$ used is added, and the mixture is slowly heated till HgCl sublimes (Planche, *A. Ch.* 66, 168)—3. A well-pulverised mixture of 1 pt. MnO_2, $1\frac{1}{3}$ pts. NaCl, and $2\frac{1}{3}$ pts. Hg is heated with $2\frac{1}{3}$ pts. conc. H_2SO_4, until HgCl sublimes. 4. A warm *dilute* solution of $HgNO_3Aq$, mixed with a little HNO_3 to prevent formation of basic salts, is ppd. by *excess* of dilute NaClAq containing a little HCl; the liquid is heated for some time in contact with the pp. which is then thoroughly washed with cold water in the dark (Scheele; *cf.* Frantwein, *R. P.* 11, 72; 12, 155; Mialhe, *J. Ph.* 22, 586).—5. Cl is passed into $HgNO_3Aq$; the pp. of HgCl mixed with $HgCl_2$ is washed with hot water till $HgCl_2$ is all dissolved; the HgCl is then crystallised from warm $HgNO_3Aq$ (Sievers, *B.* 21, 647).

Properties.—White, semi-transparent, tetragonal, prisms; if sublimed quickly, forms a fibrous mass of small crystals. When powdered, calomel shows a slight lemon-yellow colour. Highly refractive and dispersive. Tasteless and inodorous. Sublimes without melting. Almost quite insol. water, alcohol, ether, and dilute acids. Sl. sol. cold, more sol. hot, $HgNO_3Aq$ (*v.* Debray, *C. R.* 70, 995; *cf.* Drechsel, *J. pr.* [2] 24, 44). Boiled with HClAq, $HgCl_2$ goes into solution, and Hg is separated; with conc. hot H_2SO_4, $HgCl_2$ and $HgSO_4$ are formed. HgCl is decomposed by solutions of alkalis, alkaline earths, and alkaline carbonates, with ppn. of Hg_2O. For experiments on V.D. of calomel, *v. supra*.

Reactions.—1. Exposed to *sunlight*, HgCl darkens with separation of Hg (for action of *heat* on HgCl *v. supra*).—2. Partly decomposed by *aqueous vapour* or *boiling water*, with production of $HgCl_2$ and Hg.—3. Decomposed by many *metals* when heated with them in presence or absence of water, giving metallic chlorides and Hg.—4. Triturated with *iodine* and water, $HgCl_2$ and HgI_2 are produced (Planche a. Soubeiran, *J. Ph.* 12, 651).—5. Heated with a little *sulphur*, HgS and $HgCl_2$ are formed; with excess of S, the products are HgS and S_2Cl_2.—6. Heated in *phosphorus* vapour, HgCl yields PCl_3 and Hg phosphite (Davy).—7. By heating an intimate mixture of 3 pts. HgCl with 1 pt. *arsenic*, a sublimate is obtained consisting in part of yellow tetrahedral crystals; according to Capitaine (*J. pr.* 18, 422) these crystals are *mercuri-arsenic chloride* AsHgCl. The compound is decomposed by hot water to As-Hg amalgam, As_2O_3 and HCl; it is partly decomposed by heat, giving Hg, As, and $AsCl_3$.—8. Reduced by *sulphurous acid*, also by hot *stannous chloride* solution, with separation of Hg.—9. Cold *sulphuric acid* has no action on HgCl; the hot conc. acid forms $HgCl_2$, $HgSO_4$, and SO_2.—10. Dissolved by hot *nitric acid* with evolution of NO; the solution contains $Hg(NO_3)_2$ and $HgCl_2$.—11. Boiling *hydrochloric acid* forms $HgCl_2$ and Hg; boiled in an open vessel with water and a little HCl, no Hg is separated, but $HgCl_2$ goes into solution.—12. Decomposed by *hydrocyanic acid* solution, forming $HgCy_2$, Hg, and HCl.—13. With solution of *alkali chlorides* forms $HgCl_2$, which combines with the excess of alkali chloride to form double salts, some of which are soluble and some insoluble.—14. Digested with solutions of *alkali iodides*, or *iodide of magnesium*, or *iron*, HgI is separated, and metallic chloride goes into solution.—15. Solutions of *alkalis* form Hg_2O and alkali chloride; heated with solid alkalis, Hg, O, and alkali chloride are produced.—16. *Ammonia* produces black NH_2Hg_2Cl (*v.* MERCURAMMONIUM COMPOUNDS).—17. Heated with *carbonates of calcium*, *barium*, or *magnesium*, Hg, Hg_2O, and HgO are separated, and CO_2 is evolved (Buchner, *R. P.* 3, 31; 4, 289; Vogel, *R. P.* [3] 1, 34).—18. With *alkali sulphites* in solution, Hg separates, and a double sulphite of Hg and alkali metal goes into solution. 19. Rubbed with *antimony tri-* or *penta-sulphide*, HgS and $SbCl_3$ are formed.

Testing calomel for impurities.—HgCl sometimes contains $HgCl_2$, $HgNO_3$, or $Hg(NO_3)_2$, or Hg. $HgCl_2$ is detected by shaking with water, filtering, and adding $SnCl_2Aq$, when a white-grey pp. is produced. Bonnewyn (*Bl.* [2] 4, 201) says that $\frac{1}{50000}$ pt. of $HgCl_2$ in HgCl may be detected by immersing a clean knife-blade in the calomel moistened with alcohol or ether; if $HgCl_2$ is present a black spot is formed on the blade. $HgNO_3$ or $Hg(NO_3)_2$ is detected by heating, when NO_2 is evolved. Hg may be detected by examination under the microscope. HgCl may be adulterated with powdered heavy spar, &c.; this remains unchanged on sublimation. Adulteration with gum or other organic material is detected by the smell produced on heating.

Combinations.—1. With *sulphur chloride*, to form $2HgCl.SCl_2$, produced by long-continued warming HgCl with S_2Cl_2; also by heating an intimate mixture of 31 pts. $HgCl_2$ and 2 pts. S in a dish covered with a funnel, on to which the double compound sublimes; also by heating As_2S_5 with $HgCl_2$ ($7HgCl_2 + As_2S_5 = 2AsCl_3 + 3HgS + 2Hg_2SCl_4$). Forms rectangular needles, which melt to a brown liquid, and volatilise without decomposition; decomposed by water (Capitaine, *J. pr.* 18, 422).—2. With *stannous chloride* to form $2HgCl.SnCl_2$. Produced by heating an amalgam of 3 pts. Sn with 1 pt. Hg mixed with 24 pts. HgCl, and subliming. Forms white dendritic crystals; partially decomposed by heat;

wholly decomposed by water, with formation of $SnCl_2$ which reduces the HgCl (Capitaine, *J. pr.* 18, 422).—3. H. Rose (*P.* 44, 325) states that HgCl combines with *sulphur dioxide*.

MERCURIC CHLORIDE. $HgCl_2$. (*Perchloride of mercury. Corrosive sublimate.*) Mol. w. 270·54. [288°] (Carnelley, *C. J.* 33, 276). (303°) (Carnelley a. Williams, *C. J.* 33, 282). S.G. 6·223 (Playfair a. Joule, *C. S. Mem.* 2, 401); 5·448 (Schröder, *P.* 107, 113). V.D. 136·3 (Mitscherlich, *P.* 29, 193). S.H. 12°–45° ·064 (Kopp, *Tr.* 155, 71); 13°–98° ·06889 (Regnault, *A. Ch.* [3] 1, 129). S. 5·73 at 0°, 6·57 at 10°, 7·39 at 20°, 8·43 at 30°, 9·62 at 40°, 11·34 at 50°, 13·86 at 60°, 17·29 at 70°, 24·32 at 80°, 37·05 at 90°, 53·96 at 100° (Poggiale, *A. Ch.* [3] 8, 463). S. cold alcohol 43·5, boiling alcohol 86·2; S. ether 33; S. glycerin 7 (Fairley, *M. S.* [3] 9, 685). Crystallises in two forms belonging to the trimetric system: (i) crystals from alcoholic solution, $a:b:c = \cdot7254:1:1\cdot0686$; (ii) crystals by sublimation, $a:b:c = \cdot9347:1:\cdot3396$ (*v.* Mitscherlich, *P.* 28, 118; Von Lang, *W. A. B.* 45, 119). H.F. $[Hg,Cl^2] = 54{,}490$ (Thomsen, *Z. P. C.* 2, 21).

Occurrence.—In a volcanic district on Ternate, one of the Molucca islands (Frenzel, *Min. Mittheil.* 1877. 305).

Formation.—1. By heating Hg in excess of Cl. 2. By dissolving HgO in hot HClAq, and evaporating.—3. By dissolving Hg in hot HClAq containing some HNO_3, evaporating, and recrystallising from hot water.—4. By adding excess of Cl to a slightly acid solution of $Hg(NO_3)_2$ (Sievers, *B.* 21, 647).

Preparation.—1. An intimate mixture of equal parts NaCl and $HgSO_4$ (obtained by boiling 4 pts. Hg with 5 pts. conc. H_2SO_4 till a dry mass is formed), to which a little MnO_2 has been added (to prevent formation of HgCl from Hg_2SO_4 which may be present), is slowly heated in a long-necked flask or retort; $HgCl_2$ sublimes on the cooler parts of the apparatus. The operation must be conducted in a good draught-cupboard because of the very poisonous nature of $HgCl_2$.—2. Boiling conc. $HgNO_3Aq$ is mixed with conc. HClAq as long as a pp. forms; the pp. of HgCl is boiled with as much HClAq as was used in its formation ($HgNO_3Aq + 2HCl = HgCl_2Aq + H_2O + NO_2$); crystals of $HgCl_2$ separate on cooling; they may be recrystallised from hot water.

Properties.—Translucent crystals, forming a white powder when crushed. $HgCl_2$ has a disagreeable metallic taste; it is extremely poisonous. Melts at 288° (*v. supra*) to a colourless liquid; according to Haass, $HgCl_2$ does not melt when heated if the pressure is less than 120 mm. (*B.* 13, 2203). Easily sol. water; sol. alcohol, ether, and glycerin (*v. supra*). Schröder (*J. R.* 1886. 18) gives the following table, showing the S.G. of aqueous and alcoholic solutions of $HgBl_2$, and the percentage of $HgCl_2$ in these solutions:—

Aqueous solutions of $HgCl_2$.

P.c. $HgCl_2$	*S.G. compared with water at 4°* 0°	10°	20°	30°
1·22	1·01008	1·0099	1·00835	1·00575
2·434	1·02035	1·02018	1·01856	1·01585
3·578	1·0305	1·03022	1·02855	1·02577
4·725	1·0407	1·04033	1·03856	1·03566

Alcoholic solutions.

P.c. $HgCl_2$	*S.G. compared with water at 4°* 0°	10°	20°	30°	*Coefficient of change of S.G.*
0	·8315	·82286	·81435	·80594	·000849
1·22	·8397	·8312	·8228	·8141	·000854
2·38	·8484	·8399	·8314	·8227	·000858
4·42	·8635	·8549	·8403	·8375	·000867
8·56	·8966	·8877	·8789	·8698	·000891
2·43	·9308	·9213	·9119	·9024	·000946
15·91	·9620	·9523	·9425	·9329	·000971
19·32	·9951	·9852	·9753	·9652	·000997
22·46	1·0285	1·0184	1·0083	·9982	·001013

$HgCl_2Aq$ reacts slightly acid to litmus. On boiling $HgCl_2Aq$ some $HgCl_2$ passes off with the steam. $HgCl_2Aq$ is decomposed by light with evolution of O and formation of HCl and Hg oxychloride (*cf.* V. Meyer, *B.* 20, 2970).

Reactions.—1. Many *metals* decompose $HgCl_2$ when heated with it, forming HgCl or Hg; such metals are Sb, As, Bi, Cu, Fe, Pb, Ni, Sn. Many metals also reduce $HgCl_2$ in aqueous solution, generally ppg. HgCl and Hg; Cd, Fe, and Zn pp. Hg only.—2. *Reducing agents, e.g.* $SnCl_2Aq$, SO_2Aq, formic acid, oxalic acid, produce HgCl (*cf.* Eder, *B.* 13, 166; also Wurtz's *Dictionnaire, Suppl.* p. 1066).—3. With many *carbon compounds*, $HgCl_2$ forms HgCl and HCl (the H being withdrawn from the C compound).—4. $HgCl_2$ is not decomposed by *sulphuric* or *nitric acid*; it dissolves fairly easily in HNO_3Aq.—5. Dissolves in hot conc. *hydrochloric acid*; on cooling, a white crystalline mass is obtained which has the composition $2HgCl_2.HCl$ according to Boullay (*A. Ch.* 34, 243; *cf. Combinations*, No. 1).—6. According to Fairley (*B. A.* 1875. 42), *hypochlorites* reduce $HgCl_2$ to HgCl.—7. *Albumen* is rapidly coagulated and ppd. by $HgCl_2Aq$; white of egg serves as an antidote to poisoning by corrosive sublimate.—8. Boiled with *mercuric oxide*, oxychlorides are obtained (*v.* MERCURY, OXYCHLORIDES OF, p. 223).—9. *Alkalis* produce HgO and alkali chloride.—10. *Normal potassium* or *sodium carbonate* ppts. HgO; K(or Na)HCO_3 is also formed, and this reacts with the rest of the $HgCl_2$ to pp. oxychlorides.—11. *Potassium* (or *sodium*) *hydrogen carbonate* produces various oxychlorides (*q.v.* p. 223).—12. *Phosphorus trihydride* produces a black pp. when passed into $HgCl_2$ dissolved in water or alcohol; on continuing the passage of PH_3, the pp. becomes yellow, and then has the composition $P_2Hg_3.3HgCl_2.3H_2O = 2(PHg_2Cl.HgCl_2).3H_2O$; the solution contains HCl. This compound is known as *dimercuriphosphonium-mercuric chloride*; it must be washed quickly with cold water, and dried over H_2SO_4 *in vacuo*; it is decomposed by hot water, giving Hg, HCl, and H_3PO_3; heat produces HCl, Hg, and H_3PO_4 (H. Rose, *P.* 40, 75).—13. *Arsenic trihydride* produces a brown-yellow pp. in $HgCl_2Aq$. This pp. has the composition $AsHg_2Cl.HgCl_2$; it is known as *dimercuriarsonium-mercuric chloride*. The pp. is washed with cold water and quickly dried over H_2SO_4 *in vacuo*; it is decomposed by water to Hg, As_2O_3, and HCl (H. Rose, *P.* 51, 423).

Combinations.—1. With *hydrochloric acid*; according to Boullay (*A. Ch.* 34, 243) the compound $2HgCl_2.HCl$ is obtained by dissolving $HgCl_2$ in hot conc. HClAq, and cooling; this

compound forms a crystalline lustrous mass which melts by the heat of the hand (*v.* also Ditte, *C. R.* 92, 353). Neumann (*M.* 10, 236) obtained *chloromercuric acid* $HHgCl_3$ by gently warming excess of $HgCl_2$ with HClAq, filtering through asbestos, and cooling to between 0° and −4°. This acid is very readily decomposed by heat or moisture. Solutions of $HgCl_2$ in HClAq react with alkalis to form $HgCl_2.2MX$ (M = alkali metal); the heat produced in the reaction is c. 27,200 for 2MOH; the solution of $HgCl_2$ in HClAq probably contains the acid H_2HgCl_4. Dry HCl passed over well-cooled $HgCl_2$ has no action (N., *l.c.*).—2. With many *chlorides* and with some other *salts*. The chief *compounds with other chlorides* are the following (*v.* Von Bonsdorff, *P.* 17, 115):—

(i) With *phosphorus pentachloride*: $3HgCl_2.2PCl_5$. Pearl-white needles; sublimes unchanged; decomposed by water; formed by heating the constituents together (Baudrimont, *A. Ch.* [4] 2, 45).

(ii) With *alkali chlorides*. (*a*) With *potassium chloride*: $2KCl.HgCl_2.H_2O$; $KCl.HgCl_2.H_2O$; $KCl.2HgCl_2.2H_2O$. The first salt is formed by saturating KClAq with $HgCl_2$ at 30°, adding as much KCl as originally used, and evaporating. The second salt is produced by evaporating a solution of equal equivalents of KCl and $HgCl_2$ (Rammelsberg, *P.* 90, 34). The third salt results by saturating KClAq at 60° with $HgCl_2$ and allowing to cool. The compound $6KCl.3HgCl_2.CuCl_2.2H_2O$ was obtained by Von Bonsdorff (*P.* 33, 81) by adding $CuCl_2Aq$ to a dilute solution of $KCl.HgCl_2$. (*b*) With *sodium chloride*: $2(NaCl.HgCl_2).3H_2O$; $2NaCl.HgCl_2$. The first salt is obtained by adding NaCl to NaClAq saturated with $HgCl_2$. The second salt is produced by adding alcohol to saturated NaClAq shaken with powdered $HgCl_2$. (*c*) With *rubidium chloride*: $2RbCl.HgCl_2$; $RbCl.2HgCl_2$; $RbCl.HgCl_2$. Obtained, respectively, by evaporating a neutral solution of RbCl and $HgCl_2$, by evaporating a solution of equal parts of the constituent salts, and by heating the second salt to 50° (Godeffroy, *Ar. Ph.* [3] 12, 47). (*d*) With *ammonium chloride*: $2NH_4Cl.HgCl_2.H_2O$ (*sal alembroth*) is obtained by evaporating a solution of 1 pt. NH_4Cl and 2 pts. $HgCl_2$; loses H_2O in dry air; isomorphous with the corresponding K salt. The other salts obtained are $NH_4Cl.HgCl_2$, $2NH_4Cl.2HgCl_2.2H_2O$ (Kane); $2NH_4Cl.9HgCl_2$, and $2NH_4Cl.3HgCl_2.4H_2O$ (Holmes, *C. N.* 5, 351).

(iii) With *alkaline earth chlorides*. (*a*) With *calcium chloride*: $CaCl_2.5HgCl_2.8H_2O$; by saturating warm $CaCl_2Aq$ with $HgCl_2$, and cooling; by evaporating the mother-liquor the salt $CaCl_2.2HgCl_2.6H_2O$ is obtained. (*b*) With *strontium chloride*: $SrCl_2.2HgCl_2.2H_2O$. (*c*) With *barium chloride*: $BaCl_2.2HgCl_2.2H_2O$. (*d*) With *magnesium chloride*: $MgCl_2.3HgCl_2.5H_2O$ and $MgCl_2.HgCl_2.6H_2O$.

(iv) With *chloride of zinc*: $ZnCl_2.HgCl_2.4H_2O$; by evaporating a mixed solution of the constituents. Analogous salts with $CuCl_2$, $CoCl_2$, $NiCl_2$, and $FeCl_2$ have been obtained.

The chief *compounds with oxysalts* are the following:—

(i) With *ammonium sulphite*: $3HgCl_2.2(NH_4)_2SO_3$. By adding hot saturated $HgCl_2Aq$ to cold $(NH_4)_2SO_3Aq$ (P. de Saint-Gilles, *A.* 84, 266, 269).

(ii) With *potassium chromate*, and *dichromate*: (*a*) $HgCl_2.K_2Cr_2O_7$; by cooling a warm solution of equivalents of the two salts (Millon, *A. Ch.* [3] 18, 388; Darby, *C. S. Mem.* 1, 24). (*b*) $2HgCl_2.K_2CrO_4$; by mixing solutions of the constituent salts in the ratio $2HgCl_2:K_2CrO_4$, adding HClAq sufficient to dissolve ppd. $HgCrO_4$, and evaporating (Darby, *l.c.*).

(iii) With *ammonium dichromate*: (*a*) $HgCl_2.(NH_4)_2Cr_2O_7.H_2O$; by evaporating a solution of the constituents (Abel a. Richmond, *C. J.* 3, 202; *cf.* Darby, *C. S. Mem.* 1, 24; Zepharovich, *W. A. B.* 39, 17). (*b*) $HgCl_2.3(NH_4)_2Cr_2O_7$; by evaporating the mother-liquor from the first salt (A. a. R., *l.c.*; *cf.* Clarke a. Stern, *Am. Ch.* 3, 351).

(iv) With *copper acetate*: $2HgCl_2.Cu(C_2H_3O_2)_2.CuO$; deposited from a mixture of cold saturated solutions of $HgCl_2$ and $Cu(C_2H_3O_2)_2$ (Hutteroth a. Wöhler, *A.* 53, 142).

(v) With *chlorochromtetrammonium chloride*: $6HgCl_2.Cl_2Cr_28NH_3.Cl_4$; by spontaneous evaporation of a mixed solution of the two salts (Clève, *J.* 1862. 150).

3. Compounds of $HgCl_2$ with PHg_2Cl and $AsHg_2Cl$ are known. (*a*) *Dimercuriphosphonium-mercuric chloride* $2(PHg_2Cl.HgCl_2).3H_2O$; a yellow solid formed by passing PH_3 into $HgCl_2$ dissolved in water or alcohol (*v. Reactions*, No. 12). (*b*) *Dimercuriarsonium - mercuric chloride* $AsHg_2Cl.HgCl_2$; a brown-yellow pp. by passing AsH_3 into $HgCl_2Aq$ (*v. Reactions*, No. 13).—4. A compound of $HgCl_2$ with *mercuric sulphocyanide* —$HgCl_2.Hg(CSN)_2$—is obtained by the reaction of $SOCl_2$ with $Hg(SCN)_2$ (McMurtroy, *C. J.* 55, 50).

Mercury, chlorocyanide of; *v. Mercury, cyanochloride of, infra.*

Mercury, chlorosulphides of; *v. Mercuric sulphide, Combinations*, No. 4, p. 225.

Mercury, chloro-iodides of; *v. Mercury, iodochlorides of*, p. 221.

Mercury, chromates of; *v.* vol. ii. p. 155.

Mercury, cyanides of; *v.* vol. ii. p. 342.

Mercury, cyanochloride of. HgCyCl. Quadratic prisms; stable in air; produced by evaporating an aqueous solution of equivalent weights of $HgCl_2$ and $HgCy_2$ (Liebig, *S.* 49, 253; Poggiale, *C. R.* 23, 762; *cf.* Weeren, *J. pr.* 64, 63).

Mercury, cyanoselenides and cyanosulphides of; *v. Mercury, selenocyanides* and *sulphocyanides of*, under Cyanides, vol. ii. pp. 348 and 350.

Mercury, ferrocyanides of; *v.* vol. ii. p. 335.

Mercury, fluorides of. Two are known, HgF and HgF_2; the V.D. of neither has been determined. These fluorides are remarkably unstable both as regards the action of water and of heat.

Mercurous fluoride. HgF or Hg_2F_2. Prepared by adding freshly ppd. Hg_2CO_3 to HFAq so long as the salt is dissolved, and evaporating; also by adding recently prepared HgCl to a solution of Ag_2CO_3 in HFAq, filtering from AgCl, and evaporating on a steam-bath (Finkener, *A.* 110, 142). Berzelius obtained HgF, mixed with HgCl, by subliming a mixture of HgCl with NaF. HgF is a light yellow, crystalline, powder. It is partly

dissolved, and partly decomposed to HF and Hg_2O, by water. Exposed to light when moist it is blackened. HgF may be heated to c. 200° without change; above this temperature Hg sublimes and the glass vessel is corroded. HgF is decomposed by alkalis with separation of Hg_2O; the action of NH_3Aq is more complex. HgF absorbs NH_3 gas forming $N_2H_6Hg_2F_2$ (*v. Mercurammonium compounds*, p. 206). Combines with SiF_4 to form *Mercurous silicofluoride* $Hg_2SiF_6.2H_2O$ (*v. Mercury, silicofluorides of*, p. 224).

Mercuric fluoride. HgF_2. According to Fremy (*A. Ch.* [3] 47, 5), crystals of this compound are obtained by dissolving HgO in excess of HFAq, and evaporating the solution slowly over lime. Finkener (*P.* 110, 628) obtained an *oxyfluoride*, $HgF_2.HgO.H_2O$, by this method; by adding conc. HFAq (50 p.c.) to this oxyfluoride, it was suddenly changed to a white crystalline mass of $HgF_2.2H_2O$ (Finkener, *l.c.*). The hydrated fluoride is decomposed at 30°, giving H_2O, HF, and $HgO.HgF_2.H_2O$ (F.). HgF_2 is decomposed by water with separation of HgO. Addition of slight excess of NH_3Aq to HgF_2 in HFAq ppts. $NH_2Hg_2OF.HF$ (Finkener, *P.* 110, 632). *Mercuric silicofluoride* $HgSiF_6.6H_2O$ probably exists (*v. Mercury, silicofluorides of*, p. 224). Berzelius obtained a compound of HgF_2 with NH_4F by treating HgF_2 with NH_3Aq. HgF_2 combines with HgS (*v. Mercuric sulphide, Combinations*, No. 6, p. 225).

Mercury, fluosulphide of; *v. Mercuric sulphide, Combinations*, No. 6, p. 225.

Mercury, fulminate of; *v.* vol. ii. p. 317.

Mercury, haloid compounds of. Two series of these compounds exist, HgX and HgX_2. The molecular weights of $HgCl_2$, $HgBr_2$, and HgI_2 are known; the molecular weights of HgCl, HgBr, and HgI are probably as represented by these formulæ. The compound $HgI.HgI_2$ also exists, and a periodide of Hg has been isolated. The mercurous compounds HgX are insoluble in water, except HgF, which is partly dissolved, and partly decomposed, by water; the mercuric compounds HgX_2 are soluble in water, with the exception of HgF_2, which is decomposed by water. The Hg haloid compounds combine with many other haloid compounds, and also with oxysalts, to form numerous double salts. The double salts of the type $HgX_2.M^IX$ and $HgX_2.2M^IX$ are best regarded as salts of the mercur-halogen acids $HHgX_3$ and H_2HgX_4 respectively; the acids $HHgX_3$ have been isolated, and probably also the acids H_2HgX_4. The heats of formation of HgX and HgX_2 decrease as the atomic weight of X increases. Thomsen gives the following data (*Z. P. C.* 2, 21):—

X	[Hg,X]	X	[Hg,X²]
Cl	32,605	Cl	54,490
Br	25,475	Br	41,880
I	15,550	I	25,640.

An iodochloride HgICl, and an iodobromide HgIBr, have been isolated.

Mercury, hydrated oxide of. According to Carnelley a. Walker (*C. J.* 53, 80), the hydrate $HgO.H_2O$ is obtained by ppg. $HgCl_2Aq$ by NaOHAq, and drying in air; it is stable to about 100°, and is completely dehydrated at c. 175°. According to Schaffner (*A.* 51, 181) the yellow pp. formed by adding KOHAq to solution of a mercuric salt is $HgO.3H_2O$ (*v. Mercuric oxide*, p. 222). But according to Millon (*B. J.* 27, 112), Marchand (*J. pr.* 37, 277), Rammelsberg (*J. pr.* [2] 38, 559), and Wallace (*Chem. Gazette*, 1858. 345), the pp. obtained from Hg salts by KOHAq is HgO.

Mercury, iodides of. Besides the iodides HgI and HgI_2, corresponding with the chlorides, bromides, and fluorides, of Hg, there is said to exist a definite mercuro-mercuric iodide, $HgI.HgI_2$, and a hexa-iodide HgI_6. Hg and I combine directly with production of heat.

Mercurous iodide. HgI or Hg_2I_2. Mol. w. not known with certainty. Melts at c. 290° (with partial decomposition according to Stroman, *B.* 20, 2818). Boils at c. 310° with partial decomposition (Yvon, *C. R.* 76, 1607). S.G. 7·75 (Boullay, *A. Ch.* [2] 43, 266). S.H. 17°–99° ·03949 (Regnault, *A. Ch.* [3] 1, 129). Crystallises in tetragonal forms, $a:c = 1:1·6726$ (Des Cloizeaux, *C. R.* 84, 1418). H.F. [Hg,I] = 15,550 (Thomsen, *Z. P. C.* 2, 21).

Formation.—1. By rubbing together Hg and I, in the ratio Hg:I, moistened with a few drops of alcohol, and removing the small quantity of HgI_2 which is always formed by treatment with alcohol, in which HgI_2 is soluble but HgI is insoluble.—2. By rubbing together HgI_2 and Hg in the ratio HgI_2:Hg, and dissolving out unchanged HgI_2 by alcohol.—3. By heating 10 parts I with $15\frac{3}{4}$ parts Hg in a retort, on a sand-bath, to not above 250°; HgI sublimes in red crystals, becoming yellow when cold (Yvon, *C. R.* 76, 1607). 4. By adding KIAq to solution of a mercuric salt, preferably the acetate (*v.* Lefort, *Ph.* [3] 3, 823).

Preparation.—A conc. solution of $HgNO_3$, containing a little HNO_3 and free from basic nitrate, is heated to boiling with excess of I; when the I is partially dissolved the liquid is carefully decanted into a warm basin; on cooling, very lustrous, transparent, yellow tablets of HgI separate. The crystals are brought on to a filter (best in the dark), washed with cold water containing a little HNO_3, and then with pure cold water, and dried in the dark at ordinary summer-temperature by placing them on filter paper which is frequently changed (Stroman, *B.* 20, 2818). HgI is obtained as a flocculent pp. by rapidly adding a fairly conc. solution of I in alcohol to cold conc. $HgNO_3Aq$ (S., *l.c.*).

Properties and Reactions.—HgI crystallises in yellow tetragonal tablets, isomorphous with HgCl. HgI is sometimes described as a green powder. Stroman (*l.c.*) says that green preparations are impure. When heated, the yellow crystals become dark yellow, then orange, and finally garnet-red. Yvon (*C. R.* 76, 1607) says that the change of colour begins at 70°, and assigns a definite temperature for each change of colour. Stroman (*B.* 20, 2818) could not connect the different colours with definite intervals of temperature; he says that the salt prepared by him was pure yellow at 100°. Sublimation begins at c. 190° according to Yvon, at c. 110°–120° according to Stroman. HgI when moist is rapidly blackened by light. HgI is very slightly soluble in water; insoluble in alcohol. It is easily decomposed to Hg and HgI_2, *e.g.* by HIAq, KIAq, and similar iodides. Heated rapidly HgI gives a sublimate of Hg and $HgI.HgI_2$. HgI

is used in medicine. For medicinal purposes it must be quite free from HgI_2, which is a violent poison.

MERCURO-MERCURIC IODIDE. $HgI.HgI_2$. A compound of Hg and I of this composition was obtained by Boullay (*A. Ch.* [2] 34, 345) by adding KIAq containing I, in the ratio KI:½I, to $HgNO_3Aq$. The same compound is said to be obtained by adding KIAq to $HgNO_3Aq$ and digesting the pp. for some time in the liquid; also by rubbing together HgI_2 and I in the ratio $3HgI_2$:Hg. Mercuro-mercuric iodide is described as a yellow powder, insol. water and alcohol; unchanged in the dark, but becoming dark when exposed to light. When heated, it turns red, then melts, and may be sublimed unchanged, yielding crystals which are red when hot but become yellow on cooling. HIAq, and various iodides in solution, dissolve HgI_2 leaving HgI, and then decompose the HgI with separatiou of Hg.

MERCURIC IODIDE. HgI_2. Mol. w. 452·86. [238°] (Carnelley a. Williams, *C. J.* 33, 283). (339°–359°) (C. a. W., *l.c.*). S.G. red variety 6·2941 to 6·3004 at 0°, 6·276 at 126°; yellow variety 6·225 at 126° (Rodwell a. Elder, *Pr.* 28, 284); 6·179 at 200° solid; 5·286 at 200° molten (R. a. E., *l.c.*). V.D. 225·7 to 234·4 (Mitscherlich, *P.* 29, 193). S.H. 18°–99° ·04197 (Regnault, *A. Ch.* [3] 1, 129). Crystallises in tetragonal forms (red), $a:c = 1:1·9955$; also in rhombic forms (yellow), $p:p = 114° 30'$. H.F. $[Hg,I^2] = 25,640$ (Thomsen, *Z. P. C.* 2, 21). Change of yellow to red crystals is accompanied by production of heat; 3000 gram-units (Berthelot, *Bl.* [2] 39, 17; *cf.* Weber, *P.* 100, 127). S. ·004 at 17·5°, ·005 at 22°; S. ·286 50 p.c. alcohol at 18°, 1·186 absolute alcohol at 18° (Bourgoin, *Bl.* [2] 42, 620).

Formation.—1. By the action of I on Hg; Dublanc (*Ph. C.* 1849. 656) says that pure HgI_2 is obtained by pouring 1,000 pts. alcohol (93 p.c.) on to 100 pts. Hg, aud adding 124 pts. I in portions of 10 pts. at a time; after each addition of I, the whole is agitated until the alcohol becomes colourless; the addition of the last portion of I should leave the alcohol coloured; the HgI_2 is washed with alcohol.—2. By adding KIAq or FeI_2Aq to $HgCl_2Aq$.

Preparation.—1. 8 pts. $HgCl_2$ and 10 pts. KI are dissolved, separately, in water; the solutions are mixed, and the pp. is thoroughly washed with cold water. Any excess of KI dissolves some HgI_2, and any excess of $HgCl_2$ produces a yellowish pp. containing more or less $HgCl_2$. Williams (*Ph.* [3] 3, 1015) dissolves 8 pts. $HgCl_2$ in 4 pts. NH_4Cl in water, and then adds 10 pts. KI in water.—2. 10 pts. I are suspended in water, and Fe filings are added until all the I is changed to FeI_2; the solution is at once added to a solution of 10¾ pts. $HgCl_2$ iu water, the pp. of HgI_2 is rapidly separated from the liquid (to prevent formation of Fe oxychlorides) and washed with cold water. By crystallising from hot KIAq, or, better, from hot conc. HClAq (Köhler, *B.* 12, 608), HgI_2 is obtained in very lustrous, red tetragonal prisms, with a greenish reflection.

Properties.—HgI_2 obtained by ppn. is a pure scarlet-coloured, crystalline, heavy powder. It is sl. sol. water; S. = ·66 (Wurtz). Sol. hot alcohol; somewhat sol. glycerin (in 340 pts., Fairley, *M. S.* [3] 9, 685); also in ether, and some oils. Sol. KIAq, also in conc. hot HClAq; from these solutions HgI_2 separates in well-formed crystals. HgI_2 is dimorphous. Red (tetragonal) HgI_2 is changed to the yellow (rhombic) modification by heat; the change occurs at 126° (Rodwell a. Elder, *Pr.* 28, 284); it is accompanied by a sudden, and then by a regular, expansion. S.G., red at 126° = 6·276, yellow at 126° = 6·225 (R. a. E.). HgI_2 melts at 238° (Carnelley a. Williams, *C. J.* 33, 283), at 253°–254° according to Köhler (*B.* 12, 608), to a blood-red liquid; melting is attended with considerable expansion. At c. 339°–359° the liquid boils, and sublimes to yellow rhombic plates. The yellow variety passes into the red at the ordinary temperature; this change is hastened by rubbiug or scratching the red crystals; heat is produced in the process, 3,000 gram-units according to Berthelot (*cf.* Weber, *P.* 100, 127). The HgI_2 obtained by adding cold KIAq to cold $HgCl_2Aq$ appears at first yellow, but it quickly changes to red; the change of crystalline form in this case may be observed under the microscope. Solutions of HgI_2 in alcohol, ether, or KIAq are colourless; if the HgI_2 is allowed to form slowly from these solutious, the crystals are red; but if the ppn. is made rapid, *e.g.* by pouring an alcoholic solution into water, the crystals appear yellow for a moment, but they quickly change to red (*cf.* Schiff, *A.* 111, 371; Selmi, *J.* 1855. 417).

Reactions.—1. HgI_2 dissolves in *hydriodic acid* solution with production of heat (*v.* Berthelot, *Bl.* 38, 369). This solution has about the same heat of neutralisation as HIAq (Thomsen); with alkalis it forms salts $HgI_2.2MI$; the solution very probably contains the acid H_2HgI_4 (*cf. Combinations*, No. 2). An *iodomercuric acid*, $HHgI_3$, has been obtained by slightly warming excess of HgI_2 with HIAq, filtering through asbestos, and cooling to between 0° and −4° (Neumann, *M.* 10, 236); this acid is very readily decomposed by moisture and by heat. According to Boullay (*A. Ch.* [2] 34, 345) a solution of HgI_2 in hot HIAq deposits I on cooling, and then crystals of $2HgI_2.3HI$.—2. Most *heavy metals*, *e.g.* Zn, Sn, wheu triturated with HgI_2 remove I and leave Hg; *potassium* acts in the same way.—3. HgI_2Aq is decomposed by *alkalis*, with separation of HgO and formation iu solution of a double salt $xHgI_2.yMI$. *Baryta* and *strontia* react similarly to alkalis.—4. *Lime*, *sodium carbonate*, aud *potassium carbonate* do not decompose HgI_2Aq; but a solution of HgI_2 in alcohol is decomposed by these reagents.—5. HgI_2 dissolves in hot *calcium hypochlorite* solution; on cooliug Ca periodate is deposited and $HgCl_2$ remains in solution (Rammelsberg). 6. When HgI_2 is boiled with *nitric acid*, S.G. 1·5–1·4, $Hg(IO_3)_2$ is formed; with acid S.G. 1·3, white leaflets of $HgI_2.Hg(NO_3)_2$ separate; with acid S.G. 1·2, crystals of unchanged HgI_2 are obtained, together with some of the compound $HgI_2.Hg(NO_3)_2$ (Kraut, *B.* 18, 3461).—7. *Chlorine*, passed into water containing HgI_2 in suspension, produces a yellow solution containing $HgCl_2$ and ICl_3 (Filhol).

Combinations.—1. With *hydriodic acid* (*v. Reactions*, No. 1).—2. With various metallic iodides to form double salts, regarded by Von Bonsdorff as *iodomercurates* (*P.* 17, 265).

These salts have been examined chiefly by Boullay (*A. Ch.* [2] 34, 345). They are generally obtained by dissolving HgI_2 in a solution of the other iodide and evaporating. The following are the most important:—

(i) With *alkali iodides.* (*a*) With *potassium iodide*: $2HgI_2.2KI.3H_2O$; $HgI_2.2KI$. The former is produced by saturating boiling KIAq with HgI_2, filtering, separating from HgI_2 which crystallises out, and evaporating. Sol. alcohol and ether. Decomposed by water, with formation of HgI_2, and $HgI_2.2KI$ which separates on evaporation. These soluble salts may be prepared by boiling KIAq with HgO; the solution contains the double salts and also KOH (*cf.* Jehn, *Ar. Ph.* [3] 1, 97). (*b*) With *sodium iodide*: NaIAq reacts with HgI_2 similarly to KIAq; the compositions of the double salts of NaI with HgI_2 have not been satisfactorily determined. (*c*) With *ammonium iodide*: $2(NH_4I.HgI_2).3H_2O$; obtained, as yellow needles, by dissolving HgI_2 in hot NH_4IAq, separating from HgI_2 which forms on cooling, and evaporating.

(ii) With *other metallic iodides.* BaI_2, SrI_2, CaI_2, and MgI_2 solutions react with HgI_2 similarly to KIAq; the double salts are probably $MI_2.HgI_2$. HgI_2 appears to form double compounds with CdI_2 and FeI_2. The compound $2HgI_2.Cu_2I_2$ was obtained by Hess (*D. P. J.* 218, 183).—3. HgI_2 combines with *mercuric chloride*, also with *mercuric bromide* (*v. Mercury, iodochlorides* and *iodobromide of, infra*).—4. Combines with *mercuric sulphide* (*v. Mercuric sulphide, Combinations*, No. 5, p. 225).

Mercury, hexa-iodide of. HgI_6. This periodide is said by Jörgensen (*J. pr.* [2] 2, 357) to be obtained by adding cold $HgCl_2Aq$, followed by addition of water, to an alcoholic solution of KI_3 heated to 50°. If the solutions are mixed hot, large rhombic crystals of HgI_6 are formed, but they are always mixed with HgI_2. HgI_6 is decomposed quickly by alcohol, slowly by water, with formation of red HgI_2. HgI_6 possesses most of the optical properties of *tourmalin.*

Mercury, iodobromide of. HgIBr. Sulphur-yellow, translucent, rhombic prisms, $a:b:c = \cdot6443:1:\cdot9194$ (Groth, *B.* 2, 574). Melts at c. 229°, and boils at c. 360°; crystallisable from ether; may be sublimed unchanged. Produced by crystallising a mixture of HgI_2 and $HgBr_2$ from ether or acetone; also by the reaction of an alkyl iodide, *e.g.* EtI, on $HgBr_2$ dissolved in acetone (Oppenheim, *B.* 2, 571).

Mercury, iodochlorides of. Two iodochlorides of Hg have been isolated. (i) $HgI_2.2HgCl_2$ $(= Hg_3I_2Cl_4)$. Obtained by dissolving HgI_2 in hot $HgCl_2$, and cooling (Liebig, *S.* 49, 252); also by boiling HgCl with excess of I and much water until I vapour is no longer given off (Selmi, *J.* 1855. 417). (ii) HgICl. Prepared by heating, in a closed tube at 140°–160°, HgI_2, $HgCl_2$, and a little water, until no HgI_2 remains unchanged (Köhler, *B.* 12, 1187). Boullay (*P.* 48, 175) said that HgICl is produced by saturating hot $HgCl_2Aq$ with HgI_2; but Köhler found that very little was formed in this way. HgICl forms a citron-yellow crystalline mass, which becomes red after about 12 hours. The red modification forms tetragonal, the yellow forms rhombic, crystals. HgICl is citron-yellow at c. 125°; it melts at c. 153° to a golden-coloured liquid which solidifies at c. 146°; it is slightly soluble, with partial decomposition, in hot water, more soluble in alcohol. HgICl may be sublimed, with only slight decomposition, in a stream of HCl, SO_2, or H_2S. From a solution of HgICl in dilute HClAq, H_2S ppts. a yellow solid, probably HgICl.HgS (Köhler, *l.c.*).

Mercury, iodosulphides of; *v. Mercuric sulphide, Combinations*, No. 5, p. 225.

Mercury, nitride of. Hg_3N_2. (*Trimercuramine.*) This compound was first isolated by Plantamour (*A.* 40, 115). Ppd. HgO is dried at 40°–50°, and then heated at 100° in a stream of dry NH_3 so long as water is evolved (Hirzel, *J.* 1852. 419). Plantamour directed to pass NH_3 over cold HgO, then to heat to 150° in NH_3, and finally to remove unchanged HgO by HNO_3Aq; Hirzel found that HNO_3Aq reacts with Hg_3N_2. Mercury nitride is a brown powder, very explosive, but requires a higher temperature, or a stronger blow, than nitrogen iodide to explode it. Hg_3N_2 is not acted on by cold dilute H_2SO_4Aq; the hot acid decomposes it. Conc. H_2SO_4 reacts energetically and explosively. Conc. HNO_3Aq forms $Hg(NO_3)_2$ and NH_4NO_3; dilute HNO_3Aq forms a white powder; HClAq forms $HgCl_2$ and NH_4Cl. Mixed with KOH and heated, NH_3 and Hg are formed. Moist Hg_3N_2 is slowly decomposed by light; in water it is changed, after 24 hours, to a white powder.

Mercury, oxides of. Two oxides of Hg are known, Hg_2O and HgO; it is doubtful whether Hg_2O has been obtained free from Hg and HgO. Neither oxide has been gasified, and the mol. w. of neither is known with certainty.

Mercurous oxide. Hg_2O. (*Suboxide*, or *black oxide, of mercury.*) This oxide is prepared by adding NaOHAq or KOHAq to solution of a mercurous salt, or to HgCl suspended in water. The best salt to use seems to be $HgNO_3$; it should be dissolved in water with a very little HNO_3, the solution being made dilute; ppn. with KOHAq, and washing with cold water, should be performed in the dark, and the black pp. should be dried in the dark without heating. Guibourt (*A. Ch.* [2] 1, 422) says that Hg_2O cannot be obtained quite free from Hg and HgO; this is confirmed by Bruns a. O. v. d. Pfordten (*B.* 21, 2010), who assert that Hg_2O oxidises to HgO at the ordinary temperature. Barfoed (*J. pr.* [2] 38, 441) says that the product of the action of NaOHAq on mercurous salts is a mixture of Hg, Hg_2O, and HgO in varying proportions. The descriptions of Hg_2O probably apply to Hg_2O mixed with more or less Hg and some HgO.

Mercurous oxide is a black powder; S.G. 10·69 (Herapath, *P. M.* 64, 321); 8·95 (Karsten, *S.* 65, 394). H.F. $[Hg^2,O] = 24{,}860$ (Thomsen, *Z. P. C.* 2, 21). Hg_2O is decomposed very easily by light or heat, giving HgO and Hg; strongly heated gives Hg and O. Dilute HClAq produces HgCl. Hg_2O is soluble in conc. acetic acid. With dilute acids Hg_2O generally yields mercurous salts; with H_3PO_3Aq it gives H_3PO_4Aq and Hg. Boiled with KIAq, Hg and $HgI_2.2KIAq$ are formed (Berthemot, *J. Ph.* 14, 189). With conc. NH_4ClAq, NH_3 is evolved and Hg and $HgCl_2$ are produced (Pagenstecher, *R. P.* 27, 27; Thompson, *P. M.* [3] 10, 179).

MERCURIC OXIDE. HgO. (*Red oxide of mercury. Red precipitate.*) Mol. w. unknown, as compound has not been gasified. S.G. 11·074 at 17·5° (Herapath, *P. M.* 64, 321); 11·136 to 11·344 at 4° (Playfair a. Joule, *C. S. Mem.* 3, 84, and *C. J.* 1, 137); 11·29 at 4° *in vacuo* (Le Royer a. Dumas, in Böttger's *Tabellarische Uebersicht der Spec. Gewichte der Körper*, Frankfurt, 1837). S.H. 19°–52° = ·053 (Kopp, *T.* 155, 71); 5°–98° = ·0518 (Regnault, *A. Ch.* [3] 1, 129). H.F. [Hg,O] = 22,000 (Thomsen, *Z. P. C.* 2, 21). Crystallises in rhombic forms $a:b:c$ = ·6523:1:·9456 (Nordenskjöld, *P.* 114, 621); in monoclinic forms according to Des Cloiseaux (*A. Ch.* [4] 20, 201). C.E. (0°–100°) ·0058 (Playfair a. Joule, *C. J.* 1, 137).

HgO was known to the Arabians in the eighth century; Geber prepared it by calcining the nitrate; and towards the end of the seventeenth century Boyle obtained it by strongly heating Hg in air.

Formation.—By heating Hg to near its B.P. in a loosely covered vessel for a long time.

Preparation.—1. Hg is dissolved in HNO_3Aq, the solution is evaporated to dryness, the residue is powdered and then heated on a sand-tray so long as N oxides are evolved, the temperature being slowly raised, and the heating continued till a porcelain plate held over the vessel shows a slight deposit of Hg. HgO thus prepared forms red lustrous scales.—2. One of the oxychlorides $2HgO.HgCl_2$, and the oxychloride $4HgO.HgCl_2$, when treated with KOHAq, give red HgO; another oxychloride $2HgO.HgCl_2$, and also the oxychloride $3HgO.HgCl_2$, give yellow HgO by treatment with KOHAq. The compound $2HgO.HgCl_2$ which yields *red* HgO is prepared by mixing 1 vol. $KHCO_3Aq$, free from K_2CO_3, saturated at 15°, with 3 vols. $HgCl_2Aq$, also saturated at 15°, stirring with a glass rod till black streaks appear where the rod rubs the glass, pouring off, adding a fresh quantity of the mixed solution, and again stirring. The compound $2HgO.HgCl_2$ which gives the *yellow* HgO is prepared by stirring a mixture of 1 vol. $KHCO_3Aq$, saturated at 15°, with 6 to 10 vols. $HgCl_2Aq$, also saturated at 15°. The compound $4HgO.HgCl_2$ is prepared by mixing 1 vol. $HgCl_2Aq$ (saturated at 15°) with a large excess (4 to 6 vols.) $KHCO_3Aq$ (saturated at 15°), and allowing to stand for some time (*cf. Mercury, oxychlorides of*, p. 223).—3. $Hg(NO_3)_2Aq$, or $HgCl_2Aq$, is poured into KOHAq; the pp. is thoroughly washed and dried at 100°–120°. HgO thus prepared forms a yellow compact solid.

Properties.—HgO exhibits allotropy; it forms heavy, red, crystalline scales, or a somewhat more bulky, amorphous, yellow powder (*v. supra*). HgO is a violent irritant poison. HgO is very slightly soluble in water; 1 pt. dissolves in 200,000 cold water, or in 125,000 pts. if the water is boiled with HgO and then allowed to cool (Wallace, *Chem. Gazette*, 1858. 345). The solution has a metallic taste. Heated to redness, Hg is separated into Hg and O. Heated below the temperature of decomposition, HgO turns black, but recovers its original colour on cooling. HgO is slowly blackened and decomposed to Hg and O by the action of light. There are differences in the reactions of Cl, $HgCl_2$ in alcoholic solution, and oxalic acid, with the two varieties of HgO (*v. Reactions*, Nos. 8, 9, 10).

Reactions.—1. Decomposed by *heating to redness*, giving Hg and O; Pelouze (*C. R.* 16, 50) said that yellow HgO is decomposed at a lower temperature than the red variety, but this was not confirmed by Gay-Lussac (*C. R.* 16, 309), nor by Millon (*B. J.* 27, 112). Carnelley a. Walker (*C. J.* 53, 80) found that HgO, ppd. by NaOHAq from $HgCl_2Aq$, began to give off O at a little above 175°, and that evolution of O became rapid at c. 415°, at which temperature red HgO was formed and decomposed. Myers's results (obtained by measuring vapour pressures of O from HgO; *B.* 6, 11) agree with those of C. a. W. Debray (*C. R.* 77, 123) found that when a tube containing HgO was sealed, and the whole tube was heated to 440°, the O evolved was almost wholly again absorbed.—2. A mixture of HgO with such *easily oxidised bodies* as P, S, Sb, detonates when heated more or less violently. Some organic compounds are oxidised by boiling in solution with HgO. SO_2Aq boiled with HgO produces SO_3Aq and Hg. $SnCl_2Aq$ forms $SnCl_4Aq$ and Hg.—3. HgO is decomposed, rapidly and somewhat violently, by heating with *magnesium*, in the ratio HgO:Mg, with formation of MgO and Hg (Winkler, *B.* 23, 128).—4. Heated with *sodium*, Na amalgam and the compound $Na_2O.HgO$ are formed (Beketoff, *B.* 13, 2392); the compound $Na_2O.HgO$ is not decomposed by heat, but very quickly by water.—5. HgO dissolves in *molten potash*. If the KOH is nearly saturated with HgO, allowed to cool slowly, and lixiviated with a little cold water, a heavy violet crystalline powder and a lighter greyish-green powder are obtained. The violet powder is said to consist of $K_2O.HgO$, and the greyish powder to contain from 2 to 5 p.c. K_2O; the S.G. of $K_2O.HgO$ is 10·31; it is decomposed at high temperatures, also by continued washing with water, but less completely by alcohol (St.-Meunier, *C. R.* 60, 557).—6. According to Fouberg (*A. Ch.* [4] 1, 300), saturated solutions of the *alkali and alkaline earth haloid compounds* are decomposed, with separation of alkali or alkaline oxides, by boiling with HgO (*cf.* Melsens, *A. Ch.* [3] 26, 220; and H. Rose, *P.* 107, 298). André, however, says that boiling saturated solutions of alkaline earth chlorides react with HgO to form either oxychlorides $x HgCl_2.y HgO$, or compounds of HgO with the alkaline chloride (*C. R.* 104, 431; *v. Mercury oxychlorides of*, p. 223; and also *infra*, *Combinations*, No. 1). According to John (*Ar. Ph.* [3] 1, 97), HgO boiled with KIAq produces KOHAq and the double iodide $HgI_2.KI$.—7. HgO reacts with most *acids* to form mercuric salts HgX_2 ($X = NO_3$, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c.).—8. The reaction of *chlorine* with HgO differs according to the conditions, and the variety of HgO used. Cl scarcely reacts with red crystalline HgO; with yellow HgO, prepared by ppn. and dried at c. 100°, Cl reacts energetically forming $HgCl_2$ and O; with the yellow oxide, dried at 300° and cooled, Cl reacts more slowly, forming Cl_2O and $HgCl_2$, or, if water be present, forming HClOAq and $HgO.HgCl_2$ (*cf.* vol. ii. pp. 12, 16).—9. An *alcoholic solution of mercuric chloride* heated with yellow HgO at once produces black oxychloride $HgO.HgCl_2$; the same oxychloride is formed from the red variety of

HgO only after prolonged action of boiling alcoholic $HgCl_2$ solution.—10. *Oxalic acid solution* reacts with yellow HgO, to form oxalate, in the cold; but the red variety is unchanged when boiled with $H_2C_2O_4Aq$.

Combinations. — 1. With *alkaline earth chlorides*; obtained by the reaction of HgO with solutions of $CaCl_2$, $BaCl_2$, and $SrCl_2$. The compounds $2HgO.CaCl_2.4H_2O$, $HgO.BaCl_2.6H_2O$, and $HgO.SrCl_2.6H_2O$, are described by André (*C. R.* 104, 431).—2. With *ammonia*, to form $2HgO.NH_3.H_2O = NHg_2OH.2H_2O$; this compound reacts with acids as a base forming *dimercuri-ammonium salts* (*v.* MERCURAMMONIUM COMPOUNDS, p. 206).

Mercury, oxybromide of. $3HgO.HgBr_2 = Hg_4O_3Br_2$. (*Basic mercuric bromide.*) A yellow, crystalline, powder; obtained by boiling $HgBr_2Aq$ with HgO, filtering, and allowing to crystallise; or by partial ppn. of $HgBr_2Aq$ by $KOHAq$, and boiling the liquid in contact with the pp. (Löwig, *P.* 14, 485; *cf.* Rammelsberg, *P.* 55, 248).

For H.F. of oxybromides of Hg *v.* André, *Bl.* [2] 41, 274.

Mercury, oxychlorides of. $Hg_xO_yCl_z$. (*Basic mercury chlorides*). Several oxychlorides of Hg are known; they are produced by the reaction of HgO with $HgCl_2Aq$, by partial ppn. of $HgCl_2Aq$ by $KOHAq$ or $NaOHAq$, by mixing $KHCO_3Aq$ and $HgCl_2Aq$ in different proportions, and by the reaction of Cl with yellow HgO.

Millon (*A. Ch.* [3] 27, 253) described oxychlorides obtained by mixing solutions of $KHCO_3$ (free from K_2CO_3) and $HgCl_2$, both saturated at 15°. (i.) $2HgO.HgCl_2$; by adding 1 vol. $KHCO_3Aq$ to 6–10 vols. $HgCl_2Aq$; also by adding 1 vol. $KHCO_3Aq$ to 3 vols. $HgCl_2Aq$, stirring till ppn. begins on the sides of the vessel, pouring off the liquid, adding a fresh quantity of the same mixture, and stirring again. The compound obtained by the first process forms a red non-crystalline powder, and yields *yellow* HgO when acted on by $KOHAq$; as obtained by the second process, the compound is a heavy, black, lustrous solid, which yields *red* HgO with $KOHAq$. (ii.) $3HgO.HgCl_2$; by mixing equal volumes of the solutions of $KHCO_3$ and $HgCl_2$, and allowing to stand; a golden-yellow crystalline pp., yielding *yellow* HgO with $KOHAq$. (iii.) $4HgO.HgCl_2$; by mixing 1 vol. $HgCl_2Aq$ with 4–6 vols. $KHCO_3Aq$, and allowing to stand; a brown crystalline solid, which yields *red* HgO with $KOHAq$.

Roucher (*A. Ch.* [3] 18, 372) described seven oxychlorides, containing $HgCl_2$ and HgO in the ratios 1, ½, ·2, 3, 4, 5, and 6; each oxychloride exists, according to Roucher, in two varieties, one derived from and giving *red* HgO, the other derived from and giving *yellow* HgO; some of the oxychlorides also exhibit other differences. Roucher described 15 different oxychlorides. A tabular statement showing the chief differences between the oxychlorides is given by Roucher.

André (*C. R.* 104, 431) described two oxychlorides, $HgCl_2.3HgO$ and $2HgCl_2.3HgO$, obtained by dissolving HgO in boiling $CaCl_2Aq$ and $MgCl_2Aq$, respectively, and pouring the solutions into large quantities of cold water.

The oxychlorides of Hg have been examined more recently by Thümmell (*Ar. Ph.* 27, 589; *v.* abstract in *C. J.* 56, 1050). T. says that only 5 definite compounds exist, viz., $HgO.2HgCl_2$, $HgO.HgCl_2$, $2HgO.HgCl_2$, $3HgO.HgCl_2$, and $4HgO.HgCl_2$. (i) $HgO.2HgCl_2$ is formed in all solutions prepared by dissolving HgO in $HgCl_2Aq$, but it is readily decomposed; it is best prepared by heating at 100° 1 pt. HgO (red or yellow), with 10 pts. $HgCl_2$, and 60 pts. water, stirring till no further separation of a yellow powder occurs, washing, drying, and then washing with ether (free from alcohol) to remove $HgCl_2$. Warm water separates $2HgO.HgCl_2$; $NaOHAq$ ppts. *red* HgO. (ii) $HgO.HgCl_2$ has not yet been obtained pure. (iii) $2HgO.HgCl_2$ exists in two varieties; (*a*) *red* variety, obtained by mixing solutions of $NaHCO_3$ and $HgCl_2$ in the ratio $2NaHCO_3 : HgCl_2$; (*b*) *black* variety, obtained by heating the red variety when dry, or by adding HgO to hot $HgCl_2Aq$, or by mixing equivalent quantities of *red* HgO and $HgCl_2$ in cold water, or by treating $3HgO.HgCl_2$ with cold $HgCl_2Aq$. (iv) $3HgO.HgCl_2$ is a yellow pp. obtained by adding alkaline carbonate (normal or acid) to $HgCl_2Aq$, avoiding excess of the carbonate, also by treating freshly ppd. *yellow* HgO with $HgCl_2Aq$ (this preparation is yellow and yields *yellow* HgO with $KOHAq$), also by treating washed *red* HgO with $HgCl_2Aq$ (this preparation is reddish yellow and yields *red* HgO by $KOHAq$). (v) $4HgO.HgCl_2$ is obtained as a brown amorphous powder, by adding $KHCO_3Aq$ to $HgCl_2Aq$, in the ratio 30 to 35 $KHCO_3 : HgCl_2$; it is also obtained, as reddish-brown crystalline plates, by shaking $HgCl_2Aq$ with red HgO in the ratio $HgCl_2 : 6HgO$; both varieties give *yellow* HgO by $KOHAq$. All these oxychlorides yield sublimates containing $HgCl$ and $HgCl_2$ when heated.

For H.F. of oxychlorides of Hg *v.* André, *Bl.* [2] 41, 274.

Mercury, oxycyanides of; *v.* CYANIDES, vol. ii. p. 342.

Mercury, oxyfluoride of. $HgO.HgF_2.H_2O$. (*Basic mercuric fluoride.*) A yellow crystalline solid; obtained by dissolving freshly ppd. HgO in $HFAq$, and digesting the solution with HgO, or evaporating the solution (Finkener, *P.* 110, 628). The oxyfluoride is also obtained by heating $HgF_2.2H_2O$ (*q. v.* p. 210) to 30° (F.). Heated above 100°, the oxyfluoride gives off H_2O and HF; it is decomposed by water with separation of HgO.

Mercury, oxyiodide of. $3HgO.HgI_2$. (*Basic mercuric iodide.*) A yellowish-brown solid; obtained by melting together HgO and HgI_2 in the ratio $3HgO:HgI_2$, also by digesting HgI_2 with dilute $KOHAq$ (Rammelsberg, *P.* 48, 182).

Mercury, oxysulphides of. Oxysulphides of Hg have been described; but according to Pollock (*B.* 22, 2859) none has been isolated, and the existence of any is very improbable.

Mercury, phosphide of. No phosphide of Hg has been isolated with certainty. By passing P hydride, prepared by boiling amorphous P with $KOHAq$, into $HgCl_2Aq$, several compounds have been obtained. Aschan (*Chem. Zeitung*, 10, 82, 102) describes a yellow compound $3Hg_3P_2.7HgCl_2$, a red compound $4Hg_3P_2.5HgCl_2$, and a black compound $Hg_3P_2.HgCl_2$. A compound probably $2PH_3.6Hg_2O$ is said by Aschan (*l.c.*) to be formed by passing P hydride over Hg_2CO_3. The pps.

formed when P hydride is passed into $Hg(NO_3)_2Aq$ are probably mixtures of different compounds of Hg, P, and HNO_3 (A.). Most of the foregoing compounds are readily decomposed, some explosively, by warming.

Mercury, salts of. Hg forms two series of salts; *mercurous salts* corresponding with Hg_2O, and *mercuric salts* corresponding with HgO. The former are obtained sometimes by dissolving Hg_2O in acids, sometimes by dissolving Hg in acids and digesting with excess of Hg, and in some cases by double decomposition from the nitrate; the mercuric salts are obtained by dissolving HgO or $HgCO_3$ in acids, or by double decomposition from the nitrate. The mercurous salts have the composition HgX, where X = NO_3, $\frac{1}{2}SO_4$, &c.; the mercuric salts have the composition HgX_2. The mercuric salts are more stable, as a class, than the mercurous salts. The normal mercurous salts are generally decomposed by water into a basic salt, which separates, and an acid salt, which goes into solution. Many basic salts and a large number of double salts are known. The salts of Hg, as a class, act as violent and irritating poisons. The principal salts of Hg are the following (*v.* Carbonates, Nitrates, Sulphates, &c.): *antimonates*, *arsenates* and *-ites*, *bromates*, *carbonates*, *chlorates* and *perchlorates*, *chromates*, *iodates* and *periodates*, *molybdates*, *nitrates* and *-ites*, *phosphates*, *selenates* and *-ites*, *sulphates* and *-ites*, *tantalates*, *thiosulphates*, *tungstates*, *vanadates*.

Mercury, selenide of. HgSe. Small quantities of more or less pure HgSe occur native in the Harz, accompanying PbSe. HgSe is produced by strongly heating together Hg and Se, and subliming at a higher temperature; forms grey, metal-like, lustrous laminæ; dissolved by *aqua regia* with formation of Hg selenite, slowly changed to the same compound by boiling conc. nitric acid (Uelsmann, *A.* 116, 126; *cf.* Little, *A.* 112, 211). HgSe is also formed by passing H_2Se for a long time into $HgCl_2Aq$; the white pp. of $2HgSe.HgCl_2$ at first produced is changed to black HgSe. S.G. of natural HgSe is 7·1 to 7·4; S.G. of artificially prepared HgSe is 8·877.

Combinations.—1. With *mercuric chloride*, to form $2HgSe.HgCl_2$; a white pp. formed by adding H_2Se, or K_2Se, to excess of $HgCl_2Aq$.—2. With *mercuric oxide*, to form 2HgSe.HgO; a black powder formed by treating $2HgSe.HgCl_2$ with NaOHAq. Decomposed by heat, yielding sublimates of HgSe and Hg (Uelsmann, *A.* 116, 126).

Mercury, selenochloride of. $Hg_3Se_2Cl_2$; *v.* *Mercury, selenide of, Combinations*, No. 1.

Mercury, selenosulphide of. A mineral approaching the composition HgSe.4HgS is found near San Onofre in Mexico; it is known as *onofrite*.

Mercury, selenocyanides of. HgSeCy and $Hg(SeCy)_2$; *v.* vol. ii. p. 348.

Mercury, silicofluorides of. Two are known, $Hg_2SiF_6.2H_2O$ and $HgSiF_6.6H_2O$.

Mercurous silicofluoride, $Hg_2SiF_6.2H_2O$. Clear prismatic crystals; obtained by dissolving Hg_2CO_3 in H_2SiF_6Aq, evaporating, washing with a little water, and pressing between paper (Finkener, *P.* 111, 246; *cf.* Berzelius, *P.* 1, 200).

Mercuric silicofluoride, ? $HgSiF_6.6H_2O$. Obtained by dissolving HgO in H_2SiF_6Aq, evaporating till yellow needles ($HgSiF_6.HgO.3H_2O$) begin to separate, and then allowing to stand at a temperature not above 15°. Forms clear, colourless, rhombohedral crystals; very unstable; deliquescent in air, and efflorescent over H_2SO_4; composition doubtful (Finkener, *P.* 111, 246). The compound $HgSiF_6.HgO.3H_2O$ (Finkener) was described by Berzelius (*P.* 1, 200) as the normal salt.

Mercury, sulphides of. Two are known, Hg_2S and HgS; the latter reacts towards the alkali sulphides as an acidic sulphide, it also combines with many Hg compounds to form double compounds.

Mercurous sulphide, Hg_2S. This sulphide is best prepared, according to Berzelius, by dropping mercurous acetate solution into Na or NH_4 sulphide solution (*cf.* Brande, *Q. J. S.* 18, 292). $HgNO_3Aq$ should not be used, as the HNO_3 produced oxidises the Hg_2S. Hg_2S is a black powder, easily decomposed by heat to HgS and Hg. According to Barfoed (*Bl.* [2] 3, 183) the substance described as Hg_2S always contains some Hg, however it may be prepared.

Mercuric sulphide, HgS. Mol. w. uncertain. H.F. [Hg,S] = 8,220 (Thomsen, *Z. P. C.* 2, 21). This compound exists in two forms: a black amorphous pp., and a red crystalline body known as *vermilion* or *cinnabar*.

Occurrence.—In Illyria, Spain, Bohemia, Ural mountains, China, Japan, Mexico, California, Chili, and Peru.

Formation.—1. By rubbing or heating together 1 pt. S and $6\frac{1}{4}$ pts. Hg.—2. By adding H_2S, or an alkaline sulphide, to solution of a mercuric salt.—3. By digesting Hg with an alkaline polysulphide.—4. By subliming a mixture of S and HgO or $HgSO_4$.

Preparation.—1. Amorphous black mercuric sulphide is prepared by passing excess of H_2S into slightly acidified $HgCl_2Aq$ or $Hg(NO_3)_2Aq$, washing the pp. thoroughly with dilute HNO_3Aq and then with water, and drying at a low temperature.—2. Red crystalline mercuric sulphide (vermilion) is prepared in different ways. (*a*) A mixture of 6 pts. Hg and 1 pt. S is heated till combination occurs (attended generally with production of heat and light and partial projection of the mass); the product is powdered, mixed with a small quantity of S, and heated for some hours in a hard glass flask, sunk in sand in a wind-furnace; the flask is loosely closed by a charcoal stopper and is arranged so that the upper part is kept comparatively cold; red HgS sublimes on to the neck of the flask. The HgS is purified by grinding, boiling with KOHAq, and washing with water. (*b*) Black amorphous HgS is heated with an alkaline persulphide. This may be done by triturating 100 pts. Hg with 38 pts. S for some hours, till black HgS is produced, heating with 25 pts. KOH in 130–150 pts. water to 45°–50° for several hours (the water being replaced as it evaporates, and the mass being stirred from time to time) until reddening begins, after which the temperature is maintained at 45° till the whole is bright-red. The red HgS is washed, and any Hg present is removed by levigation (Brunner, *P.* 15, 593; *cf.* Dobereiner, *S.* 61, 380;

Firmenich, *D. P. J.* 172, 370; Liebig, *A.* 5, 289; 7, 49; Raab, *N. R. P.* 24, 39). (*c*) $HgCl_2Aq$ is poured into excess of dilute NH_3Aq; to the pp. of NH_2HgCl thus produced is added conc. $Na_2S_2O_3Aq$ in quantity rather more than sufficient to dissolve the pp., and the whole is heated for some time to 70°–80° (Hausmann, *B.* 7, 1746). For details of the manufacture of *Vermilion v.* DICTIONARY OF APPLIED CHEMISTRY.—3. Colloidal mercuric sulphide, soluble in water, is obtained by ppg. a dilute solution of a mercuric salt by H_2S, and washing with water or dilute H_2SAq for a long time (Winssinger, *Bl.* [2] 49, 452).

Properties.—The black sulphide is an amorphous, heavy powder; heated in a closed vessel, it yields a sublimate of red HgS; heated in air, Hg sublimes and SO_2 is formed; it is not acted on by dilute acids. The red sulphide crystallises in hexagonal forms, $a:c = 1:1·145$; S.G. 8·1 to 8·99; polarises light; blackens by exposure to light (*v.* Heumann, *B.* 7, 750); heated to the sublimation-temperature, red HgS is changed to the black variety (Fuchs, *P.* 31, 581). Mitscherlich (*A.* 12, 168) found V.D. of HgS at 670° to be 85·3; V. and C. Meyer found V.D. at 1560° to be 78; the formula HgS requires V.D. 116; a mixture of Hg + Hg + 2S requires V.D. 77·3. The red sulphide reacts with acids more slowly than the black variety. The colloidal sulphide is soluble in water, forming a solution which is black and opaque when conc., but brown, with a greenish tint by reflected light, when dilute; a very dilute solution may be boiled till all H_2S is expelled, or kept for some time, without change.

Reactions.—1. *Heated in a closed vessel*, HgS sublimes.—2. *Heated in air*, SO_2 is formed, and Hg sublimes.—3. Heated with solid *alkalis* or *alkaline carbonates*, Hg sublimes and alkaline sulphide remains.—4. Heated with *iron*, *tin*, *antimony*, *copper*, *zinc* (and some other metals), a metallic sulphide and Hg are produced; HgS is decomposed by heating with finely divided Cu and water (*v.* Heumann, *B.* 7, 1388, 1486).—5. Digested for some time with *iodine* in KIAq, HgS is decomposed with formation of $HgI_2.2KI$ and separation of S (Wagner, *J. pr.* 98, 23).—6. HgS is decomposed to Hg and SO_2 by heating with *lead monoxide*, Pb being separated.—7. HgS is scarcely attacked by *dilute acids*; *conc. nitric acid* produces $Hg(NO_3)_2$ mixed with $HgSO_4$; HNO_3Aq S.G. c. 1·2 produces a white compound $2HgS.Hg(NO_3)_2$.—8. According to Bolley (*A.* 75, 239) HgS is at once decomposed by an *ammoniacal solution of silver nitrate*, with formation of a mercurammonium salt and Ag_2S.—9. HgS is insoluble in *caustic soda* or *sodium monosulphide* solution; but it dissolves in a mixture of the two, *i.e.* in *sodium hydrosulphide* solution. This solution contains a sulpho- salt (*sulphohydrargyrate of sodium*). The solution is readily obtained by adding KOHAq to ppd. HgS, and passing in H_2S (excess of H_2S causes reppn. of HgS). On evaporation, white crystals $HgS.K_2S.5H_2O$ separate, mixed with KOH; these crystals are decomposed by water (Weber, *P.* 97, 76; *cf.* Brunner, *P.* 15, 596). By ppg. $HgCl_2Aq$ with NH_4 sulphide, and adding KOHAq, a solution is obtained, which, on evaporation, yields KCl, and then a sulpho- salt mixed with KOH. According to Schneider (*P.* 127, 488) the crystals of the sulpho- salt, when kept for some years in KOHAq, form six-sided, lustrous, olive-green tablets having the composition $2HgS.K_2S$.

Combinations.—1. With *alkali sulphides*; *v. supra, Reactions* No. 9.—2. Forms a compound with *hydrogen sulphide*; $31HgS.H_2S$. Produced in solution by passing H_2S into HgS suspended in boiled water (Linder a. Picton, *C. J. Proc.* 1890. 49).—3. With *cuprous chloride* to form $2HgS.Cu_2Cl_2$; a yellow solid, obtained by boiling HgS with $CuCl_2Aq$ and HClAq, and removing S by CS_2 (? $3HgS + 2CuCl_2 = 2HgS.Cu_2Cl_2 + HgCl_2 + S$). This compound is decomposed by boiling conc. HClAq with evolution of a little H_2S and formation of Cu_2Cl_2 and $HgCl_2$ in solution; dilute hot H_2SO_4Aq has no action, but with boiling conc. H_2SO_4, HCl and SO_2 are evolved and a compound of $HgSO_4$ and HgS is formed. NaOHAq produces NaCl, HgS, and Cu_2O (*v.* Heumann, *B.* 7, 1390). 4. With *mercuric chloride*, and also with *mercuric bromide*, to form compounds $2HgS.HgX_2$ (X = Cl or Br). These sulphohaloid compounds are formed (*a*) by passing H_2S into excess of $HgCl_2Aq$ or $HgBr_2Aq$, (*b*) by digesting freshly ppd. HgS with boiling $HgCl_2Aq$ or $HgBr_2Aq$ (H. Rose, *P.* 13, 59), (*c*) by adding HCl (or HBr), or solution of a metallic chloride (or bromide), to HgS dissolved in mercuric acetate solution (Palm, *C. C.* 1863. 120), (*d*) by heating HgS with 8–10 parts $HgCl_2$ or $HgBr_2$, till the whole melts, and washing the cold mass with boiling water (Schneider, *P.* 115, 167). The compounds are yellow-white crystalline powders; decomposed by slow heating to HgS and HgX_2; decomposed by alkali solutions, but not by HNO_3Aq or H_2SO_4Aq (*cf.* Barfoed, *J. pr.* 93, 230).—5. With *mercuric iodide* to form the sulpho-iodide $HgS.HgI_2$; a yellow solid obtained by digesting HgI_2 with less H_2SAq than suffices for complete decomposition (H. Rose, *P.* 13, 59); also by ppg. HgO and HgI_2 in HClAq by a small quantity of H_2S (Rammelsberg, *P.* 48, 175); also by saturating HgI_2 in HIAq with H_2S, and diluting (Kekulé). Palm (*C. C.* 1863. 121) says that the yellow-red pp. obtained by adding HIAq, or a solution of an alkali iodide, to HgS dissolved in mercuric acetate solution, has the composition $2HgS.HgI_2$.—6. With *mercuric fluoride*, to form the sulphofluoride $2HgS.HgF_2$; obtained by passing a little H_2S into HgF_2 dissolved in HFAq (H. Rose, *P.* 13, 59).—7. With *mercuric sulphate*, to form several compounds, the chief of which are (1) $HgSO_4.HgS$, (2) $HgSO_4.2HgS$, and (3) $HgSO_4.3HgS$. These compounds are obtained, (1) by treating red HgS with warm H_2SO_4Aq (Palm, *J.* 1862. 220); (2) by treating $2HgS.HgNO_3$ (obtained by passing a little H_2S into $Hg(NO_3)_2Aq$) with H_2SO_4Aq (Barfoed, *J.* 1864. 282; Kessler, *A. Ch.* [2] 6, 615); (3) by adding $H_2S_4O_6Aq$ to $Hg(NO_3)_2Aq$ and removing S by washing with CS_2 (Spring, *A.* 199, 116; Wackenroder, *A.* 60, 190).—8. With *mercuric nitrate*, to form $2HgS.Hg(NO_3)_2$; a white solid, obtained by passing a little H_2S into $Hg(NO_3)_2Aq$, or by digesting freshly ppd. HgS with $Hg(NO_3)_2Aq$, or by ppg. a solution of HgS in mercuric acetate by HNO_3Aq or alkali nitrate solution (H. Rose, Barfoed, Palm, *l.c.*). By heating HgS with HNO_3Aq, S.G. 1·2, to 120° in a closed tube, Gramp

(*J. pr.* [2] 14, 299) obtained a white crystalline mass of $6HgS.HgO.2Hg(NO_3)_2.12H_2O$.

Mercury, sulphobromide of; *v. Mercuric sulphide, Combinations*, No. 4.

Mercury, sulphochloride of; *v. Mercuric sulphide, Combinations*, No. 4.

Mercury, sulphocyanides of; *v.* vol. ii. p. 350.

Mercury, sulphofluoride of; *v. Mercuric sulphide, Combinations*, No. 6.

Mercury, sulpho-iodides of; *v. Mercuric sulphide, Combinations*, No. 5.

Mercury, sulphoselenide of; *v. Mercury, selenosulphide of*, p. 224.

M. M. P. M.

MERCURY COMPOUNDS, ORGANIC. Mercury forms compounds with two identical alcohol radicles, or with one alcohol radicle and one acid residue. Compounds of mercury with two different alcohol radicles appear to split up at the moment of their formation, *e.g.* 2HgEtMe $= HgMe_2 + HgEt_2$ (Frankland, *A.* 111, 57).

Mercury dimethide $Hg(CH_3)_2$. *Mercury dimethyl.* Mol. w. 230. V.D. 8·29 (calc. 7·97). (93°–96°).

Formation.—1. When mercury is exposed with MeI to sunlight for a week, crystalline CH_3HgI is formed (Frankland, *A.* 85, 361). When this body is distilled with KOH, lime, or KCy, mercury dimethide passes over as a heavy liquid which may be purified by washing with water and rectifying over $CaCl_2$ (Buckton, *Pr.* 9, 91; *A.* 108, 103).—2. By the action of sodium-amalgam on MeI (10 pts.) in presence of acetic ether (1 pt.) (Frankland a. Duppa, *C. J.* 17, 415; *A.* 130, 105).

Properties.—Colourless oil, with faint but mawkish taste. Insol. water, v. sol. alcohol and ether. Dissolves phosphorus, resins, and caoutchouc. Very inflammable, burning with a bright flame.

Reactions.—1. *Iodine* forms CH_3HgI and methane. Bromine acts in like manner.—2. $SnCl_4$ forms a crystalline compound which is decomposed by water with formation of CH_3HgCl.—3. Conc. HClAq gives methane and CH_3HgCl.—4. Conc. H_2SO_4 gives methane and $(CH_3Hg)_2SO_4$.—5. PCl_3 gives $CH_3.HgCl$.—6. $KMnO_4$ oxidises it to $CH_3.Hg.OH$ (Seidel).

Mercuric chloro-methide $CH_3.HgCl$. [170°] (Seidel, *J. pr.* [2] 29, 135). S.G. 4·063 (Schröder, *B.* 12, 563). Formed from $HgMe_2$ by the action of HCl. Laminæ.

Mercuric iodomethide $CH_3.HgI$. [143°]. From MeI and Hg in sunlight (Frankland). Formed also by heating $HgMe_2$ with HgI_2. Small nacreous laminæ (from ether), insol. water, m. sol. alcohol, v. sol. ether and MeI. Slightly volatile, emitting an unpleasant odour, and leaving a persistent nauseous taste. May be sublimed.

Mercuric nitromethide $CH_3.HgNO_3$. [100°]. From an alcoholic solution of $CH_3.HgI$ and $AgNO_3$. Nacreous laminæ, v. sol. water, sl. sol. alcohol. Its solution is not ppd. by KOH or baryta-water, but HCl and soluble chlorides ppt. CH_3HgCl (Strecker, *A.* 92, 79).

Mercuric acetomethide $CH_3.Hg.OAc$. [143°]. Obtained by heating $HgMe_2$ with acetic acid at 130° (Otto, *Z.* [2] 6, 25). Thin tables, with very offensive odour, nearly insol. boiling water and cold HOAc.

Mercuric chloro-methylo-iodide $CH_2Cl.HgI$. [129°]. Obtained by boiling $CH_2I.HgI$ with alcoholic $HgCl_2$ (Sakurai, *C. J.* 41, 360). Silky plates (from alcohol). Decomposed by iodine into methylene chloro-iodide and $HgCl_2$.

Mercuric iodo-methylo-iodide $CH_2I.HgI$. [109°]. Formed by leaving mercury and a little mercurous iodide in contact with methylene iodide in a sealed tube for several days (Wanklyn a. Von Than, *C. J.* 12, 258; Sakurai, *C. J.* 37, 658). White crystals (from CH_2I_2); insol. water, cold alcohol, ether, chloroform, EtI, and benzene; sl. sol. boiling alcohol; v. sol. methylene iodide. When heated with iodine dissolved in aqueous KI it is decomposed into CH_2I_2 and HgI_2. Chlorine and bromine act in like manner. When heated with HClAq it is reduced to $CH_3.HgI$.

Di-mercuric methyleno-di-iodide $CH_2(HgI)_2$. [c. 230°]. Obtained by exposing a mixture of an ethereal solution of methylene iodide with a little HgI_2 and an excess of mercury to sunlight (Sakurai, *C. J.* 39, 487). Formed also by the action of mercury on $CH_2I.HgI$. Yellowish crystalline powder, insol. all ordinary solvents, sl. sol. hot methylene iodide. When heated with dilute HClAq or with KIAq it yields $CH_3.HgI$. Iodine forms HgI_2 and methylene iodide.

Mercuric methenylo-tri-iodide $CH(HgI)_3$. From iodoform, mercury, and alcohol, by exposure to sunlight (Sakurai, *C. J.* 39, 488). Yellow mass, insol. ordinary solvents and in CH_2I_2. Gives iodoform when treated with iodine.

Mercuric diethide $HgEt_2$. Mol. w. 258. (159°). S.G. 2·46. V.D. 9·97 (calc. 9·4). Strecker (*C. R.* 39, 57; *A.* 92, 97) by acting on EtI with mercury obtained the compound EtHgI. Dünhaupt (*Chem. Gaz.* 1854, 263; *A.* 92, 379) obtained the corresponding EtHgCl and EtHgBr by decomposing bismuth triethide with $HgCl_2$ or $HgBr_2$. Buckton (*A.* 109, 218; *C. J.* 16, 17) obtained $HgEt_2$ by the action of $ZnEt_2$ on $HgCl_2$; and, lastly, Frankland and Duppa showed that mercuric diethide can be more easily obtained by the action of sodium-amalgam on EtI in presence of acetic ether. The acetic ether remains in undiminished quantity at the end of the process; but nevertheless its presence is essential.

Preparation.—Ethyl iodide (10 pts.) is mixed with EtOAc (1 pt.) and poured upon $\frac{1}{5}$ p.c. sodium-amalgam, the flask being shaken and cooled in water. When separation of NaI has rendered the liquid pasty it is distilled off from a water-bath and shaken with fresh amalgam. Finally it is mixed with water, and the oil dried over $CaCl_2$ and rectified.

Properties.—Transparent colourless liquid, with faint ethereal odour; insol. water, sl. sol. alcohol and ether. Very poisonous. Burns with smoky flame. Takes fire in chlorine.

Reactions.—1. Acts violently on *bromine* and *iodine*, forming EtHgBr and EtHgI (Buckton, *A.* 112, 220).—2. Alcoholic $HgCl_2$ forms EtHgCl. 3. Conc. HClAq forms ethane and EtHgCl.—4. H_2SO_4 gives ethane and $(EtHg)_2SO_4$.—5. *Sodium* forms a bulky grey spongy mass, which

takes fire in air and violently decomposes when heated.—6. Heated with finely granulated zinc it yields $ZnEt_2$ and mercury (Frankland a. Duppa, *C. J.* 17, 29). *Cadmium* forms $CdEt_2$. *Bismuth* gives $BiEt_3$.—7. Mercuric ethide is decomposed when heated at 150° with *copper*, *iron*, *silver*, or *gold*; but ethides of these metals are not formed. 8. $KMnO_4$ forms EtHgOH.—9. When heated with PCl_3 it forms $PEtCl_2$.—10. *Iodoform* at 90° gives acetylene and ethylene (Suida, *M.* 1, 716).

Mercuric chloro-ethide EtHgCl. [190°] (Seidel). S.G. 3·48. Formed by the action of $HgCl_2$ on $BiEt_3$; by treating $HgEt_2$ with alcoholic $HgCl_2$, and by the action of $HgCl_2$ on $ZnEt_2$. Ppd. by adding NaCl to an aqueous solution of $EtHgNO_3$. Obtained also by treating EtHgOH with HCl. Light iridescent laminæ (from alcohol). Nearly insol. water, sl. sol. ether, v. sol. boiling alcohol. Sublimes at 40°. With Ag_2CO_3 it gives $(EtHg)_2CO_3$, which crystallises with difficulty and is easily decomposed by heat and by acids. Ag_3PO_4 gives a very soluble phosphate (Dünhaupt).

Mercuric iodomethide EtHgI. Formed by the action of mercury on EtI in diffused daylight. Decomposed by direct sunlight (Strecker, *A.* 92, 75). Shining laminæ; insol. water, sol. alcohol and ether. Sublimes at 100°. Dissolves without change in aqueous NH_3 or KOH. With $ZnEt_2$ it yields ZnI_2 and $HgEt_2$.

Mercuric ethylo-hydroxide EtHgOH. Obtained by adding moist Ag_2O to a boiling alcoholic solution of EtHgCl, filtering, and evaporating *in vacuo*. Strongly alkaline liquid, which blisters the skin. V. sol. water. Decomposes ammonium salts with expulsion of NH_3. It does not liberate KOH or MgO from their salts, but it ppts. salts of Al, Zn, Sn, Cu, Au, and Pt. With a large excess of H_2S it forms a white pp. turning through orange to black. With metallic zinc it forms $ZnEt_2$. With acids it forms crystalline salts; *e.g.* HCl yields EtHgCl.

Mercuric bromo-ethide EtHgBr. *Mercuric ethylo-bromide.* Formed from $BiEt_3$ and $HgBr_2$, or by treating EtHgOH with HBr (Dünhaupt, *A.* 92, 379). Resembles EtHgCl.

Mercuric ethylo-cyanide EtHgCy. Formed by saturating an alcoholic solution of EtHgOH with HCy. Crystallises readily; v. sol. alcohol and ether. Very volatile. Gives off a repulsive odour when heated.

Mercuric ethylo-nitrate $EtHgNO_3$. *Mercuric nitro-ethide.* From EtHgI and $AgNO_3$. Colourless prisms, v. e. sol. water, m. sol. alcohol (Strecker).

Mercuric ethylo-sulphate $(EtHg)_2SO_4$. Formed from EtHgCl and Ag_2SO_4. Shining laminæ (from alcohol).

Mercuric ethylo-sulphide $(EtHg)_2S$. Obtained by adding ammonium sulphide to an alcoholic solution of EtHgCl. Yellowish-white powder, v. sol. alcohol, ether, and CS_2. The alcoholic solution is decomposed by evaporation, leaving HgS.

Mercuric ethylo-acetate EtHgOAc. [178°]. Obtained by dissolving $HgEt_2$ in HOAc (Otto, *Z.* 1870, 25).

Mercuric dipropyl $HgPr_2$. (190°) (C.); (180°) (Schtscherbakoff, *J. R.* 13, 353). S.G. $\frac{16}{}$ 2·214. Formed by the action of propyl iodide on sodium-amalgam in presence of acetic ether (Cahours, *C. R.* 76, 133, 1383). Oil, sl. sol. alcohol, v. sol. ether. With iodine and bromine it forms products which may be crystallised from alcohol. The effect of small additions of $HgPr_2$, of $Hg(C_4H_9)_2$, of $Hg(C_5H_{11})_2$, and of $HgPh_2$ on the freezing-point of ethylene bromide has been studied by Louise and Roux (*C. R.* 107, 600).

Mercuric di-isobutyl $Hg(CH_2Pr)_2$. (206°). S.G. $\frac{15}{}$ 1·835. Obtained by treating a mixture of isobutyl iodide and acetic ether with 2 p.c. sodium-amalgam (Cahours). Colourless liquid. Iodine forms $CH_2Pr.HgI$, whence Ag_2O forms $CH_2Pr.HgOH$. Bromine acts in like manner.

Mercuric di-isoamyl $Hg(C_5H_{11})_2$. S.G. $\frac{0}{}$ 1·666. From isoamyl iodide (5 pts.), acetic ether (1 pt.), and sodium-amalgam (Frankland a. Duppa, *A.* 130, 110). Colourless oil, decomposed on distillation even *in vacuo*. May be distilled with steam. Insol. water, v. sl. sol. alcohol, v. sol. ether. With chlorine it forms dense fumes of $C_5H_{11}HgCl$. It reacts with great violence with bromine and iodine. With an alcoholic solution of $HgCl_2$ it readily forms $C_5H_{11}HgCl$ [86°], which crystallises from alcohol in hair-like needles. An ethereal solution of $Hg(C_5H_{11})_2$ treated first with an alcoholic solution of iodine and then with solid iodine forms isoamyl iodide and $C_5H_{11}HgI$ [122°], which crystallises from alcohol in pearly scales. With zinc at 130° $C_5H_{11}HgI$ forms zinc isoamyl and zinc-amalgam.

Mercuric-di-octyl $Hg(C_8H_{17})_2$. S.G. $\frac{17}{}$ 1·342. Prepared by the action of sodium-amalgam on octyl iodide in presence of a little acetic ether (Eichler, *B.* 12, 1880). Liquid. Insol. water, sol. alcohol, ether, and C_6H_6. Decomposes at 200° into Hg and hexadecane (dioctyl).

Mercuric octylo-iodide $C_8H_{17}HgI$: white silky pp. Prepared by the action of an alcoholic solution of iodine on mercury-dioctyl.

Mercuric octylo-chloride $C_8H_{17}HgCl$. White pp. Prepared by the action of mercuric chloride on mercury-dioctyl.

Mercuric octylo-hydroxide $C_8H_{17}HgOH$. [75°]. Prepared by the action of silver oxide on an alcoholic solution of mercury-dioctyl (Eichler, *B.* 12, 1881). Yellow leaflets. Insol. cold, sl. sol. hot, water, v. sol. alcohol. Alkaline.

Mercuric allylo-iodide C_3H_5HgI. [135°]. S. (CS_2) 18·7 at 49°. Formed by shaking allyl iodide with mercury, and extracting the resulting yellow mass with hot alcohol or ether (Zinin, *A.* 96, 363; *cf.* Linnemann, *A.* 140, 180). It is best to mix the allyl iodide with an equal volume of alcohol (Oppenheim, *B.* 4, 670). Silvery scales, which turn yellow on exposure to light, especially on drying. It even turns yellow in the dark. Sublimes at 100°. Sl. sol. cold alcohol, nearly insol. water. Decomposes above its melting-point. $AgNO_3$ added to its alcoholic solution ppts. all the iodine as AgI. Moist Ag_2O ppts. AgI, and the filtrate on evaporation leaves a strongly alkaline syrupy mass which forms salts with acids. HI easily decomposes it, forming HgI_2 and propylene. Iodine forms HgI_2 and allyl iodide (Linnemann, *A.* 133, 133; *Suppl.* 3, 262). PBr_3, acetyl chloride, and BzCl have no action on mercury allyl-iodide. On shaking it with a solution of $ZnEt_2$ in ether an energetic reaction sets in, the products being mercury, ZnI_2, diallyl, and $HgEt_2$. A solution

of KCy acts quickly in the cold, forming diallyl, mercury, $HgCy_2$, and KI; if in distilling off the diallyl the distillation is not stopped in time an explosion occurs. Aqueous KI at 100° forms mercury, diallyl, and $KHgI_3$. The mercury allyl compounds attack the skin, producing blisters which appear after the lapse of 7 hours. The compound C_3H_5HgCl obtained by the action of HCl on the hydroxide is sparingly soluble (Krasowsky, *Z.* 6, 527).

Mercuric propargyl iodide C_3H_3HgI. From propargyl iodide and mercury (Henry, *B.* 17, 1132). Small yellowish crystalline masses.

Mercuric diphenyl $Hg(C_6H_5)_2$. [120°]. (above 300°). S.G. 2·318. Formed by heating a mixture of bromo-benzene, benzene, $HgCl_2$, and sodium (Michaelis a. Reese, *B.* 15, 2876). Prepared by boiling for some time a solution of bromo-benzene (10 pts.) in an equal volume of xylene with 2·7 p.c. sodium amalgam and a little acetic ether (1 pt.). The product is recrystallised from benzene (Dreher a. Otto, *Z.* [2] 4, 685; 6, 9; *A.* 154, 93). Small white needles or prisms, turning yellow in daylight. Insol. water, v. sol. chloroform, CS_2, and benzene, m. sol. ether and boiling alcohol. May be sublimed. Partly decomposed on distillation into mercury, diphenyl, benzene, and charcoal.

Reactions.—1. Dry HCl gives benzene and $HgCl_2$. HI, nitric acid, HBr, and H_2SO_4 act in like manner.—2. When melted with *sulphur* (2 at.) the products are HgS and phenyl mercaptan.—3. *Iodine* (2 at.) in alcoholic or CS_2 solution forms PhHgI and iodobenzene. Excess of iodine forms HgI_2 and iodo-benzene.—4. *Chlorine* forms PhHgCl and chloro-benzene. Br acts in like manner.—5. Glacial *acetic acid* yields benzene and PhHgOAc.—6. *Aluminium foil* at 130° forms $AlEt_3$ [230°] (Friedel a. Crafts, *A. Ch.* [6] 14, 460).—7. Alcoholic $HgCl_2$ at 100° gives PhHgCl.—8. When boiled with *sodium*, benzene and sodium-amalgam are formed.—9. SO_3 gives mercuric benzene sulphonate (Otto, *J. pr.* [2] 1, 179).—10. *Allyl iodide* forms diallyl, diphenyl, and PhHgI (Suida, *M. I.* 715).—11. $C_6H_5SO_2Cl$ at 160° forms $C_6H_5SO_2C_6H_5$ and PhHgCl (Otto, *B.* 18, 246).—12. $COCl.CO_2Et$ forms phenyl-glyoxylic ether (Claisen a. Morley, *B.* 11, 1596). 13. When oxidised by $KMnO_4$ the hydroxide PhHgOH is probably first formed, but on adding HCl this is changed to PhHgCl (Seidel, *J. pr.* [2] 29, 134; Otto, *J. pr.* [2] 29, 136).

Mercuric phenylo-chloride $C_6H_5.HgCl$. *Mercuric chlorophenylide.* [250°]. Obtained by slowly passing chlorine over $HgPh_2$ or into its solution in CS_2. Prepared by heating $HgPh_2$ with $HgCl_2$ in alcoholic solution at 110°. Trimetric tables (from benzene). May be sublimed. Sl. sol. alcohol and benzene, insol. water.

Mercuric phenylo-bromide C_6H_5HgBr. [275°]. Resembles the preceding in preparation and properties. Br forms $HgBr_2$ and bromo-benzene. When heated with an alcoholic solution of K_2S the products are KBr, HgS, and $HgPh_2$.

Mercuric phenylo-iodide C_6H_5HgI. [266°]. From $HgPh_2$ and I in alcohol. Satiny tables (from alcohol-benzene). Insol. water, nearly insol. cold alcohol, ether, and benzene, m. sol. hot benzene and chloroform, v. sol. CS_2. May be partially sublimed. Sodium-amalgam reduces it in alcoholic solution to $HgPh_2$.

Mercuric phenylo-hydroxide C_6H_5HgOH. From PhHgCl by boiling with alcohol and moist Ag_2O. White trimetric prisms (from alcohol), sol. boiling water, alcohol, and benzene, sl. sol. cold water. Softens at 160°, but is not melted at 200°. The aqueous solution is alkaline in reaction. Expels NH_3 from its salts; ppts. alumina from alum, and absorbs CO_2 from the air.

Mercuric phenylo-cyanide PhHgCy. [204°]. From $HgPh_2$ and $HgCy_2$ in alcoholic solution at 128°. Long slender trimetric prisms; v. sl. sol. boiling water, m. sol. boiling alcohol and benzene. Conc. HClAq at 120° forms $HgCl_2$, formic acid, benzene, and NH_3. Alcoholic KOH forms mercury, benzene, and potassium cyanate. Iodine forms PhHgI and ICy. H_2S forms HgS, benzene, and HCy.

Mercuric phenylo-sulphocyanide PhHgSCy. [227°]. From $HgPh_2$ and $Hg(SCy)_2$. Silky plates; sol. boiling alcohol.

Mercuric phenylo-nitrate $PhHgNO_3$. [c. 167°]. From PhHgCl and $AgNO_3$ in alcohol. Trimetric silky plates; v. sl. sol. boiling water. Conc. HClAq gives benzene and mercuric nitrate.

Mercuric phenylo-carbonate $(PhHg)_2CO_3$. From PhHgCl and Ag_2CO_3. Small white needles; sl. sol. boiling water, m. sol. boiling alcohol and benzene. Not decomposed on fusion.

Mercuric phenylo-formate PhHgO.CHO. [171°]. From $HgPh_2$ and concentrated formic acid. Small tables.

Mercuric phenylo-acetate PhHgOAc. [149°]. Obtained by boiling $HgPh_2$ with excess of HOAc, ppg. with water, and crystallising from hot water. Radiate groups of prisms; sl. sol. cold, m. sol. hot, water; m. sol. alcohol and benzene. Decomposed by distillation yielding diphenyl, benzene, Ac_2O, HOAc, carbon, and mercury. Boiling aqueous HCl forms benzene, $HgCl_2$, and HOAc. Other mineral acids act in like manner. Sodium-amalgam reduces it in alcoholic solution to benzene. Iodine, acting on its aqueous solution, forms HgI_2, iodo-benzene, and HOAc. H_2S forms HgS, benzene, and HOAc.

Mercuric phenylo-propionate $PhHgOC_3H_5O$. [c. 166°]. From $HgPh_2$ and boiling propionic acid. Crystals; sol. hot water, alcohol, and benzene.

Mercuric phenylo-myristate $PhHgOC_{14}H_{27}O$ From $HgPh_2$, myristic acid, and alcohol at 120°. Small scales; sol. boiling alcohol and benzene. Boiling HClAq splits it up into $HgCl_2$, benzene, and myristic acid (Otto, *J. pr.* [2] 1, 179).

Mercuric tetra-methyl-di-amido-di-phenyl $(NMe_2.C_6H_4)_2Hg$. [169°]. Formed by the action of sodium-amalgam in presence of EtOAc on *p*-bromo-di-methyl-aniline dissolved in xylene (Schenk a. Michaelis, *B.* 21, 1501). Colourless crystals, turning green in air. Crystallises from benzene with C_6H_6 (1 mol.). V. e. sol. chloroform, and benzene, v. sl. sol. alcohol and ether.

Mercuric di-*o*-tolyl $Hg(C_6H_4Me)_2$. [107°]. From o-bromo-toluene sodium-amalgam, and

acetic ether (Ladenburg, *A.* 173, 162). Large triclinic tables (from benzene).

Mercuric o-tolylo-chloride [2:1]$C_6H_4Me.HgCl$. *o-Tolyl-mercuric chloride.* [146°]. Formed by treating mercuric di-*o*-tolyl with $HgCl_2$ in ethereal solution (Michaelis a. Genzken, *A.* 242, 180). Needles; v. sol. chloroform, m. sol. alcohol and benzene, sl. sol. ether and petroleum-ether. Sublimes with partial decomposition.

Mercuric *m*-tolylo-chloride [3:1]$C_6H_4Me.HgCl$. [160°]. Obtained by boiling $(C_6H_4Me)_3SbHgCl_2$ with alcohol (M. a. G.). Needles (from alcohol); v. sol. chloroform and benzene, m. sol. alcohol. H_2S passed into its alcoholic solution ppts. HgS.

Mercuric di-*p*-tolyl $Hg(C_6H_4Me)_2$. [238°]. Formed from *p*-bromo-toluene, sodium-amalgam, and EtOAc (Dreher a. Otto, *A.* 154, 171; Ladenburg, *A.* 173, 163). Needles or tables; insol. water, sl. sol. cold alcohol, m. sol. hot benzene, CS_2, and $CHCl_3$. May be distilled. Boiling conc. HClAq gives toluene and $HgCl_2$

Mercuric p-tolylo-chloride $C_6H_4Me.HgCl$. [187°]. Small tables (Otto, *J.pr.* [2] 1, 185).

Mercuric p-tolylo-iodide $C_6H_4Me.HgI$. [220°]. From mercuric di-*p*-tolyl and iodine. Trimetric satiny tables; insol. water, sl. sol. boiling alcohol, m. sol. hot benzene. May be sublimed.

Mercuric p-tolylo-acetate $C_6H_4Me.HgOAc$. [153°]. Small trimetric prisms; nearly insol. cold water, sl. sol. boiling water, m. sol. alcohol. Behaves like the corresponding phenyl compound.

Mercuric-di-*p*-xylyl $(C_6H_3Me_2)_2Hg$. [123°]. Prepared by the action of sodium-amalgam on bromo-*p*-xylene (Jacobsen, *B.* 14, 2112). Thick prisms; sol. CS_2, chloroform, and benzene, sl. sol. alcohol and ether.

Mercuric di-*m*-xylyl [1:3:4] $(C_6H_3Me_2)_2Hg$. [170°]. From bromo-*m*-xylene and 2 p.c. sodium-amalgam by heating at 145° for 12 hours (Weller, *B.*20, 1718). Slender felted needles; sl. sol. ether, alcohol, and cold benzene; v. sol. hot benzene. Boiling HClAq gives $HgCl_2$ and *m*-xylene. PCl_3 forms $C_6H_3Me_2PCl_2$ (257°) and $C_6H_3Me_2HgCl$.

Mercuric di-*n*-propyl-di-phenyl $Hg(C_6H_4Pr)_2$. [110°]. From $Br.C_6H_4.Pr$ [1:4] and sodium-amalgam (R. Meyer, *J. pr.* [2] 34, 103). Long needles.

Mercuric di-cymyl $Hg(C_{10}H_{13})_2$. [134°]. Formed by heating a mixture of bromo-cymene with xylene and sodium-amalgam with addition of a little acetic ether (Paternò a. Colombo, *B.* 10, 1749). Long slender needles; m. sol. boiling alcohol, benzene, and xylene.

Mercuric di-pentamethyl-phenyl $Hg(C_6Me_5)_2$. [266°]. From bromo-pentamethyl-benzene, chloroformic ether, and sodium-amalgam (Jacobsen, *B.* 22, 1220). Prisms (from xylene); v. sl. sol. alcohol and ether, v. sol. hot xylene.

Mercuric di-naphthyl $Hg(C_{10}H_7)_2$. Mol. w. 454. [243°]. S.G. 1·93 (Schröder, *B.* 12, 564). Formed by boiling (α)-bromo-naphthalene with several times its volume of crude xylene, pasty sodium-amalgam, and a little acetic ether for 19 hours, and filtering while hot (Otto a. Mörics, *A.* 147, 164; *Z.* [2] 3, 377; 4, 162). Small minute, trimetric prisms (from benzene or CS_2). Not affected by air or light. Insol. water, sl. sol. boiling alcohol, cold benzene or ether, m. sol. hot CS_2, chloroform, and benzene. Decomposed by heat. Conc. HIAq forms HgI_2 and naphthalene. HCl and HBr act in a similar way. Iodine forms HgI_2, $C_{10}H_7HgI$, and ultimately $C_{10}H_7I$. It does not react with $HgCl_2$.

Mercuric naphthylo-bromide $C_{10}H_7HgBr$. [196°]. From $Hg(C_{10}H_7)_2$ and bromine. Formed also by heating $Hg(C_{10}H_7)_2$ with $HgBr_2$. Needles; insol. water, sol. hot alcohol.

Mercuric naphthylo-iodide $C_{10}H_7HgI$. [185°]. From mercuric di-naphthyl and iodine (1 mol.) in CS_2. Soft satiny needles or dendritic groups. Not altered by light; insol. water, sl. sol. hot alcohol and benzene. Sodium-amalgam converts it into mercuric di-naphthyl.

Mercuric naphthylo-acetate $C_{10}H_7HgOAc$. [154°]. Formed, together with naphthalene, by heating mercuric di-naphthyl with excess of HOAc. Small needles (from alcohol); insol. water, v. sol. hot HOAc, alcohol, CS_2, benzene, and chloroform, m. sol. ether. Hot HClAq gives naphthalene and HOAc. Sodium-amalgam acting on its alcoholic solution forms naphthalene and HOAc. Water at 140° has no action.

Mercuric naphthylo-butyrate $C_{10}H_7.Hg.OC_4H_7O$. [200°]. Very slender needles; sol. hot water.

MESACONIC ACID $C_5H_6O_4$ *i.e.* $CH_3.C(CO_2H):CH.CO_2H$. Mol. w. 130. [202°]. S. 2·7 at 18°; 118 at 100° (Pebal, *A.* 78, 130); 2·6 at 14°; 3·4 at 22° (Baup, *A.* 81, 97). S. (90 p.c. alcohol) 30·6 at 17°; 95·7 at 78° (P.); (88 p.c. alcohol) 38 at 22° (B.). R_∞ 46·9 in a 3·69 p.c. aqueous solution (Kanonnikoff, *J.pr.* [2] 31, 349). *Heat of solution* −5493. *Heat of combustion* 27,334 (Gal a. Werner, *Bl.* [2] 47, 159). H.C. 479,063 (Louguinine, *C. R.* 106, 1291).

Formation.—1. By boiling a dilute solution of citraconic acid for half an hour with one-sixth of its volume of nitric acid. Mesaconic acid is deposited on cooling (Gottlieb, *A.* 77, 268; Pebal, *A.* 78, 129; Baup, *A.* 81, 96).—2. By boiling citric acid with conc. HIAq or HBrAq (Kekulé, *A. Suppl.* 2, 94; Fittig, *A.* 188, 77, 80). 3. By heating a conc. aqueous solution of itaconic or citraconic acid at 180° to 200°, CO_2 and an empyreumatic oil being also formed (Swarts, *Bull. Acad. Royale Belgique,* [2] 36, No. 7). 4. From *citra-* and *mesa*-di-bromo-pyrotartaric acids by heating with KI and copper at 150° (Swarts, *Z.* 1868, 259).—5. The mono-anilide is heated with (3 mol. of) KOH and a little water for 1½ hours in the water-bath. The aniline separates out and is removed by means of ether, the acid being ppd. by means of SO_4H_2 (Anschütz, *A.* 254, 136).—6. 'Oxy-tetric acid,' which is formed from methyl-aceto-acetic acid by successive treatment with bromine and alcoholic potash (Demarçay, *A. Ch.* [5] 20, 473), is identical with mesaconic acid (Gorboff, *J. R.* 1887, 605; Cloëz, *Bl.* [3] 3, 598, 602).

Preparation.—By evaporating a mixture of citraconic anhydride (10 pts.), water (22 pts.), and conc. HNO_3 (3 pts.), until red fumes begin to appear. The product is crystallised from water (Fittig, *A.* 188, 73).

Properties.—Slender needles (from water) or

prisms (from alcohol); sl. sol. cold, v. sol. hot, water. V. sol. alcohol and ether. May be sublimed without decomposition. Its molecular weight, determined by Raoult's method, is identical with that of citraconic and of itaconic acid (Paternò, *B.* 21, 2157). Mesaconic acid is slightly coloured by $FeCl_3$, and the solution when boiled yields a brown gelatinous pp. which re-dissolves on cooling. The addition of more $FeCl_3$ prevents its re-dissolving. Neutral solutions of mesaconates give a brown pp. with $FeCl_3$, insoluble in excess of the reagent or when heated.

Reactions.—1. Conc. HIAq at 160° forms pyrotartaric acid.—2. *Sodium amalgam* also reduces it to pyrotartaric acid. The same reduction may be effected by zinc-dust (Böttinger, *B.* 9, 1821).—3. *Bromine* has no action in the cold (difference from citraconic acid) but above 60° it combines, forming mesa-di-bromo-pyrotartaric acid [170°] (Kekulé, *A. Suppl.* 2, 85).—4. *Chlorine* passed into water in which mesaconic acid is suspended forms a solution which when evaporated leaves chloro-citramalic acid $C_5H_7ClO_5$ (chloro-oxy-pyrotartaric acid). The same acid is formed, together with tri-chloro-acetone, by passing chlorine into an aqueous solution of sodium mesaconate.—5. Does not combine with HBr in the cold, but by prolonged heating with HBrAq at 100° or 140° it is converted into *citra*-bromo-pyrotartaric acid; an acid that is formed also by the union of HBr with citraconic acid in the cold. — 6. When repeatedly heated with fuming HClAq at 160° it is converted into *citra*-chloro-pyrotartaric acid [130°], which is decomposed by boiling water into HCl and mesaconic acid (Swarts).—7. The *electrolysis* of potassium mesaconate yields, at the positive pole, CO_2 and allylene (Aarland, *J. pr.* [2] 6, 256; 7, 142).—8. AcCl forms citraconic anhydride. Mesaconic anhydride has not been obtained (Petri, *B.* 14, 1636).—9. On evaporating a solution of the *aniline* salt water is not eliminated from the molecule (difference from citraconic acid).

Salts.—NH_4HA''. S. 12·5 at 15°. Very small prisms.—$BaA''4aq$: monoclinic crystals, more sol. water than barium citraconate and itaconate (Petri, *B.* 14, 1634).—$BaH_2A''_2 2aq$: pearly hexagonal plates.—$CaA''aq$. S. 6 at 20°. Very small needles, insol. alcohol.—$PbA'' 1\frac{1}{2}aq$: deposited in the cold as a crystalline pp., v. sl. sol. water.—$PbA''aq$: deposited from a hot solution as an amorphous pp.—$PbH_2A''_2$ (dried at 100°). Small needles.—$(HO.Pb)_2A''_2$: ppd. by adding lead subacetate to a solution of sodium mesaconate (Otto, *A.* 127, 182).—$CuA''2aq$.—Ag_2A'': crystalline pp., sl. sol. water.—$AgHA''$: needles, m. sol. hot water.

Methyl ether Me_2A'' (205° i. V.). S. ·8 at 15°. S.G. $\frac{15}{15}$ 1·1254; $\frac{30}{30}$ 1·1138. M.M. 1·154 at 21°. μ_D 1·4564 at 16° (Gladstone); 1·4570 at 17° (Knops, *A.* 248, 195); μ_H 1·4813 at 16° (Gladstone). From the acid, MeOH, and HCl (Perkin, *C. J.* 39, 556).

Ethyl ether (229° i. V.). S.G. $\frac{15}{15}$ 1·051; $\frac{30}{30}$ 1·039 (Perkin); $\frac{20}{4}$ 1·0468 (Knops, *A.* 248, 196). M.M. 1·168 at 25°. μ_D 1·4433; μ_H 1·4727 at 16° (Gladstone; *cf.* Knops). Formed by the action of alcohol and HCl on mesaconic and on citraconic acids.

Chloride $C_3H_4(COCl)_2$. (80° at 17 mm.). Prepared by the action of PCl_5 on mesaconic acid or citraconic anhydride (Petri, *B.* 14, 1634). Colourless liquid.

Amide $C_5H_4O_2(NH_2)_2$: [177°]; colourless flat crystals, sol. water.

Anilide $C_5H_4O_2(NHPh)_2$: [186°]; flat white silky needles, sol. alcohol and ether, sl. sol. water. Heated to 268° it decomposes into aniline and citraconanil (the phenylimide of citraconic acid) (O. Strecker, *B.* 15, 1639).

Mono-anilide $C_3H_4(CO_2H)(CONHPh)$. [153°]. Formed by heating citraconic anhydride with aniline at 170°, rectifying *in vacuo* the resulting phenylimide (172° at 12 mm.), dissolving it in baryta-water, ppg. excess of barium by CO_2, and then adding HCl (Anschütz, *A.* 254, 133). Identical with the product which separates from an aqueous solution of acid aniline citraconate on standing. White powder. Converted by heating in a sealed tube with KOH into mesaconic acid.

Constitution.—Mesaconic acid stands to citraconic acid in the same relation that fumaric stands to maleic acid. This is shown by their behaviour towards Br, HBr, and aniline, and by the physical constants of their ethers. Hence mesaconic acid is methyl-fumaric acid, while citraconic acid is methyl-maleic acid. The constitution of mesaconic acid will therefore be known as soon as that of fumaric acid has been satisfactorily determined (*v.* MALEÏC ACID).

MESA-DI-BROMO-PYROTARTARIC ACID *v.* DI-BROMO-PYROTARTARIC ACID.

TRIMESIC ACID $C_9H_6O_6$ *i.e.* $C_6H_3(CO_2H)_3$ [1:3:5]. *Benzene-s-tri-carboxylic acid.* Mol. w. 210. [c. 325°]. H.C.v. 768,500. H.C.p. 767,600. H.F. 285,400 (Stohmann, Kleber a. Langbein, *J. pr.* [2] 40, 140).

Formation.—1. By the oxidation of mesitylene or mesitylenic acid by chromic acid mixture (Fittig, *A.* 141, 153).—2. By the oxidation of uvitic acid (Baeyer, *Z.* 1868, 119; Fittig, *A.* 147, 301), and of *s*-tri-ethyl-benzene (Jacobsen, *B.* 7, 1435; Friedel a. Balsohn, *Bl.* [2] 34, 636) by chromic acid mixture.—3. One of the products obtained by heating hydromellitic or iso-hydromellitic acid with conc. H_2SO_4 (Baeyer, *A. Suppl.* 7, 40, 48).—4. By heating mellitic acid with glycerin (Baeyer, *A.* 166, 340).—5. In very small quantity by fusing the corresponding bromo-benzene sulphonic acid with sodium formate (Böttinger, *B.* 7, 1781).—6. By fusing benzene *s*-trisulphonic acid with KCy, and saponifying the resulting nitrile with KOH (Jackson a. Wing, *Am.* 9, 347).—7. From di-sodium salicylate $C_6H_4(ONa).CO_2Na$ by heating in a current of carbonic acid, converting the resulting $C_6H_2(OH)(CO_2H)_3$ into $C_6H_2Cl(CO_2H)_3$, and reducing with zinc and dilute acids.—8. By the polymerisation of propiolic acid, which takes place to some extent when it is exposed for some weeks to sunlight, air being excluded (Baeyer, *B.* 19, 2185).—9. Trimesic ether is formed by the action of sodium upon a mixture of ethyl formate and ethyl acetate; formyl-acetic ether $HCO.CH_2.CO_2Et$ is probably first formed and subsequently condensed (Piutti, *B.* 20, 537). When mixtures of methyl formate and ethyl acetate, or of ethyl formate with methyl acetate

are used a mixture of ethyl and methyl trimesates is obtained.

Properties.—Colourless prisms (from water); partially sublimes before melting. M. sol. cold water and ether, v. sol. hot water, v. e. sol. alcohol. When distilled with lime it yields benzene.

Salts.—NaH_2A''': plates, sl. sol. cold water. —Na_3A'''.—KH_2A''': needles, sl. sol. cold water.— $Ca_3A'''_2aq$: nodules.—$Ba_3A'''_2aq$ (dried at 150°): needles, almost insol. cold, v. sl. sol. boiling water (difference from mesitylenic acid).— $BaH_4A'''_2 4aq$: slender hair-like needles, sl. sol. cold water.—$Zn_3A'''_2 2aq$: glittering prisms, almost insol. cold water.—$Cu_3A'''_2 aq$ (dried over H_2SO_4). Pale-blue pp.—Ag_3A'''.

Methyl ether Me_3A'''. [143°]. Small silky needles. H.F. 249,500 (Stohmann, *J. pr.* [2] 40, 353).

Ethyl ether Et_3A'''. [133°]. Prepared by adding a mixture of formic and acetic ethers by drops to twice the amount of ether, in which sodium is placed. On adding dilute H_2SO_4 an oil is obtained, which gives a blue-violet colour with $FeCl_3$, and on standing in a desiccator deposits crystals of trimesic ether (Wislicenus, *B.* 20, 2930). Long glistening prisms. A mixture of this ether and the preceding in equal proportions melts at 105° to 110°.

Sulpho-trimesic acid. *Amide.* $C_6H_2(SO_2NH_2)(CO_2H)_3$. Formed by oxidising the amide of either of the sulpho-mesitylenic acids with $KMnO_4$ (Jacobsen, *A.* 206, 203).— KH_2A''' 2aq: crystalline mass, m. sol. water. Conc. HClAq at 210° gives trimesic acid, NH_3, and H_2SO_4. Potash-fusion gives oxy-trimesic acid.

MESICERIN *v.* TRI-OXY-MESITYLENE.

MESIDIC ACID *v.* UVITIC ACID.

MESIDINE $C_9H_{13}N$ *i.e.* $C_6H_2(CH_3)_3NH_2$ [1:3:5:6]. *Amido-mesitylene.* (229°) (Ladenburg, *A.* 179, 172). S.G. ·963.

Formation.—1. By boiling nitro-mesitylene with tin and HClAq (Fittig a. Storer, *A.* 147, 1).— 2. From di-methyl-aniline methylo-iodide, by heating in a sealed tube at 335° (Hofmann, *B.* 5, 715; 8, 61).—3. By heating *u-m*-xylidine hydrochloride or *c-m*-xylidine hydrochloride with methyl alcohol at 300° (Eisenberg, *B.* 15, 1012; Nölting a. Forel, *B.* 18, 2681).—4. By heating aniline hydrochloride with MeOH at 300° (Limpach, *B.* 21, 640).

Properties.—Liquid. Gives *m*-xyloquinone on oxidation. When heated with MeOH and HCl for forty-eight hours at 230° it yields di-methyl-mesidine (c. 215°). $ClCO_2Et$ yields $C_6H_2Me_3.NH.CO_2Et$ [62°] (Eisenberg, *B.* 15, 1016).

Salts.—B'HCl: feathery crystals or prisms, v. sol. water and alcohol.—$B'_2H_2SnCl_4$. Sparingly soluble needles.—$B'_2H_2PtCl_6$.—$B'_2H_2C_2O_4$: plates, sl. sol. cold water.

Acetyl derivative $C_6H_2(CH_3)_3NHAc$. [217°]. Prisms (from alcohol). May be sublimed.

Benzoyl derivative $C_6H_2(CH_3)_3NHBz$. [204°]. Needles (Schack, *B.* 10, 1711).

MESIDINE SULPHONIC ACID $C_9H_{13}NSO_3$ *i.e.* $C_6H(NH_2)(CH_3)_3SO_3H$ [6:1:3:5:4]. *Amido-mesitylene sulphonic acid.* From nitro-mesitylene sulphonic acid by reduction with NH_3 and H_2S (Rose, *A.* 164, 70). Slender prisms or needles (containing aq) (from water), v. sol. hot alcohol, sl. sol. cold water. Does not combine with HCl or H_2SO_4.—BaA'_2: nodules, m. sol. cold water.—MgA'_2 3aq.—ZnA'_2 5aq.—PbA'_2 aq: crystalline; v. sol. cold water.—AgA'.

MESITENE LACTONE *v.* vol. i. p. 21 and BROMO-MESITENE LACTONE.

TRI-MESITIC ACID *v.* PYRIDINE TRI-CARBOXYLIC ACID.

MESITOL $C_9H_{12}O$ *i.e.* $C_6H_2(CH_3)_3(OH)$ [1:3:5:6]. *Oxy-mesitylene.* [69°]. (219·5° i. V.). Obtained from mesidene by the diazo- reaction, and by fusing mesitylene sulphonic acid with potash (Biedermann a. Ledoux, *B.* 8, 57, 250; Jacobsen, *A.* 195, 268). Crystals, v. e. sol. alcohol and ether. Volatile with steam. Insol. NH_3Aq and aqueous Na_2CO_3; v. sol. NaOHAq. Not coloured by $FeCl_3$. Forms a sulphonic acid, which has an easily soluble barium salt, coloured deeply by $FeCl_3$. This sulphonic acid yields oxy-mesitylenic acid by potash-fusion.

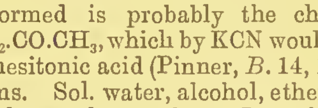
Methyl derivative $C_6H_2(CH_3)_3(OCH_3)$. (c. 202°). Liquid. Bromine gives a bromo-derivative [80°]. *V.* AMIDO- and BROMO-MESITOL.

MESITONIC ACID $C_7H_{12}O_3$ or $(CH_3)_2C(CO_2H).CH_2.CO.CH_3$ (?). *Di-α-methyl-β-acetyl-propionic acid.* [74°] (Anschütz). [90°] (P.). (138° at 15 mm.). (230°–240°) at 760 mm. Prepared, together with an acid ($C_8H_{13}NO_3$) and phoronic nitrile ($C_{11}H_{18}N_2O_2$), by boiling the product of the action of gaseous HCl on acetone, with alcoholic KCN. In this reaction the substance first formed is probably the chloride $(CH_3)_2CCl.CH_2.CO.CH_3$, which by KCN would give the nitrile of mesitonic acid (Pinner, *B.* 14, 1071). Plates or prisms. Sol. water, alcohol, ether, and benzene, sl. sol. petroleum-ether. Its salts are v. e. sol. water. On distillation it splits off water, forming mesito-lactone $C_7H_{10}O_2$. Yields di-methyl-malonic acid on oxidation with HNO_3 (Anschütz, *A.* 247, 103). On reduction it yields the lactone of γ-oxy-di-α-methyl-valeric acid $(CH_3)_2C.CH_2.CHMe.O.CO$ [52°].

Ethyl ether $C_6H_{10}(OH).CO_2Et$. (210°). Colourless liquid.

Acetyl derivative of the *ethyl ether* $C_6H_{10}(OAc).CO_2Et$. (206°). Liquid (Pinner, *B.* 15, 578).

Phenyl hydrazide $PhHN_2{:}CMe.CH_2.CMe_2.CO_2H$. [121·5°]. Small prisms (from benzene or dilute alcohol). On boiling with a few drops of HClAq it yields crystalline $C_{13}H_{16}N_2O$ [84°].

Compound with Hydrogen Cyanide $C_8H_{13}NO_3$ *i.e.* 

Mesitylic acid. [174°]. Prepared, together with mesitonic acid and phoronic nitrile, by boiling the product of the action of HCl on acetone with alcoholic KCN. In this reaction it is probably formed by the addition of HCN to mesitonic acid or its nitrile (Simpson, *A.* 148, 351; Pinner, *B.* 14, 1071; 15, 580). Distils undecomposed at a high temperature. Large flat prisms (containing aq). Very stable body. Forms easily soluble salts. By heating with HCl to 140° CO_2 and NH_3 are split off. Heated with concentrated H_2SO_4 to 150° it is converted

into mesitonic acid. On oxidation with $KMnO_4$ in acid solution it gives di-methyl-succinimide and di-methyl-malonamic acid [107°].

Ethyl ether A'Et. [90°]. Colourless prisms. Sol. alcohol and in acid, sl. sol. water.

Amide $C_8H_{14}N_2O_2$. [222°]. Colourless crystals. Sol. water and alcohol.

Mesito-lactone $C_7H_{10}O_2$ *i.e.*

$(CH_3)_2.C.CH:C.CH_3$
 | |
CO—O

. *Lactone* of *Oxy-heptenoic acid.* [24°]. (167°). Prepared by distillation of mesitonic acid (Pinner, *B.* 15, 579). Large colourless prisms, sl. sol. water. Neutral body. By boiling with KOH it is reconverted into mesitonic acid. It combines with bromine.

MESITYL. This name was given by Kane (*P.* 44, 476) to a radicle C_3H_5, of which he supposed acetone to be the hydroxide and MESITYL OXIDE (*q. v.*) the oxide. More recently it has been employed to denote both *s*-di-methyl-benzyl and *s*-tri-methyl-phenyl.

MESITYL ALCOHOL *v.* ω-OXY-MESITYLENE.

MESITYL BROMIDE *v.* BROMO-MESITYLENE.

MESITYLENE C_9H_{12} *i.e.* $C_6H_3Me_3$ [1:3:5]. *s-Tri-methyl-benzene.* Mol. w. 120. (164·5°) (Schiff, *A.* 220, 94). S.G. $\frac{9\cdot8}{4}$ ·8694 (S.); $\frac{20}{4}$ ·8558 (Brühl, *A.* 200, 190). C.E. (9·8° to 164·5°) ·001159 (S.). V.D. 4·4 (obs. and calc.). S.V. 162·4 (Schiff); 162·2 (Ramsay). $\mu_\beta = 1{\cdot}5015$. $R_\infty = 65{\cdot}75$ (B.). H.C. = 1,251,660 [C,O_2 = 94,000; H_2,O = 69,000] (Stohmann, *J. pr.* [2] 35, 41); 1,282,310 (Thomsen, *Th.* 4, 63). H.F.p. = 490. H.F.v. = −2410 (*Th.*).

Occurs in coal-tar oil (Fittig a. Wackenroder, *A.* 151, 292; Jacobsen, *A.* 184, 179; *B.* 9, 256; 10, 855). It is also one of the products of the manufacture of oil-gas (Armstrong, *C. J.* 49, 74). Occurs in all kinds of petroleum (American, Russian, &c.) (Engler, *B.* 18, 2234).

Formation.—1. By distilling acetone with H_2SO_4 (Kane, *P.* 44, 474; Hofmann, *C. J.* 2, 104; Cahours, *C. R.* 24, 255; *C. J.* 3, 17).—2. By the action of H_2SO_4 on allylene (Fittig a. Schrohe, *B.* 8, 17).—3. By treating toluene with MeCl in presence of $AlCl_3$, ψ-cumene being also formed (Friedel a. Crafts, *A. Ch.* [6] 1, 461; Ador a. Rilliet, *B.* 12, 329).

Preparation.—1. By mixing 180 g. acetone with 300 g. sulphuric acid, allowing to stand for an hour, then distilling gently, using a current of steam at the end of the operation. The yield is 40 g. (Varenne, *Bl.* [2] 40, 266).—2. H_2SO_4 (2 vols.) diluted with water (1 vol.) is slowly added to a mixture of crude acetone (2 vols.) and sand. After 24 hours the mixture is distilled. The oil thus obtained is washed with aqueous NaOH and rectified (Fittig a. Brückner, *A.* 147, 42).—3. The fraction of coal-tar oil boiling between 160° and 168° is agitated with H_2SO_4 and the resulting sulphonic acids converted first into Ba salts and then into Na salts. The Na salts are then treated with PCl_5, and the resulting chlorides converted into amides by NH_3Aq. On crystallising from alcohol, the ψ-cumene sulphonamide separates first, and then mesitylene sulphonamide. The mesitylene sulphonamide is then heated with conc. HClAq at 160° (Jacobsen).—4. The sulphonic acids of ψ-cumene and of mesitylene may also be separated by heating with HClAq at 100° for 1 hour, when mesitylene sulphonic acid is decomposed into mesitylene and H_2SO_4, while ψ-cumene sulphonic acid is not affected (Armstrong, *B.* 11, 1697).—5. When steam is passed through a heated solution of mesitylene sulphonic acid in dilute H_2SO_4, hydrolysis into mesitylene and H_2SO_4 begins as soon as the temperature reaches 100° (Armstrong a. Miller, *C. J.* 45, 148).

Properties.—Light oil.

Reactions.—1. Br and Cl form crystalline substitution-products.—2. Fuming HNO_3 mixed with fuming H_2SO_4 forms tri-nitro-mesitylene. 3. Boiling dilute HNO_3 oxidises it to mesitylenic acid and uvitic acid (Fittig, *A.* 141, 142).—4. $K_2Cr_2O_7$ and H_2SO_4 yield acetic acid (Fittig). 5. $KMnO_4$ oxidises it to uvitic and trimesic acids (Jacobsen, *A.* 184, 191).—6. When heated with $AlCl_3$ in a current of HCl it yields MeCl and *m*-xylene, toluene, and benzene (Jacobsen, *B.* 18, 342).—7. MeI in presence of $AlCl_3$ yields (1, 2, 4, 5)-tetra-methyl-benzene (durene) (Barbier a. Roux, *Bl.* [3] 2, 4).—8. *Benzyl chloride* and $AlCl_3$ at 100° form benzyl-mesitylene (*q. v.*). 9. *Benzoyl chloride* in presence of aluminium chloride forms phenyl tri-methyl-phenyl ketone $C_6H_5.CO.C_6H_2Me_3$ [36°] and the compounds $(C_6H_5.CO)_2C_6HMe_3$ [117°] and $(C_6H_5CO)_3C_6Me_3$ [215°] (Louise, *A. Ch.* [6] 6, 200).—10. PCl_5 at 180° gives a small quantity of $C_6H_3(CH_2Cl)_3$ (Colson a. Gautier, *Bl.* [2] 45, 6).—11. Mesitylene is very readily attacked by *halogens.* In the *dark*, mono- di- or tri- (*eso*)-bromo-mesitylene ($C_6H_2Me_3Br$, C_6HMe_3Br, and $C_6Me_3Br_3$) are formed according as 1, 2, or 3 mols. of bromine are employed. Chlorine acts similarly. The presence of iodine, though not required, does not effect the reaction. At the *boiling-point* the bromine, as usual, enters the side-chains, 1 mol. Br forming ω-bromo-mesitylene (mesityl bromide) $C_6(CH_3)_2CH_2Br$ melting at [38°]. Direct *sunshine*, which usually acts like heat, in the case of mesitylene, owing to the great tendency to displacement of the nucleal hydrogen, produces a different result; (*eso*)-mono-bromo-mesitylene is first produced but is partly attacked by the rest of the bromine forming the liquid *p*-ω-di-bromo-mesitylene (*p*-bromo-mesityl-bromide) $C_6H_2(CH_3)_2Br(CH_2Br)$ [5:3:4:1]. If *eso*-bromo-mesitylene be exposed to further bromination in sunshine, the reaction proceeds normally, producing *p*-ω-di-bromo-mesitylene (as above), and, on further action, *p*-ω_1-ω_2-tri-bromo-mesitylene $C_6H_2(CH_3)Br(CH_2Br)_2$ [5:4:3:1] melting at [122°] (Schramm, *B.* 19, 212).—12. When a 10 p.c. solution of mesitylene in CS_2 is mixed with a similar solution of chromyl chloride CrO_2Cl_2 a pp. $(C_6H_3Me_3)(CrO_2Cl_2)$ is obtained which when decomposed by water yields di-methyl-benzoic aldehyde (221°), which is oxidised by air to mesitylenic acid (Etard, *C. R.* 97, 909).—13. The diacetyl derivative of *ortho-formic aldehyde* (1 pt.) mixed with mesitylene (1 pt.) and HOAc (10 pts.) condenses on adding a mixture of HOAc (10 pts.) with an equal volume of H_2SO_4; and after 24 hours crystals of $(C_6H_2Me_3)_2CH_2$ [130°] separate. The formation of this body may be used as a test for mesitylene, a mixture of methyl alcohol and CrO_3 in HOAc being used instead of $CH_2(OAc)_2$ (Baeyer, *B.* 5, 1094; 6, 220).

Constitution.—The explanation of the for-

mation of mesitylene by condensation of acetone was first given by Baeyer (*A.* 140, 306). That the three methyls are symmetrically situated in the benzene nucleus would appear from the existence of only one mono-derivative derived by displacing an atom of hydrogen in the nucleus, *e.g.* there is only one nitro-mesitylene. A systematic proof of the symmetry of mesitylene has been given by Ladenburg (*A.* 179, 163). He prepares in succession $C_6Me_3(NO_2)(NO_2)H$, $C_6Me_3(NO_2)(NH_2)H$, $C_6Me_3(NO_2)(NH_2)(NO_2)$, and $C_6Me_3(NO_2)H(NO_2)$. Since the last di-nitro-mesitylene is identical with the first, the second and third hydrogen atoms are similarly situated in the nucleus. Again, from the above nitro-mesidine $C_6Me_3(NO_2)(NH_2)H$ Ladenburg obtained $C_6Me_3(NO_2)HH$ and, by reducing this, mesidine $C_6Me_3(NH_2)HH$. Nitro-mesidine, obtained by nitrating $C_6Me_3(NH_2)HH$, must be either $C_6Me_3(NH_2)(NO_2)H$ or $C_6Me_3(NH_2)H(NO_2)$. But since it has been shown that the second and third atoms of hydrogen are similarly situated, these two formulæ are identical. And since the nitro-mesidine is found to be identical with the $C_6Me_3(NO_2)(NH_2)H$ prepared from the di-nitro-mesitylene $C_6Me_3(NO_2)(NO_2)H$, it follows that the first and second atoms of hydrogen are similarly situated. Hence all three atoms of hydrogen are similarly situated, and the formula will be $C_6Me_3H_3$ [1:3:5].

Mesitylene hexahydride C_9H_{18} *i.e.* $C_6Me_3H_9$. (c. 137°). Obtained by heating mesitylene with PH_4I at 280° (Baeyer, *Z.* [2] 5, 320; *A.* 155, 273). Oil, smelling like petroleum. Converted by prolonged heating with fuming HNO_3 into tri-nitro-mesitylene.

References.—Di-amido-, Benzyl-, Bromo-, Bromo-nitro-, Bromo-oxy-, Chloro-, Di-chloro-bromo-, Chloro-nitro-, Nitro-, Nitro-benzyl-, Di-oxy- and Tri-oxy- mesitylene. *V.* also Mesidine, Mesitol, and Azo- compounds.

MESITYLENE-DIAMINE *v.* Di-amido-mesitylene; vol. i. p. 166.

MESITYLENE CARBOXYLIC ACID *v.* (β)-*Iso*-cuminic acid.

MESITYLENE GLYCOL *v.* Di-oxy-mesitylene.

MESITYLENE PHTHALOYLIC ACID *v.* Phenyl tri-methyl-phenyl ketone carboxylic acid.

MESITYLENE SULPHINIC ACID $C_6H_2Me_3.SO_2H$ [1:3:5:6]. [99°]. Formed by adding a mixture of sodium-amalgam and $C_6H_2Me_3SO_2Cl$ to a dry mixture of benzene and toluene, and decomposing the resulting pulpy mass with HCl (Holtmeyer, *Z.* 1867, 686). Fan-shaped groups of needles.—BaA'_2 *x*aq.—AgA'.

MESITYLENE SULPHONIC ACID $C_9H_{12}SO_3$ *i.e.* $C_6H_2Me_3SO_3H$. [c. 77°]. Formed by dissolving mesitylene in warm H_2SO_4 (Hofmann, *C. J.* 2, 113; Jacobsen, *A.* 146, 85; 184, 185; Beilstein a. Kögler, *A.* 137, 317; Fittig, *J.* 1866, 610; *Z.* [2] 4, 583). Trimetric six-sided tables (containing 2aq) (Rose, *Z.* [2] 6, 341; *A.* 164, 53; Bodewig, *J.* 1879, 737). Decomposed by distillation with dilute H_2SO_4 into mesitylene and H_2SO_4, the hydrolysis beginning at 100° (Armstrong a. Miller, *C. J.* 45, 148). Gives mesitol on potash-fusion (Jacobsen, *A.* 195, 265).

Salts.—KA'aq. Roundish groups of silky laminæ. S. 14 at 12°.—NH_4A' aq. [250°]. Plates, v. sol. water and alcohol.—$CaA'_2$5aq: efflorescent crystals.—BaA'_2 9aq. S. 6·6 at 18°; 5·5 at 11·5°.—$SrA'_2$7aq.—$MgA'_2$6aq.—$CoA'_2$6aq: flesh-coloured laminæ, v. sol. water and alcohol. —$CuA'_2$4aq. Pale-green laminæ. S. 6 at 10°.—PbA'_2 9aq. Pearly plates. S. 15 at 20°.

Chloride $C_6H_2Me_3SO_2Cl$. [57°]. Wedge-shaped tables (from ether), insol. water, v. sol. alcohol and ether (Holtmeyer, *Z.* 1867, 686).

Amide $C_6H_2Me_3SO_2NH_2$. [142°]. S. ·033 at 0°; ·54 at 100°. S. (83 p.c. alcohol) 5·5 at 0°; 114 at 78°. Fibrous mass (from alcohol) or hair-like needles (from ether). May be oxidised to $C_6H_2Me(CO_2H)_2.SO_2NH_2$ and an acid $C_6H_2Me_2(CO_2H).SO_2NH_2$, and the anhydride of an isomeric acid $C_6H_2Me_2<\genfrac{}{}{0pt}{}{SO_2}{CO}>NH$ (Hall a. Remsen, *Am.* 2, 130; Emerson, *Am.* 8, 268).

Imide $(C_6H_2Me_3SO_2)_2NH$. [124°]. Formed by heating the amide with a little HCl in a sealed tube. Long needles, m. sol. hot water, sol. NaOHAq, and reppd. by HCl.

Mesitylene disulphonic acid $C_6HMe_3(SO_3H)_2$. Formed by dissolving mesitylene (1 pt.) in fuming H_2SO_4 (10 pts.) and adding P_2O_5 (3 pts.), the temperature being kept low during the operation (Barth a. Herzig, *M.* 1, 807). Deliquescent needles. Gives oxy-mesitylenic acid on potash-fusion. — K_2A'' 2aq. — Na_2A'' 1½aq: needles. — BaA'' 3aq: needles.—CuA'' (dried over H_2SO_4): greenish-white needles.

Reference.—Bromo-mesitylene sulphonic acid.

MESITYLENIC ACID $C_9H_{10}O_2$ *i.e.* $C_6H_3Me_2.CO_2H$. *Di-methyl-benzoic acid.* Mol. w. 150. [166°]. H.C.v. 1,084,300. H.C.p. 1,085,200. H.F. 105,800 (Stohmann, Kleber, a. Langbein, *J. pr.* [2] 40, 135). Colourless plates.

Formation.—1. By boiling mesitylene with dilute HNO_3 (1 vol. of S.G. 1·4 and 2 vols. water) for 18 hours. The product is distilled with steam, boiled with a little tin and HClAq to remove a nitro- compound, and crystallised from alcohol (Fittig, *A.* 141, 144; Fittig a. Brückner, *Z.* [2] 4, 493; *A.* 147, 45).—2. By boiling *s*-di-methyl-ethyl-benzene with nitric acid (S.G. 1·1) (Jacobsen, *B.* 7, 1430; Wroblewsky, *B.* 9, 495). 3. By passing CO over a mixture of NaOEt and NaOAc at 205°; or by heating such a mixture with zinc-dust (Geuther a. Fröhlich, *A.* 202, 310).

Properties.—Monoclinic crystals (from alcohol); v. sl. sol. water, v. sol. alcohol. Sublimes below its melting-point. Distillation with lime yields *m*-xylene. Chromic acid mixture oxidises it to trimesic acid.

Salts.—NaA' (dried at 130°). V. sol. water and alcohol.—CaA'_2 ½aq. Not more soluble in hot than cold water. — BaA'_2: silky prisms.—$MgA'_2$5aq: groups of monoclinic prisms.—ZnA'_2 (dried at 130°): laminæ or needles, sl. sol. water.—MnA'_2.—NiA'_2 (dried at 130°).—AgA'_2. Minute needles, sol. hot water.—AgA'_2aq (Hall a. Remsen, *Am.* 2, 130).

Ethyl ether EtA'. (241°). Heavy oil; solidifies below 0°.

Amide $C_6H_3Me_2.CONH_2$. [133°]. Needles; v. sl. sol. cold water.

References.—Amido- bromo-, and chloro-mesitylenic acid.

MESITYLENIC GLYCOL *v.* DI-OXY-MESITYLENE.

MESITYLENIC GLYCERIN *v.* TRI-OXY-MESITYLENE.

MESITYLIC ACID *v.* compound of MESITONIC ACID with HCy.

MESITYL MERCAPTAN *v.* TRI-METHYL-PHENYL MERCAPTAN.

MESITYL OXIDE $C_6H_{10}O$ *i.e.* $(CH_3)_2C:CH.CO.CH_3$. *Methyl isobutenyl ketone. Isopropylidene-acetone.* (132°) at 751 mm. S.G. $\frac{20}{4}$ ·8578. μ_D 1·4440. V.D. 3·67 (calc. 3·39). R_∞ 49·7 (Kanonnikoff, *J. pr.* [2] 31, 352).

Formation.—1. One of the products of the action of H_2SO_4 on acetone (Kane, *P.* 44, 476). 2. Together with phorone by leaving acetone for several weeks in contact with quicklime (Fittig, *A.* 110, 32).—3. One of the products of the action of $ZnEt_2$ or $ZnMe_2$ on acetone (Pawlow, *B.* 9, 1311; *A.* 188, 130).—4. In small quantity, together with other bases, by distilling diacetonamine (Heintz, *A.* 174, 133; 181, 70; *B.* 8, 89).—5. By boiling with lime the lactonic products of condensation of aceto-acetic ether (Hantsch, *A.* 222, 21).—6. By boiling acetyl chloride with acetone (Beilstein a. Wiegand, *Bl.* [2] 38, 167).–7. Among the products of the distillation of glycerin with BaO (Destrem, *A. Ch.* [5] 27, 5).

Preparation.—Acetone is saturated with HCl and then left to itself for a fortnight. The product is mixed with water, and the heavy oil, containing hydrochlorides of mesityl oxide and phorone, decomposed by alcoholic or conc. aqueous KOH, and distilled with steam. The product is fractionally distilled (Baeyer, *A.* 140, 297).

Properties.—Oil, smelling like peppermint; insol. water, miscible with alcohol and ether.

Reactions.—1. Boiling dilute *sulphuric acid* forms acetone. Conc. H_2SO_4 gives mesitylene (Claisen, *B.* 7, 1168).—2. Boiling dilute *nitric acid* yields acetic and oxalic acids.—3. $KMnO_4$ oxidises it to acetic and oxy-isobutyric acid (Pinner, *B.* 15, 591).—4. Slowly combines with $NaHSO_3$ forming $NaC_6H_{11}SO_4aq$, the sodium salt of methyl isobutyl ketone sulphonic acid $CH_3.CO.CH_2.CMe_2.SO_3H$, which is decomposed by conc. NaOHAq regenerating mesityl oxide (Pinner, *B.* 16, 1727).—5. *Bromine* acts violently. But when it is added to a solution of mesityl oxide in CS_2 oily $C_6H_{10}Br_2O$ is formed. This can be distilled with steam, but in the dry state soon gives off HBr.—6. A solution in dilute alcohol is strongly attacked by *sodium-amalgam* and water then ppts. a heavy oil $C_{12}H_{20}O$ 'mesitic ether' or 'mesitic camphor' (c. 215°) smelling like camphor. A small quantity of a solid [110°–120°] is also formed (Claisen, *A.* 180, 7).—7. PCl_5 forms 'mesityl chloride' $C_6H_{10}Cl_2$, which separates on adding water as a heavy oil, smelling like oil of turpentine. It resinifies on exposure to air, and is decomposed by distillation over KOH, baryta, or lime into HCl and C_6H_9Cl, a liquid (130°) smelling like turpentine. 8. *Ammonia* forms diacetonamine $C_6H_{13}NO$.—9. *Hydriodic acid* forms a heavy oil $C_6H_{11}IO$ decomposed by alcoholic KOH into HI and mesitylene (Pawlow, *A.* 188, 138).—10. HCl passed into a mixture of mesitylene and benzoic aldehyde forms $C_4H_7.CO.CH:CHPh$ (Claisen a. Claparède, *B.* 14, 349).—11. With *acetamide* and $ZnCl_2$ it forms oxy-tri-methyl-pyridine dihydride (Canzoneri a. Spica, *G.* 14, 349; *B.* 19, 818; *cf.* Engler a. Riehm, *B.* 19, 40).—12. With amyl nitrite and alcoholic NaOEt it forms the nitroso- derivative $CMe_2:CH.CO.CH:NOH$, crystallising in colourless prisms [102°] (Claisen a. Manasse, *B.* 22, 529).

Oxim $C_6H_{11}NO$ *i.e.* $(CH_3)_2C:CH.C(N.OH).CH_3$. (c. 185°). Formed by the action of hydroxylamine on mesityl oxide (Nägeli, *B.* 16, 495). Oil. Sol. alcohol, ether, benzene, CS_2, ligroin, alkalis and acids. On warming with acids it is resolved into its constituents.

MESOCAMPHORIC ACID *v.* CAMPHORIC ACID.

MESORCIN *v.* TRI-METHYL-RESORCIN.

MESOTARTARIC ACID *v.* TARTARIC ACID.

MESOXALIC ACID $C_3H_2O_5aq$ *i.e.* $CO_2H.CO.CO_2H + aq$ or $CO_2H.C(OH)_2.CO_2H$ (Petrieff, *B.* 11, 414). Mol. w. 136. [115°] (Deichsel); [108°] (Böttinger, *A.* 203, 140); [120°] (Fischer).

Formation.—1. Together with urea, by boiling alloxan or alloxanic acid with baryta. The resulting Ba salt is recrystallised and decomposed by H_2SO_4 (Liebig a. Wöhler, *A.* 26, 298; Svanberg, *B. J.* 27, 165; Deichsel, *B. B.* 1864, 587).—2. By treating amido-malonic acid with iodine and water (Baeyer, *A.* 131, 298).—3. By boiling di-bromo-malonamide $CBr_2(CO.NH_2)_2$ with precipitated Ag_2O (Freund, *B.* 17, 782).—4. By boiling di-bromo-malonic acid with baryta-water (Petrieff, *J. R.* 10, 72).—5. By heating caffuric acid with concentrated aqueous lead subacetate (E. Fischer, *A.* 215, 283).

Properties.—Very deliquescent prisms, melting without loss of aq. M. sol. alcohol and ether, v. e. sol. water. Its concentrated aqueous solution decomposes above 80° into CO_2, glycollic, oxalic, and glyoxylic acid (Böttinger, *A.* 203, 138). With acetates of Ba and Pb it gives flocculent pps. gradually becoming crystalline. In neutral solutions $CaCl_2$ and $BaCl_2$ give pps. It reduces hot ammoniacal $AgNO_3$.

Reactions.—1. H_2S passed into an aqueous solution to which silver oxide has been added forms thio-glycollic acid $CH_2(SH).CO_2H$ and thio-di-glycollic acid (sulphido-diacetic acid) $S(CH_2.CO_2H)_2$ (Böttinger).—2. *Sodium amalgam* acting on its dilute aqueous solution forms tartronic acid $CO_2H.CH(OH).CO_2H$.—3. Silver mesoxalate boiled with water yields CO_2, oxalic acid, and silver.—4. *Urea* at 100° gives allantoïn $C_4H_6N_4O_3$.—5. *Hydroxylamine* yields the oxim which is identical with nitroso-malonic acid.

Salts. — $[A'' = C_3O_5]$.—$(NH_4)_2A''$: granular crystals turning red in air (Deichsel; *cf.* Engel, *C. R.* 98, 628).—$(NH_4)_2A''aq$. Obtained by evaporation *in vacuo* over H_2SO_4.—Needles (Petrieff).—$Na_2A''aq$: thin laminæ, v. sol. water.—$CaA''aq$: white pp. insol. dilute acetic acid.—$CaA''4aq$ (dried at 100°) (Petrieff).—$BaA''aq$ (dried at 110°). White crystalline powder, v. sl. sol. water.—$BaA''1\frac{1}{2}aq$.—BaA'' (dried at 180°).—$(HO.Pb)_2A''$: nearly insol. water.—$Ag_2A''aq$: amorphous pp. changing to minute needles. Explodes when heated.

Ethyl ether $Et_2A''aq$. From the silver salt and EtI. Oil.

Di-acetyl derivative of the ethyl ether $(CO_2Et)_2C(OAc)_2$. [145°]. From the ether (1 mol.) and AcCl (2 mols.) at 100° (P.). Long needles. Partially decomposed by fusion and by solution in water.

Di-acetyl derivative $C(OAc)_2(CO_2H)_2$. [130°]. From $(CO_2Et)_2C(OAc)_2$ and dilute alcoholic KOH. Needles. Its alkaline salts are v. sol. water; its silver salt $Ag_2C_7H_6O_8$ is an insoluble powder.

Amide $C(OH)_2(CONH_2)_2$. Deliquescent tables, which turn red in the air.

Phenyl-hydrazide $PhHN_2:C(CO_2H)_2$. [158°–164°]. From mesoxalic acid and phenyl-hydrazine hydrochloride in dilute acid solution (Elbers, *A.* 227, 355). Crystals.

Phenyl-hydrazide of the Nitrile $PhHN_2:C(CN)_2$. [135°]. May be formed from the oxim-phenyl-hydrazide of glyoxylyl-cyanide $HO.N:CH.C(N_2HPh).CN$ by dissolving in $POCl_3$, heating with PCl_5, pouring into ice, and treating the crystals with ether and alkali (Von Pechmann a. Wehsarg, *B.* 21, 3001). Yellow needles (from ether-ligroïn). Turns brown at 126°. Sol. hot water, alkalis, and the usual menstrua. Conc. H_2SO_4 forms a blood-red solution not changed by $FeCl_3$. On warming with conc. HClAq it forms yellow needles of $C_9H_8N_4O$ [245°].

MESOXALIC ALDEHYDE CHO.CO.CHO.

Oxim HON:CH.CO.CH:NOH or $ON.CH_2.CO.CH_2.NO$ *v.* Di-nitroso-acetone.

Mesoxalic semi-aldehyde $^{\times}CHO.CO.CO_2H$. *Glyoxylyl carboxylic acid.*

Diphenyl-hydrazide $CH(N_2HPh).C(N_2HPh).CO_2H$. [203°]. From di-bromo-pyruvic acid in aqueous solution and phenyl-hydrazine hydrochloride (Nastvogel, *A.* 248, 87). Reddish-yellow needles (from hot alcohol), almost insol. water, sl. sol. ether and chloroform, v. sol. hot alcohol, acetone, benzene and HOAc. Dyes wool and silk yellow. Cold conc. H_2SO_4 forms a dark-red solution from which it is ppd. by water unaltered.

Di-p-tolyl-hydrazide $CH(N_2HC_6H_4Me).C(N_2HC_6H_4Me).CO_2H$. [188°]. Formed in like manner. Golden needles (from benzene). Its alkaline salts are v. sol. hot, sl. sol. cold, water.

Nitrile $^{\times}$CHO.CO.CN *v. Glyoxylyl cyanide.*

Mesoxalic bromo-semi-aldehyde $^{\times}CBrO.CO.CO_2H$.

Methyl ether of the oxim $CBrO.C(NOH).CO_2Me$. [c. 170°]. From di-methyl di-bromo-pyrrole di-carboxylate and HNO_3 at −18° (Ciamician a. Silber, *B.* 20, 2601). Crystalline; sol. alcohol, m. sol. cold water, insol. petroleum-ether. Decomposed by fusion and by boiling with water.

MESOXALYL-UREA is Alloxan. See also its compounds with methyl-aniline, naphthyl-amine, and pyrrole.

META. *Use of this prefix applied to inorganic compounds*; for *Meta-acids* and *Meta-salts v.* the acids or salts to the name of which *Meta-* is prefixed. Thus *Meta-phosphoric acid* will be found under Phosphoric acids, and *Meta-stannates* under *stannates*, a subdivision of the article Tin.

Names of *organic bodies* beginning with 'meta' will be found under the word to which 'meta' is prefixed.

METACETONE. The mixture obtained by distilling sugar with quicklime, called metacetone by Fremy (*A. Ch.* [2] 59, 6), is composed according to E. Fischer a. Laycock (*B.* 22, 101) of propionic aldehyde, di-methyl-furfurane, and hydrocarbons.

METACETONIC ACID. An old name for Propionic acid.

METALBUMIN *v.* Proteïds, *Appendix C.*

METALDEHYDE *v.* Aldehyde.

METALLIC ACIDS. In the article Acids (vol. i. p. 47; *cf.* Classification, vol. ii. pp. 201, 202), it is shown that compounds of H with certain negative elements or groups of elements react with metallic oxides, hydroxides, and carbonates, in presence of water, to produce substances composed of metal, and the elements of the hydrogen compound excepting the H or a part of the H. Such hydrogen compounds are called acids. The negative elements which are found intimately combined with H in acids are fluorine, chlorine, bromine, iodine, oxygen, sulphur, selenion, tellurium; carbon always enters into the composition of those negative groups of elements which combine with H or with H and other elements to form acids. Only a few acids are binary compounds; the greater number are compounds of H with two or three other elements, among which are always found at least one of the eight negative elements enumerated above, or at least one of the negative carbon-containing groups of elements. By far the greater number of the more stable and definite acids are composed of H combined with non-metallic elements; but some acids have been isolated which are composed of H combined with metals and one or more of the eight strongly negative elements already enumerated, or one or more of the carbon-containing negative groups of elements. The following table gives the composition of most of those acids which contain metallic elements :—

Metallic acids.

H_3AsO_4	$(?H_2TiO_2)$	$H_2PtCy_4Cl_2$
$HAsO_3$	$(?H_4TiO_4)$	H_2PtBr_4
$H_4As_2O_7$	H_2SnO_3	$H_2Pt_4S_6$
	$H_2Sn_2O_7$	H_4OsCy_6
$(?H_3AsS_4)$	H_2SnS_3	H_4RuCy_6
H_3SbO_4	$(?H_2PbO_3)$	H_3IrCy_6
$HSbO_3$	H_2PbI_4	$H_2N_2Os_2O_6$
$H_4Sb_2O_7$	H_2CrO_4	
H_3SbO_3	$(?H_3Cr(SCy)_3)$	
HVO_3	H_2MoO_4	
$(?H_4V_2O_6)$	H_2WO_4	
$H_4V_2O_7$	H_2UO_4	
$H_4Ta_2O_7$	$(?H_2M_2O_7$; M = Mo, W, U)	
$(?H_6Nb_6O_{13})$	$(?H_2M_3O_{10}$; M = Mo, W, U)	
$(?HMnO_4)$	$HAuCy_4$	$(?H_2ZnO_2)$
H_2MnCl_6	$HAuCl_4$	$HHgCl_3$
H_4MnCy_6	$HAuBr_4$	$HHgBr_3$
H_4FeCy_6	H_2PtCl_4	$HHgI_3$
H_3FeCy_6	H_2PtCl_6	H_2HgCl_4
$H_2FeCy_5.NO$	H_2PtI_6	H_2HgBr_4
H_4CoCy_6	$H_2Pt(NO_2)_4$	H_2HgI_4
H_3CoCy_6	$H_2Pt(NO_2)_4Cl_2$	$(?HZnCl_3)$
$(?H_3AlO_3)$	$H_2Pt(SCy)_6$	$(?HZn_2Cl_5)$
	H_2PtCy_4	

The isolation of some of the acids in the fore-

going list is doubtful; these acids are placed in brackets. The compounds H_3AlO_3 and H_2ZnO_2 are also bracketed, because the reactions of these bodies show that they may be classed as feeble acids and at the same time as basic hydroxides.

An examination of the composition of the metallic acids shows that the reacting atomic aggregates of these compounds all contain a number of atoms of a negative element, or group of elements, which is large relatively to the number of atoms of metal present. The accumulation of negative atoms so modifies the functions of the H atoms that these are replaceable by metals, and this notwithstanding the presence of the positive metallic atoms. The H of the metallic hydrogen - containing compounds $H_2Cr_2O_4(=Cr_2O_3.H_2O)$ and $H_2CrO_2(=CrO.H_2O)$ is not replaced by metals when these compounds react with metallic hydroxides or carbonates; but when 4 atoms of the negative O are associated with one atom of Cr and 2 atoms of H, the H of this compound (H_2CrO_4) is distinctly acidic. The negative character, or acid-forming character, of the groups CN and SCN is rendered evident by the number of acids which are formed by the union of these groups with H and metals.

If attention is paid to the general chemical characters of the metals which form acids it is seen that most of these metals occur in groups (using this term as it is used in the nomenclature of the periodic law) which also contain several distinctly non-metallic elements: thus Ti, Sn, and Pb belong to Group IV., which group contains C and Si; Cr, Mo, W, and U belong to Group VI., in which group also occur the negative elements O, S, Se, and Te; As, Sb, V, Nb, and Ta form part of Group V., which is distinctly negative in its general chemical character, and includes the markedly non-metallic elements N and P; Fe, Co, Ni, Au, and the Pt metals occupy a peculiar position in Group VIII. (*cf.* CLASSIFICATION, vol. ii. pp. 203–210; also IRON ELEMENTS, this vol. p. 65).

Several salts exist which, on account of their methods of formation and general stability, are probably best regarded as derivatives of metallic acids that have not yet been isolated; among such salts may be mentioned the stanno- and zircono-fluorides $M^I_2Sn(Zr)F_6$. Some chemists would class most, if not all, the double metallic haloid compounds as salts of metallic acids; *e.g.* $BiF_3.3KF$ as the K salt of the acid H_3BiF_6, $ZnCl_2.BaCl_2$ as the Ba salt of the acid H_2ZnCl_4, and $MgI_2.KI$ as the K salt of the acid $HMgI_3$ (*v.* especially Remsen, *Am.* 11, No. 5).

The consideration of those metal-containing compounds which are acids brings out the inadequacy of that classification which would divide the elements into two classes only, metals and non-metals; it also well illustrates the difficulties of chemical classification, as shown by the way in which the chemical properties of an element are modified according to both the nature and the number of other elementary atoms with which that element is combined (*cf.* the article METALS in this vol. and CLASSIFICATION in vol. ii.).

M. M. P. M.

METALLOIDS. This name was at one time applied, most mistakenly, to the non-metallic elements. It is sometimes used to denote those elements which on the whole are non-metallic, but yet closely approach the metals in some of their properties; As, Sb, Ti, V, Nb, Ta, for instance, are sometimes called metalloids. The term cannot be defined. There are certain elements which one chemist would class among metals, another would place with the non-metals, and a third would prefer to put into neither class, but call them metalloids.

M. M. P. M.

METALLURGICAL CHEMISTRY. The chemical reactions utilised in metallurgy are divisible into two distinct classes, viz. '*wet*,' those which take place in aqueous solutions, and '*dry*,' those which take place in furnaces, or their equivalent, at a relatively high temperature. The present tendency is more and more in the direction of combining these two methods, metals being now frequently extracted from their ores partly by wet processes and partly by dry processes.

The ore of any metal may be defined as a collection of mineral substances containing that particular metal in sufficient quantity to pay for its extraction on a commercial scale. Although each metallic element exists in nature in a great number of combinations, yet very few of these compounds occur in sufficient quantity to be of direct importance to the metallurgist, except in so far as they may tend to introduce impurities into the metal to be extracted.

Chemically, ores may be broadly divided into three classes, containing respectively—I. NATIVE METALS, *i.e.* metals uncombined with any non-metallic element. II. SULPHIDES and ARSENIDES. III. OXIDES, *including carbonates and silicates.*

Class I. NATIVE METALS. A native metal may be separated from its ores in one of four ways. (*a*) By Liquation. In order that this may be done it is essential that the metal be fusible at a temperature insufficient to cause the earthy portions of the ore to frit or agglomerate; *e.g.* Bi. (*b*) By fusing the ore, when the metal will sink to the bottom by reason of its high S.G.; *e.g.* Bi, Cu. (*c*) By dissolving the metal out by means of another metal; *e.g.* Au, Ag, Pt. These metals may be dissolved out of their ores by Pb, which is then removed by cupellation, or, in the case of Ag, the separation of the Ag from the Pb may be effected by Zn, which does not alloy with Pb, and being specifically lighter rises to the surface, carrying the Ag and some lead with it. The Zn is subsequently distilled off, and the residual Ag and Pb cupelled. Similarly, Au and Ag may be dissolved out by Hg, which may then be distilled off. (*d*) By dissolving the metal by means of an acid or a gas in solution; *e.g.* Au extracted by a solution of Cl, and Pt, Pd, Ir, Rh, and Ru by *aqua regia*. The Au and Pt may be refined by wet processes, taking advantage of the fact that Au and Pt are insoluble in sulphuric, hydrochloric, and nitric acid, when these acids are used separately, but are soluble in *aqua regia*, while the Ag, Cu, Pb, and Fe are freely soluble in one or other of the three acids named. In '*parting*' Au, sufficient Ag must be present to allow the acid free access to the impurities, which would otherwise be protected by the insoluble gold. Pt, when present in Au only in small quantity, may be separated by '*parting*' with Ag, as under these conditions the Pt is

acted on by the '*parting acid.*' If present in larger quantity, it must be ppd. from a solution. Ir may be separated from Au by difference of S.G., and from Pt it may be removed to a certain extent by using *aqua regia* of medium concentration, in which it is not freely soluble. Pt is ppd. from its solutions as a double salt of Pt and NH_4 by adding NH_4Cl. Pd, if present, may be ppd. before the Pt by neutralising with Na_2CO_3Aq and adding $HgCy_2$. Ir, if it has gone into solution, will not be ppd. with the Pt, but its double salt is difficult to wash out. Pd, Rh, Ru, and Os will also be found with the Ir in solution after the Pt has been ppd. Rh may be removed completely by fusing the platinum double chloride with $KHSO_4$ and a small quantity of NH_4HSO_4. Ir may be ppd. at the same time as platinum by KCl, and the pp. fused with K_2CO_3, which will oxidise the Ir and not the Pt. Remove the potassium salt by boiling water, and then dissolve out the platinum with *aqua regia*, in which the oxide of Ir is insoluble. Ir may also be separated from the pp. by KCy, the Ir salt being soluble while the Pt salt is insoluble. Pt is obtained in the metallic state by carefully heating the double chloride, which then breaks up. Au is ppd. from its solutions as metal by $FeSO_4Aq$, SO_2Aq, or $H_2C_2O_4Aq$. For dental purposes, Au is frequently deposited by electrical means. Ag is first thrown down as chloride, which is afterwards reduced by Cu, Zn, or Fe. Au, containing not more than 10 p.c. Ag, is also refined by Miller's process, at the Australian Mint, in the dry way, by passing Cl into the molten gold. The impurities As, Sb, Bi, Pb, and Zn are converted into chlorides, which volatilise, and the Ag becomes AgCl, which forms a fused layer on the surface of the gold.

Class II. Sulphides and Arsenides. **Dry methods.** Sulphides and arsenides are either (*a*) *infusible*, at such temperatures as can be obtained in furnaces on the large scale; (*b*) *fusible*; or (*c*) *volatile without fusion.*

(*a*) *Infusible sulphides.* In these cases the S must be replaced by O, as an infusible sulphide cannot be properly reduced to the metallic state. This is done by calcining or roasting the ore, so that air has free access to it. The sulphide is oxidised to a sulphate at low temperatures, and at higher temperatures the sulphate breaks up into SO_2 and an oxide of the metal. Practically there is only one sulphide under this head, viz. ZnS, *zinc blende.* For the subsequent treatment of the oxide *v.* '*oxide class.*'

(*b*) *Fusible sulphides.* Sulphides and arsenides of this class may be subdivided as follows:—(i) *those which are fusible at a very low temperature, insufficient to produce fritting, i.e. incipient fusion causing agglomeration of the constituents of the ore*; (ii) *those requiring a higher temperature, at which fritting would take place.* A sulphide in division (i) may be liquated out, *e.g.* Sb_2S_3. The sulphides and arsenides belonging to (ii) may be separated by fusing the ore, when the sulphide or arsenide would collect together beneath the slag; *e.g.* sulphide of copper (*copper pyrites*); arsenides of nickel and cobalt (if sufficient arsenic is not present in the ore more is added), the arsenide separates in a distinct layer from the sulphides of other metals during the fusion; sulphide of nickel obtained by fusing nickel ores, or products, free from arsenic, with iron pyrites. The sulphides and arsenides thus separated from the gangue would next be treated in one of the following ways:—1. *Converted into oxide by roasting*; *e.g.* Sb_2S_3, *copper matte*, arsenides of nickel and cobalt (the arsenious acid being condensed in coke towers), sulphides of nickel and cobalt free from arsenic; the oxides of nickel and cobalt are subsequently treated in the wet way. 2. *Partially roasted to form a certain amount of oxide and sulphate, and then fused*; the oxygen of the oxides combines with the sulphur of the sulphides and arsenides, forming SO_2 and liberating the metal; *e.g.* Sb_2S_3 and PbS. In the case of the double sulphide of Cu and Fe, the Fe is first removed by a series of calcinations and fusions, S passing to the Cu and O to the Fe, the oxide of iron thus formed uniting at the same time with silica to form slag. This process goes on so long as any iron remains. As soon as the iron is all removed, the reaction between Cu_2S, CuO, and Cu_2O takes place, liberating metallic copper. The principal impurities in copper ores likely to pass into the Cu are As, Sb, Zn, Pb, Bi, Sn, Ni, Co, Au, and Ag. The greater proportion of these present either volatilises or becomes oxidised and removed in the slags. Au and Ag, being neither appreciably volatile under the conditions nor oxidisable, become concentrated in the copper. It is particularly difficult to get rid of the last traces of As and Bi. The use of a basic lining to the furnace—say, dolomite—greatly facilitates the removal of As in the slag. The elimination of As is also assisted by the use of 'soda nitre' in refining. Bi can most readily be removed by what is known as the *best-selecting* process, in which advantage is taken of the circumstance that copper has a greater affinity than bismuth for sulphur. This process comes in just before the copper is first reduced from the sulphide. A little copper is made to separate by the reaction between sulphide and oxide; this throws out and collects as 'bottoms' the bismuth, tin, lead, and antimony.—3. *Fused in the presence of another metal which combines with, and so removes, the sulphur*; *e.g.* sulphides of Bi, Pb, and Sb treated with Fe; Ag separated by metallic Pb from sulphide of Pb containing sulphide of Ag. Copper can only be partially separated from sulphur in this way, a double sulphide forming which cannot be reduced by iron.

The operations described under (i) and (ii) are in some cases applied directly to the ore *without first separating the sulphide by liquation or fusion.*

(*c*) *Sulphides volatile without fusion.* Amongst the metallic sulphides there is only one which sublimes without fusion, viz. HgS. When heated in presence of air HgS yields SO_2 and Hg. As the Hg has no tendency to combine with oxygen under these conditions, and is volatile at a very low temperature, it distils over, and may readily be condensed. For these reasons advantage is not taken of the fact that the sulphide is itself volatile, it being simpler to distil the metallic mercury direct from the ore. The sulphur is sometimes removed by roasting the mercury ore with lime or oxide of iron.

Treatment of Sulphides by Dry Methods.

I.

Infusible.

Calcined = oxide

II.

Fusible.

(a) *Low temperature* — Liquated

(b) *High temperature* — Fused and separated as sulphide

Roasted = oxide

Partially roasted and fused = metal

Sulphur removed by means of another metal = metal

III.

Sublimed without fusion.

1. Sulphur separated by calcination alone = metal.
2. Sulphur separated by lime, oxide of iron, or iron = metal.

Wet processes for sulphides and arsenides. The sulphide and arsenide ores of Ni, Cu, and Co are partially, and those of Cu and Ag partially or wholly, treated by wet methods. In these processes the metal is first made to form a soluble compound. This may be done by roasting the ore with, or in some cases only mixing it with, some compound, which by double decomposition will convert the metal to be extracted into a soluble compound. In other cases it is done by roasting the ore alone at a low temperature, or even by simply exposing it to the action of the atmosphere without using artificially produced heat; in either case the sulphide will be converted into a sulphate; *e.g. copper pyrites* and silver ores.

Thus, soluble sulphate of copper may be formed by roasting copper pyrites or more slowly at the ordinary temperature of the atmosphere. About one-third of the copper extracted in this country is obtained from Spanish pyrites, averaging only 3-4 p.c. of copper, by roasting the burnt ore—received from the sulphuric acid works—with common salt, which reacts with the $CuSO_4$ produced during the burning, to form $CuCl_2$, which is then dissolved out, together with the chlorides of Ag, Pb, and Au, these metals being present to a small extent. The Ag is thrown down, along with Au and Pb, by a soluble iodide, KI or ZnI_2. The iodine is removed from the AgI by Zn. Finally the Cu is ppd. by addition of iron.

The reactions which take place in the wet treatment of silver ores are of special interest and importance. They are divisible into three classes.

I. *The insoluble silver compound is decomposed and the Ag amalgamated while still in the ore* ('free milling ore'), *without the aid of any furnace-operation whatever.* If there is much S or As present the ore, where practicable, is first roasted with salt. Under this head are included all the amalgamation-processes.

II. *The insoluble silver compound is converted into sulphate by roasting alone and washed out with water; or the Ag is converted into chloride by roasting with common salt, and washed out by a solvent for chloride of silver.* Under this head are included the Augustin, Ziervogel, Von Patera, and Russell processes.

III. *The insoluble silver compound is converted into a soluble compound by the action of certain salts in solution without roasting the ore or employing any furnace-operation whatever.* This class includes the Von Patera process when applied to 'amalgamation tailings,' and the Russell process applied to both ores and tailings.

The amalgamation-methods without roasting have been of great service where fuel is scarce, as in Mexico. These methods depend on the power of certain salts, such as the chlorides of Cu, to decompose Ag_2S. If mercury is present at the same time, the AgCl will be reduced and the Ag taken up by the excess of Hg, from which it can be separated by squeezing and distillation. Iron or Cu may be employed to decompose the AgCl, Hg being used only to collect the Ag. This reduces the loss of Hg, but to bring about sufficient contact, more power, and consequently more fuel, is required. Where fuel is available there is often great advantage in roasting the ore with salt before amalgamation.

Where possible the amalgamation-methods have been superseded by the other wet processes included under heads II. and III., viz. the Augustin, Ziervogel, Von Patera, and Russell methods.

The Augustin process. Ore or regulus is first partially roasted, and then undergoes further roasting with common salt, the AgCl thus formed being washed out with NaClAq and ppd. by Cu. The Ag is usually first concentrated in copper mattes.

The Ziervogel process. This method depends on the difference between the temperatures required to break up the sulphates of different metals. Thus by suitably regulating the temperature, the sulphates of Fe, Cu, &c., formed by roasting mattes at a low temperature, may be decomposed into oxides and SO_2, while the sulphate of Ag will be unaltered, and can therefore be extracted by warm water, and then ppd. as in the previous method. The regulation of the temperature throughout a large furnace is obviously a point requiring considerable skill. For this reason, in practice, mattes are usually first worked by the Ziervogel process, and the residue extracted by the Augustin method.

Von Patera process. The soluble salts produced by roasting the matte are first dissolved out with water, after which the matte is further roasted with NaCl, and the AgCl washed out with $Na_2S_2O_3Aq$ or CaS_2O_3Aq, from which solution the Ag is ppd. by a soluble sulphide or SH_2. The silver is reduced from the Ag_2S, either by roasting or by boiling with freshly slaked lime, forming calcium polysulphide. When there is much of the base metals present, more particularly lead, the Von Patera process is not so suitable. The lead is mostly present as sulphate after roasting, and this is soluble in $Na_2S_2O_3Aq$. Some of the most important objections to the Von Patera process, as applied to poor ores containing base metal, are obviated in the process next described.

The Russell process. In this process what is known as the '*extra solution*' is used, in addition to or in substitution for that ordinarily employed in the Von Patera process. The '*extra solution*' is prepared by making solutions of $Na_2S_2O_3$ and $CuSO_4$, containing respectively 18 parts of the former and 10 parts of the latter salt, and mixing them together. The pp. after washing is dissolved in a solution containing $1-2\frac{1}{2}$ p.c. $Na_2S_2O_3$. Although this '*extra solution*' is not so good a solvent for AgCl as $Na_2S_2O_3Aq$, yet it acts energetically on native silver and the compounds of silver with S, As, and Sb. Owing to the want of permanence special precautions have to be taken in using this solution. To get the best effect the solutions should be used warm. In order to obtain finer bullion by this process, advantage is taken of the fact that $PbCO_3$ is not soluble in the solution, although other salts of lead are soluble. Na_2CO_3, free from NaOH and Na_2S, is added to the solution containing the silver and lead which have been washed out. It is stated that the whole of the Pb may thus be removed. Carbonate and sulphate of Cu are the only compounds of Cu likely to occur which are soluble in the '*extra solution.*'

It is probable that this process in the near future will supersede very largely the fusion and amalgamation-processes, besides which it is applicable to ores which cannot profitably be treated by either of the other methods. The cost of the necessary chemicals is much less than that due to loss of mercury; in addition to which, lead and copper are lost in the older processes and saved in the Russell process.

In some cases the ores may be treated direct by the Russell process without previous roasting, and both the Von Patera and Russell methods are largely used in the treatment of 'tailings' from amalgamation.

Nickel and cobalt. It has been seen that these metals may be separated from others as arsenide. In practice, however, the separation is not so complete, some of the nickel and cobalt passing into the regulus, and some of the other metals into the *speise.* The following are the reactions usually employed to separate the various metals from one another. The calcined speise is treated with HClAq. The resulting solution, which will contain Ni, Co, Fe, Cu, Pb, Bi, and As, is diluted, and oxidised by bleaching-powder, the proportion added being adjusted by a rough analysis. Milk of lime is added to the requisite extent to throw the iron down as sesquioxide, any arsenic present at the same time ppg. as basic arsenate of iron. The solution is next treated with SH_2, to ppt. Cu, Pb, and Bi, after which the Co can be thrown down as sesquioxide by a further addition of bleaching-powder, and subsequently the Ni ppd. as hydrated oxide by the addition of milk of lime.

Class III. OXIDES; INCLUDING CARBONATES AND SILICATES. *Ores of this class are reduced to the metallic state by means of carbonaceous matter such as charcoal, coal, or coke, or by means of the gaseous product of the incomplete oxidation of carbonaceous matter, viz. carbon monoxide.*

The only exceptions among the oxides of the commoner metals are Al_2O_3 and MgO. These oxides cannot be reduced to the metallic state in this way; they have to be converted into double chlorides, from which, while in a state of fusion, the metals are liberated by metallic sodium, or by electrolysis. The metals, the oxides of which are in practice reduced by carbon or CO, are Sn, Fe, Ni, Co, Mn, Cr, W, and Zn. Of these Sn and Zn present the simplest reactions. The reactions in the other cases are complicated by the fact that all these metals combine more or less freely with carbon. When it is desired to obtain the metals in the most malleable condition, *i.e.* free from carbon, the fact that the oxides and the carburised metals react with one another eliminating both the carbon and the oxygen, as CO and CO_2, is utilised. Every iron- and steel-making process is dependent on this reaction. According as the conditions are made more or less favourable to carburisation, or decarburisation, so will the resultant metal be either cast-iron, hard steel, mild steel, or malleable iron. It is possible to reduce the oxides under consideration to the metallic state, and also to carburise the metals, by the action of CO, without the metals becoming fused. The oxides are first reduced, and then carburised by the dissociation of some of the CO. The liberated oxygen combines with CO and is thus removed. Nickel is thus reduced to the metallic state, more or less combined with carbon; and bars of metallic iron are carburised to produce 'cementation' steel. In a similar way a carburised metal may be decarburised by O or CO_2; in this way 'malleable cast-iron' is made. Whether the action consists of carburising or decarburising is entirely dependent on which agent preponderates at the time in the atmosphere surrounding the body.

Reactions for removal of 'impurities' from metals of oxide class. The refining of Ni and Co, as we have seen, precedes the reduction to the metallic state. The refining of Sn is effected after reduction, partly by liquation and partly by oxidation, by which means the principal impurities, Fe, As, and W, are removed. Mn and Cr are reduced directly from their ores, in the form of alloys with iron, only pure ores being used. Tungsten is either reduced directly from the ore, alloyed with iron, or undergoes a preliminary purification and ppn. as oxide in the wet way. The impurities which it is important to remove from iron are S and P. The latter can only be passed into the slag when the slag is basic, and the conditions tend to oxidation. Thus, P is removed in the primitive iron making processes; also when iron is made by the '*finery*' and the '*puddling*' processes; also in making '*ingot-iron*' by the Siemens and Bessemer processes, when a basic lining to the furnace or converter is used. P is not removed in processes in which pig-iron or high-carbon steel is made, nor in the Siemens or the Bessemer processes when the furnace or converter is lined with siliceous material, and malleable metal is being produced. In the Bessemer process, with an '*acid-lining*,' the necessary heat for the process is obtained mainly by the oxidation of silicon in the pig-iron; when a phosphoriferous pig-iron is used, and a '*basic-lining*,' most of the heat is obtained by the oxidation of the phosphorus and less silicon is required in the pig-iron. In both processes a portion of the heat is obtained from the oxidation of C. Sulphur can be removed econo-

mically only in the blast-furnace, because when treating pig-iron for the production of malleable iron the sulphur is one of the last substances to oxidise out, and its removal would result in a great waste of iron. To remove S in the blast-furnace the temperature must be high, and the conditions must be strongly reducing and carburising: *i.e.* the charge must contain plenty of charcoal, coal, or coke, and lime must be added to the charge in considerable quantity. Under these conditions the S combines with the Ca, and passes into the slag as sulphide.

Slag reactions. Slags consist of the non-metallic constituents of an ore or furnace-product, and of the useless or objectionable metallic elements. They are produced by simply fusing the ore alone, if it is in itself sufficiently fusible, or by fusing it with such materials—fluxes—as will bring about the requisite fusibility. Except in a few special cases, *e.g.* the reduction of aluminium or magnesium, slags consist of more or less complex silicates. In processes for making more or less malleable iron, the slags are composed mainly of silicates of Fe, Ca, Al, and Mg, with smaller proportions of silicates of Mn, alkalis, and alkaline earths. In pig-iron slags, the iron is comparatively small in quantity, or is even entirely absent when much lime is used. In other slags, excepting those produced in treating the 'noble metals,' iron will generally be present in large proportion.

Electro-metallurgy. Electro-metallurgical processes are divisible into two distinct classes: one class includes processes for the extraction of metals from their ores; the other includes processes for refining metals already extracted. Although a great many processes have been devised for the electrical extraction of metals, except for the extraction of aluminium and magnesium—in which cases the metals are first got into the condition of double chlorides, or, in the case of aluminium, sometimes of fluoride—there is not much prospect of such processes being successfully and economically worked, even when power can be obtained from waterfalls. By the Cowles process, according to Sterry Hunt, nearly pure Al is produced in small buttons, but up to the present it has been necessary to reduce some other metal with the Al to collect it together. In this process the Al_2O_3 and the oxide of the metal to be alloyed with the Al are mixed with carbon, and the mixture is placed round two carbon poles between which an electric discharge is made to pass.

The second class of processes has been advantageously applied to the refining of Cu, more particularly Cu containing small quantities of Au and Ag. In refining Cu electrically, the electrolyte is usually $CuSO_4Aq$, kept at as uniform a temperature and concentration as possible; the anode being formed of the copper to be refined, pure copper depositing on the cathode. The silver and gold collect at the bottom of the tank as a muddy deposit. A. K. H.

METALS. An element is a definite and distinct kind of matter which has resisted all attempts to separate it into unlike portions. The classification of the elements, in accordance with their chemical properties, necessarily carries with it the classification of many compounds, inasmuch as the chemical properties of an element cannot even be stated without considering the composition, general chemical behaviour, and conditions of formation, of compounds of that element. For instance, certain elements are placed in the same class because they all form hydroxides which are alkalis: this statement implies an acquaintance with the compositiou, methods of production, and chemical properties, of the alkalis; but one of the chemical properties of an alkali is that it neutralises acids, and in so doing forms salts; hence it is necessary to know something about acids and salts, in order to understand what is meant by an alkali, or by an alkali-forming element.

The elements may be classified in accordance with their physical properties. If a binary compound is electrolysed, one of its elements separates at the positive electrode, and the other at the negative electrode (secondary reactions which may occur are supposed to be overlooked). That element which separates at the positive electrode is said to be electro-negative to the other element. By studying the electrolysis of binary compounds, the elements may be arranged in an electrical series. This series may be divided into two parts: all the elements on one side of any chosen element are electro-positive to all the elements on the other side of the chosen element. Taking hydrogeu as the central element we are able to subdivide the elements into two classes; all the elements on one side of H are electro-positive to the elements on the other side of H. Thus we arrive at a classificatiou of the elements founded ou one chemico-physical property. Now we find that the electro-positive elements, on the whole, more resemble one another in certain physical properties, and also in their general chemical character, than they resemble the electro-negative elements. Those elements which are electro-positive to H as a class are greyish-white in colour, lustrous, fairly malleable and ductile, comparatively good conductors of heat and electricity; those elements which are electro-negative to H vary much in colour and appearance, they are not usually lustrous, they are generally brittle, and they do not conduct heat or electricity well. Turning to the chemical characters of the two classes of elements, we find that those placed in the electro-positive class generally combine with O to form basic oxides: their compounds with O and H are also usually basic; they do not, as a rule, enter into the composition of acids; very few of them form hydrides; their haloid compounds, as a whole, are tolerably stable as regards the actiou of heat, and they are not readily decomposed by water; if they are thus decomposed they generally produce oxyhaloid compounds; speaking broadly, these elements do not exist in allotropic forms. On the other hand, we find that most of the elements which are placed in the electro-negative class combine with O to form acidic oxides; their compounds with H and O are usually acids. All acids contain one or more of these elements; they generally form hydrides; many of their haloid compounds are decomposed by heat, and many of them are also decomposed by reacting with water, thereby producing haloid acids and either oxides or oxyacids of the electro-negative elements; speak-

ing broadly, these elements exhibit the phenomena of allotropy.

Hence, it would appear that the division of elements into two classes, those which are electro-positive to H, and those which are electro-negative to H, is a good classification, because with this one class-mark many other properties, both physical and chemical, are associated.

The electro-positive elements are called metals; the electro-negative elements are called non-metals.

A further examination of metals and non-metals shows that the classification implied in these terms is very far from being sufficient for chemical purposes. We cannot define the term metal; just as we cannot define any of the chemical names which are given to classes of bodies. We can sketch the ideal metal. Considered physically, the ideal metal is a hard, fairly heavy, greyish-white, lustrous, malleable, ductile, and tenacious solid, which melts only at a high temperature; it is a good conductor of heat and electricity; it crystallises in forms belonging to the regular system; its emission-spectrum consists of lines, and is comparatively simple in character. Considered chemically, the ideal metal is hardly, if at all, changed in the air, it combines with O at fairly high temperatures, and forms one or more oxides which are basic, *i.e.* which react with acids to form salts; it reacts with water or steam to produce an oxide or hydroxide and evolve H; no hydride of the ideal metal is known; it does not enter into the composition of acids, but it reacts with acids to form salts; its sulphides react with acids to produce salts and evolve H_2S, they combine with the sulphides of decidedly electro-negative elements; the salts of the ideal metal are numerous and stable; it forms but few acid salts, but the number of double salts into which it enters is large; it combines directly with the halogens, producing compounds which are volatilised without decomposition at rather high temperatures, and which dissolve in water without change; the ideal metal forms alloys with elements of its own class, which alloys belong rather to the group of physical, than to that of chemical, compounds; lastly, the ideal metal exists in only one modification, *i.e.* it does not show allotropy. The ideal non-metal is the opposite, chemically and physically, of the metal.

No element exhibits all the properties which we have placed in the category '*metal*'; nor is there any element which possesses even some of these properties without at the same time also possessing some of the properties which belong to the typical non-metal.

The elements sodium and potassium possess most of the chemical properties enumerated as characteristic of metals; but these elements are instantly oxidised by exposure to air; they probably form unstable hydrides; they are very soft, lighter than water, and melt at moderately low temperatures.

The element gold possesses most of the physical properties characteristic of metals; but its hydroxide reacts with alkalis to form salts, *e.g.* $KAuO_2$; Au also forms the acids $HAuBr_4$ and $HAuCl_4$; Au_2S combines with the sulphides of the very metallic elements K and Na to form salts. The element chromium exhibits many of the characteristic physical properties of metals; it also decomposes steam with evolution of H; it combines with the halogens to form stable compounds, some of which have been gasified at high temperatures; chromium does not form a hydride; the oxides CrO and Cr_2O_3 are basic; the element reacts with many acids to form salts, which are well marked, stable compounds; it does not exist in allotropic forms. On the other hand, CrO_3 is a distinctly acidic oxide, reacting with water to form the acid H_2CrO_4, from which is obtained a large number of salts. In other words, chromium belongs to the class metals, and also to the class non-metals. In an even more marked way than Cr, manganese combines in itself both metallic and non-metallic properties.

The chemical properties of an element depend on the properties of the other elements with which it combines, and on the relative quantities of these other elements entering into combination. It is this fact which makes it impossible to apply the definition of metal or non-metal, in its entirety, to any element. The classification of elements into metals and non-metals is nevertheless a useful one, provided it is employed with judgment and knowledge. If we find that a certain element is hard, lustrous, unchanged or only slowly changed in the air, and is a good conductor of electricity, or if we find that the oxide of a certain element is basic, and that the chloride is not decomposed by water, or if decomposed produces an oxychloride, we have at once a guide to lead us in our further examination of the element. We shall probably find that the element in question possesses several of the other physical characteristics of metals; and we shall also probably find that it reacts with acids to form salts, decomposes steam with evolution of H, produces at least one sulphide which combines with sulphides of some of the negative or non-metallic elements, and so on.

The following division of the elements usually placed in the class *metals* is that arising from the application of the periodic law.

CLASS I. *division* 1;	Li Na K Rb Cs
,, 2;	Cu Ag Au.
CLASS II. *division* 1;	Be Ca Sr Ba
,, 2;	Mg Zn Cd Hg.
CLASS III. *division* 1;	Sc Yt La Yb
,, 2;	Al Ga In Tl.
CLASS IV. *division* 1;	Ti Zr Ce Th
,, 2;	Ge Sn Pb.
CLASS V. *division* 1;	V Nb Di Ta
,, 2;	As Sb Er Bi.
CLASS VI. *division* 1;	Cr Mo W U
,, 2;	none isolated.
CLASS VII. *division* 1;	Mn
,, 2;	none isolated.
CLASS VIII. *division* 1;	Fe Ni Co (Cu)
,, 2;	Rh Ru Pd (Ag)
,, 3;	Os Ir Pt (Au)

The metals in division 1 of Class I. are generally known as the *alkali metals*. They possess in the most marked way the chemical characters of the ideal metal; none of their compounds exhibits any acidic functions; they are electro-positive to all the other elements. The metals

in division 2 of Class I. are very distinctly metallic in thoir physical properties; chemically considered they show considerable differences among themselves; several compounds of gold are almost non-metallic in their reactions, the chemical and physical analogies of this element are best represented by placing it both with Cu and Ag, and also with Os, Ir, and Pt, in division 3 of Class VIII.

The *alkaline earth metals* which form division 1 of Class II. are more metallic in their physical properties than the metals placed in division 1 of Class I.; chemically they are also distinctly metallic. Coming to Mg, Zn, Cd, and Hg, which form division 2 of Class II., we have four elements whose properties closely approach those of the ideal metal; Cd may be taken as on the whole the best actual representative of the class metal. As we pass to the higher classes we find many metals exhibiting properties characteristic of non-metals, until in Class VII. we arrive at Mn, an element which is at once distinctly metallic and decidedly non-metallic in its chemical properties.

In connexion with the subject of this article, reference should be made to the following articles wherein the different classes of metals are described:— ALKALINE EARTHS, METALS OF THE, vol. i. p. 112; ALKALIS, METALS OF THE, vol. i. p. 114; CHROMIUM GROUP OF ELEMENTS, vol. ii. p. 168; COPPER GROUP, vol. ii. p. 250; EARTHS, METALS OF THE, vol. ii. p. 424; IRON GROUP, vol. iii. p. 65; MAGNESIUM GROUP, vol. iii. p. 163; NITROGEN GROUP (for Class V., V to Bi), vol. iii. *infra*; NOBLE METALS, vol. iii. *infra*; TITANIUM GROUP, in vol. iv.; TIN GROUP, in vol. iv.

M. M. P. M.

METALS, RARE. Under this name are included a number of presumed elementary bodies concerning which our knowledge is at present very imperfect. We see that in their general properties they approximate more or less closely to cerium, yttrium, and lanthanum, but we are not sure how far we have yet obtained them in a state of purity. Consequently we are in doubt not merely as to their at. w. and S.G., but even as to their number and their rank as elements, compounds, or mere mixtures. Our ignorance is due to the great rarity of these bodies, to the high complexity of the minerals in which they are found, but most of all to the fact that they differ among themselves meroly by very minute shades.

The principal sources of the rare metals are *gadolinite*, *keilhauite*, *fergusonite*, *euxenite*, *cerite*, and *thorite*, which are Norwegian minerals, and further, *samarskite*, which was first obtained from tho Urals, but has since been found in relatively large quantities in North Carolina. It is to be noticed that specimens of any one of these minerals, if from different localities, are not identical in the earths they contain. Hence if it is desired to isolate any particular earth it is best to select as the first material that mineral in which nature has, so to speak, commenced the task of separation. (This method was proposed by the writer in his address to the chemical section of the British Association, Birmingham Meeting (*C. N.* 54, 123; *ibid.* 54, 157; *Pr.* 40, 505.) Nilson a. Krüss have since adopted and recommended the same method (*B.* 20, 2134; *C. N.* 56, 74, 85, 135, 145, 154, 165, 172).

The recognition of tho various rare earths is a matter of no little delicacy. Here spectroscopy in its several modifications renders the greatest service. In endeavouring to ascertain by this means what substances are present in a mineral containing rare earths, chemists may employ either the spark-spectrum, the absorption-spectrum, or the incandescence- or the phosphorescence-spectrum. They may further apply any of these tests either at once to the original matter, or to some of its portions after a partial separation has been effected by chemical treatment. The question of course arises, how are we to know when we have obtained any one earth separated from all other bodies, and absolutely pure? In the case of those earths and their solutions which present an absorption-spectrum, *e.g.* didymia, samaria, holmia, erbia, &c., the writer has shown that as an element approaches simplicity the absorption-spectrum of its solutions will become less and less complicated; hence it would appear that when absolutely free from its associates, each element would have an absorption-spectrum of great simplicity, in many cases consisting of one band only (the 'one band, one element' hypothesis). But as certain earths, *e.g.* lanthana, mosandra, philippia, scandia, terbia, &c., give no absorption-spectra, this test is not applicable in all cases.

Great caution is required in drawing conclusions from the examination of spectra. Concerning the influence of one body upon another little is yet known, but that little is of sufficient importance to make us very careful how we interpret absorption-spectra when not corroborated by chemical results. Lecoq de Boisbaudran a. J. Lawrence Smith have pointed out some important modifications produced in absorption-spectra by the presence of an excess of acid in the solution (*C. R.* 88, 1167). Soret subsequently verified these observations. Brauner and others have put on record experiments on mixing solutions of didymium and samarium. They find in the case of a didymium solution showing the group of three bands, 476, 469, 428 [$1/\lambda^2$ 430·4, 441·3, 454·6], that, by adding a dilute solution of samarium, these three bands vanish, without the appearance of any of the samarium bands, until a certain proportion is reached, when the samarium bands gradually come into their places (Brauner, *C. J.* 43, 286).

Many of the earths that do not yield solutions giving absorption spectra can be made to give characteristic spectra by phosphorescence. This is known as tho 'radiant matter' test. When the spark from a good induction-coil traverses a tube having a flat aluminium pole at each end, the appearance of tho spark changes according to the degree of exhaustion. If atmospheric air is the gas under exhaustion, at a pressure of about 7 mm. a narrow black space is seen to separate the luminous glow and the aluminium plate connected with the negative pole of the induction-coil. As the exhaustion proceeds this dark space increases, until at a pressure of about 0·02 mm. the dark space nearly fills the tube; the luminous cloud showing the presence of residual gas has almost disappeared, and the molecular discharge from the negative pole

begins to excite phosphorescence on the glass where it strikes the side. There is a very wide difference in the degree of exhaustion at which various substances begin to phosphoresce. Under the influence of this discharge of 'radiant matter,' a great many substances emit, more or less intensely, a phosphorescent light. On examining this light in the spectroscope, most of these bodies give a faint, continuous, spectrum with a more or less decided concentration in some one part, the superficial colour of the phosphorescing substance depending on this preponderating emission in one or other part of the spectrum. Sometimes, but less commonly, the spectrum of the phosphorescent light is discontinuous.

If we examine the rare earths by this 'radiant matter' test we find they present phenomena of a striking character. Some of them remain unaffected, and are thus at once referred to a distinct group. Others, such as thoria, do not phosphoresce and offer great obstruction to the passage of the spark. Other earths become very phosphorescent and vary greatly in their power of retaining a residual phosphorescence. On examining phosphorescent earths glowing in a vacuum tube, the writer found remarkable differences in the duration of this residual glow. Some of the earths remain luminous for many minutes after the cessation of the current, while others cease to phosphoresce immediately on the stoppage of the current. Take the case of yttria. This earth, the writer finds, can be resolved by chemical treatment into a series of simpler bodies of unequal basicity, to which he has given the provisional designations of $G\alpha$, $G\beta$, $G\delta$, $G\zeta$, $G\eta$, and $S\gamma$. The after-glow of these bodies differs somewhat in colour from that which the earth exhibits while the current is still passing. The spectrum of the after-glow also shows that some of the lines are missing. In the electrical phosphoroscope—an instrument similar to Becquerel's phosphoroscope, but having the substance acted on electrically instead of by direct light—the different bands of the new constituents of yttria (*v. infra*) do not all appear at the same speed of rotation. At the lowest speed the double greenish-blue band of $G\beta$ is first seen, followed next by the dark-blue band of $G\alpha$. As the velocity increases there follows the bright citron-yellow band of $G\delta$, and as the utmost speed approaches the red band of $G\zeta$ is seen, but not without difficulty. As another instance, if lanthanum sulphate, with traces of Sm as impurity, along with a little lime is examined in the phosphoroscope, the band of $G\epsilon$ is visible at the lowest speed; $G\delta$ follows at an interval of ·0035 second, and the $G\alpha$ band immediately afterwards. All the earths of the yttrium and samarium groups yield discontinuous spectra when submitted to the induction discharge *in vacuo*.

A modification of phosphorescence-spectroscopy is produced by the previous addition of other earths to the specially phosphorescent earths. Lime exerts a remarkable action. By itself, it phosphoresces with a continuous spectrum, while yttria phosphoresces with a discontinuous spectrum. But if these two bodies are mixed together, the phosphorescing energy of the lime does not extend over the whole spectrum, but concentrates itself in strengthening the yttria bands. These bands become broader, but at the same time less sharply defined, in proportion as the lime is increased in quantity. Lime also brings out the phosphorescent bands of samaria. It also suppresses the sharp line $S\delta$, the most striking feature in the phosphorescent spectrum shown by pure samarium sulphate. On the other hand an addition of 'old' yttria deadens the other lines of samaria, but brings out the line $S\delta$ more strongly. Lanthanum sulphate in the 'radiant matter' tube phosphoresces with a reddish colour. If lime is added to lanthanum sulphate the phosphorescence changes its colour from red to yellow. Lime also brings out the bands of yttrium and samarium if these are present as impurities. So sensitive is this test that it will show the presence of one part of yttria or samaria in more than a million parts of lime. When $G\delta$, $G\alpha$, and $G\beta$ are present in small proportions with lime the bands of $G\delta$ and $G\alpha$ become intensified, but a dark space appears instead of the green band of $G\beta$. Hence if only a small trace of $G\beta$ is present in lime the green band is not only obliterated, but the quenching action suppresses that part of the continuous lime-spectrum which has the same refrangibility as the $G\beta$ line, and thus gives a black space in the spectrum.

There are many instances of the modifications induced in the normal spectrum of one earth by the admixture of others when treated as anhydrous sulphates. One of the most striking instances is that of a mixture of samaria with yttria, since the presence of even 40 p.c. of yttria practically obliterates the spectrum of samaria. The most minute proportion of lime added to samaria causes the sharp line at $1/\lambda^2$ 269 to vanish, while at the same time it much intensifies the other bands (*Tr.*, pt. ii. 1885; *C. R.*, June 15, 1885). The action of lime upon yttria is of great use in detecting very minute traces of this earth when in admixture with elements which would otherwise prevent its phosphorescence.

Alumina is also active in inducing new spectra when mixed with the rare earths. A moderate amount of fractionation has enabled the writer to penetrate beneath the veil of red phosphorescence observed in crude alumina and to see a complicated sharp-line spectrum (*C. N.*, 56, 62, 72). The new body of which glimpses have been obtained is probably one of the unknown earths in decipia, since the new spectrum may be fairly reproduced by adding one of the fractionations of decipia to alumina. Hence, it will be seen that the performance of a long series of check and counter-check experiments often becomes necessary before the presence or the absence of any particular earth can be inferred.

The quantitative separation of the rare metals is much more difficult than their mere recognition. These substances are not linked to one another, or to other elements with which they are associated, by any strong affinities, but they are nearly identical in their behaviour and properties. Hence we have so far been unable to find any reagent or any mode of treatment which at once quantitatively separates one of these substances from all the others. We are therefore obliged to have recourse to tedious processes of fractionation.

In attempting to enumerate or describe the rare metals, we meet with the additional difficulty that the unitary character of many of them is still a matter of extreme doubt.

Several of the rare metals will be found described in their proper alphabetical order in this Dictionary, *e.g. beryllium, cerium, didymium.* Many of these, as will be seen below, are probably capable of being further split up, but as they are frequently mentioned in chemical treatises and memoirs their description as at present, or lately, known has been found necessary.

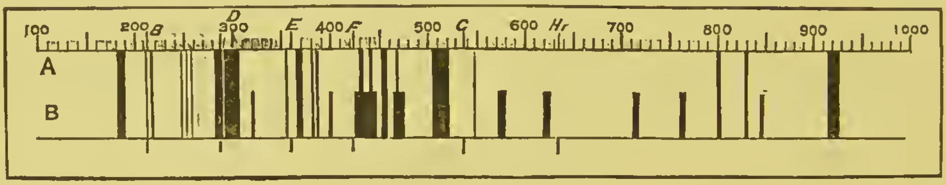
There are certain other metals which are still under discussion, *e.g.* decipium, philippium, holmium (Soret's X), and dysprosium. Roscoe has indeed proved that philippium is a mixture of terbium and yttrium, and the experiments of the writer have confirmed his results; but until we know more about the constitution of terbium and of yttrium, both of which are undoubtedly compound bodies, these experiments do not carry us much further. Samarium is also identical with a body which other chemists have named 'yttrium β.'

It has been mentioned elsewhere that the old didymium, after the elimination of Delafontaine's decipium, was found by Lecoq de Boisbaudran to contain another body, which he named samarium, characterised by the bands of Delafontaine's decipium, together with two additional bands (*cf.* figs. 1 and 2). After the removal of these bodies the residual didymium was split up by Auer von Welsbach into the two bodies, neodymium and praseodymium, the absorption-spectra of which are shown respectively in figs. 3 and 4. It will be observed, however, that two of the bands of old didymium are not to be found in the neodymium and praseodymium spectra taken conjointly. Hence it becomes extremely probable that there exists a third body distinct from neodymium and praseodymium to which one of these extra bands, or possibly both, is due. This probable metal the writer has provisionally named Dα. But we still encounter the question whether neodymium, praseodymium, and Dα are ultimate elements, or are capable of still further scission. The researches of several investigators point very decidedly in the latter direction. Thus Nilson a. Krüss in 1887 appear to have obtained from didymium no fewer than nine bodies, each of which may possibly prove to be an element. These bodies have been provisionally named by the discoverers Diα, Diβ, Diγ, Diδ, Diϵ, Diη, Diθ, Diι, and Diκ.

It seems to the writer that neodymium and praseodymium are simply the products into which the original didymium is split up by one particular mode of attack. Any single chemical operation, whether it be crystallisation, precipitation, fusion, partial solution, &c., can only separate a mixture of two bodies into two parts, just as the addition of a reagent only divides a mixture into two portions, a precipitate and a solution. These divisions will be effected on different lines according to the reagent employed. Thus, if we add ammonia to a mixture we may get a separation into two parts, but if we add oxalic acid to the same original solution we split up the mixture differently and obtain two other parts. Thus, if we crystallise a solution of old didymium, as was done by Auer von Welsbach, we divide its components into neodymium and praseodymium. But by fusing didymium nitrate we divide its components in a different way and obtain different products. Now, it is clear that so long as by different modes of attack we obtain different products, we have not yet reduced the original substance to its ultimate elements, we have not yet reached bed-rock.

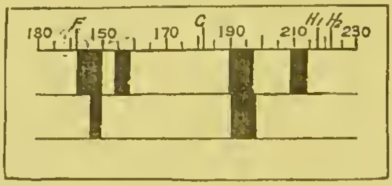
We find that a compound molecule may behave as an element, as has been shown in the case of old didymium. Chemists have a certain number of reagents, operations, or processes in regular use, and if a substance resists all these and otherwise behaves as a simple body, they call it an element. But for all this it may prove to be a compound. Hence, we may legitimately pause before conceding to neodymium and praseodymium the rank of elements. We need some criterion for an element which shall appeal to our reason more clearly than the old untrustworthy characteristic of having not as yet been decomposed; and to this point chemists would do well to turn their most serious attention.

FIG. 1.—Absorption-spectrum of Didymium.



The scale is $\frac{1}{\lambda^2}$.

FIG. 2.—Absorption-spectrum of Samarium and Decipium (De Boisbaudran).



In samarium the writer, by means of the 'radiant matter' test, has recognised four bodies, named provisionally Sδ, Gϵ, Gγ, and Gθ. Very similar observations seem to prove that, like didymium and samarium, erbium, holmium, thulium, dysprosium, &c., are compounds or mixtures of a number of closely allied bodies.

In order to ascertain the existence of supposed new elements chemists have proposed as a test that certain absorption-bands seen in different solutions follow the same variations of intensity. If this is the case we may infer that they are all characteristic of one and the same substance. But if one of the bands dies out while others remain unaltered we may judge that two or more distinct bodies are present.

In erbium the writer has detected two bodies, which he has characterised by their absorption bands λ550 and λ493. Krüss a. Nilson apply apparently to the same bodies the names Erα and Erβ. To obviate all confusion it must be remembered that the name 'erbia' has been given to two bodies which are not identical. The substance which ten years ago was called erbia, and which was then supposed to be the oxide of a simple metal, has been resolved by the investigations of Delafontaine, Marignac, Soret, Nilson, Clève, Brauner, and others into at least six distinct earths. Three of these—scandia, ytterbia, and terbia—give no absorption-spectra, while three others—erbia (new), holmia, and thulia—give absorption-spectra. The first to question the elementary character of old erbium was Delafontaine (*C. R.* 87, 559; *C. N.* 38, 202). He obtained from it and described philippia, a yellow oxide having a strong band in the violet (λ400 to 405), a broad black absorption band in the indigo-blue (about λ450), two rather fine bands in the green, and one in the red.

The history of philippium is very instructive. Soon after Delafontaine' sdiscovery, Soret (*C. R.* 89, 521; *C. N.* 40, 224) stated that he was unable to identify 'Soret's X' with Delafontaine's philippia, the latter being characterised by an absorption-band in the blue occupying the same place as one of the erbia bands. In 1880 Delafontaine (*C. R.* 90, 221; *C. N.* 41, 72) described ten new earths as present in gadolinite and samarskite, viz., mosandra, philippia, ytterbia, decipia, scandia, holmia, thulia, samaria, and two others to which he did not assign names. He concluded that the properties of philippia were identical with those of Soret's X and of Clève's holmia, and proposed that the namo holmia should be set aside in favour of philippia. In *C. R.* 91, 328 (also *C. N.* 42, 185), Clève repeated his earlier assertion that philippia was not identical with Soret's X or holmia. Delafontaine then withdrew all he had said about the absorption-spectrum of philippium and decided that it had no absorption-spectrum at all (*Archives de Genève* [3] 999, 15). Lastly Roscoe (*C. J.* 41, 277) gave an elaborate account of the earth metals in samarskite, proving philippia to be a mixture of yttria and terbia. The present writer, after prolonged chemical examination of these earths, has come to a similar conclusion; but a spectroscopic examination of the earth left on igniting some very carefully purified crystals of philippium formate, tested in the radiant matter tube, has shown that in the separation of Delafontaine's 'philippium' the yttria undergoes a partial fractionation.

Shortly after the announcement of philippium, Soret (*C. R.* 86, 1062) described an earth which he provisionally named X. It was subsequently found to be identical with Clève's holmia (*C. R.* 89, 479; *C. N.* 40, 125). The absorption-spectrum of this earth is marked by a very strong band in the extreme red (λ 804), two characteristic bands in the orange and green (λ 640 and 536), with fainter lines in the more refrangible part of the spectrum, and a number of bands in the ultra violet (see fig. 7). The claim of holmium to rank as an element has been disputed by Nilson and Krüss, who assert that it consists of, or at least contains, four distinct bodies, provisionally named Xα, Xβ, Xγ, Xδ. By submitting Soret's X to fractional precipitation, and examining the fractions spectroscopically, Lecoq de Boisbaudran found that this X, otherwise holmium, consisted of at least two elements: one of these he has named dysprosium, reserving the name holmium for the residue left after the elimination of the dysprosium. The absorption-spectrum of dysprosium shows four bands, λ 451·5, 475, 756·5, and 427·5. The absorption-spectrum of what may be called new holmium is shown in fig. 8. What relation this new holmium bears to any of the components observed in the original spectrum of holmium by Krüss and Nilson is not as yet determined.

The writer (*Pr.* 40, 502) obtained an earth by repeated fractionation, in which one of the bands ascribed to dysprosium, that namely at λ 451·5, was very strong, though the others were absent. As de Boisbaudran regards the bands λ 475 and 451·5 as both belonging to dysprosium, and as the earth obtained gives λ 451·5 strong but with scarcely a trace of λ475, dysprosium consists of at least two simpler bodies. Krüss and Nilson in fact resolve it into three bodies to which they have given the provisional names Xζ, Xε, Xη, and De Boisbaudran gives the absorption-spectrum of dysprosium as shown in fig. 9.

Simultaneously with the discovery of holmia, Clève announced the separation of a second earth from erbia, which he called thulia. Its absorption-spectrum consists of a very strong band in the red λ 680 to 707, and one in the blue λ 464·5 (fig. 10). The ultimate character of thulium is by no means established. Krüss and Nilson resolve it into two bodies, Tmα and Tmβ. Nevertheless the atomic weight of thulium has been determined as 170·7, and the composition Tm_2O_3 has been assigned to its oxide, determinations which for the present must be regarded as premature.

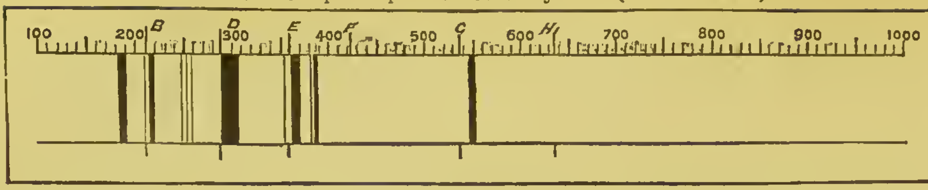
Further, it must be mentioned that the spectrum of old erbium has two faint bands, one at λ 550 and a second broader one at λ 493 (fig. 11). These bands are not to be found in the spectrum of holmium, thulium, dysprosium, or the new erbium (fig. 12). In a long-continued fractionation of the erbia group of earths, conducted with an ample supply of the old erbia, the writer finds an earth giving these two bands concentrated at one end, the bands becoming stronger, while at the same time two other bands make their appearance. This phenomenon indicates the existence of another earth as yet unknown, belonging to the erbium group.

We next come to the yttrium group, comprising the metals yttrium, terbium, gadolinium, ytterbium, scandium, mosandrium, columbium, and rogerium. Of these yttrium, terbium, ytterbium, and scandium form the subject of distinct articles in this Dictionary.

Columbium and rogerium were discovered in the samarskite of North Carolina by J. Lawrence Smith in 1879, but nothing further has been published concerning them. This columbium is perfectly distinct from an element sometimes called columbium, but better known as tantalum.

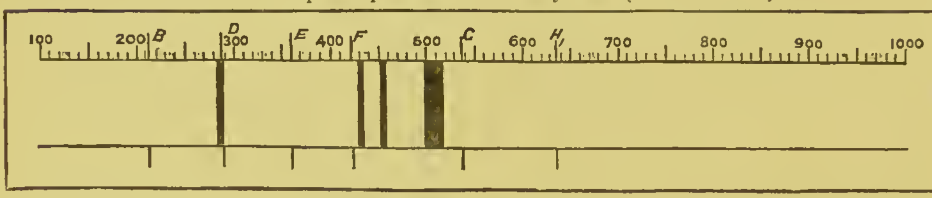
Mosandrum was also discovered by J. L. Smith, and has been the subject of a little controversy. Delafontaine pronounced it a mixture

FIG. 3.—Absorption-spectrum of Neodymium (Von Welsbach).



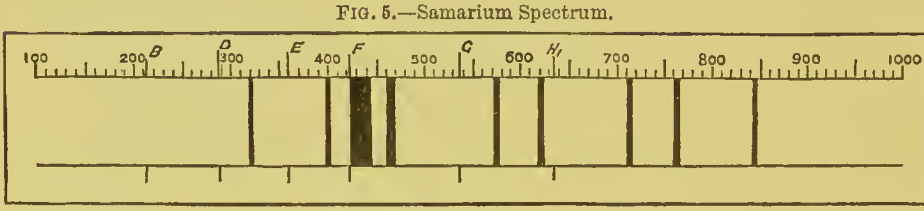
The scale is $\frac{1}{\lambda^2}$.

FIG. 4.—Absorption-spectrum of Praseodymium (Von Welsbach).



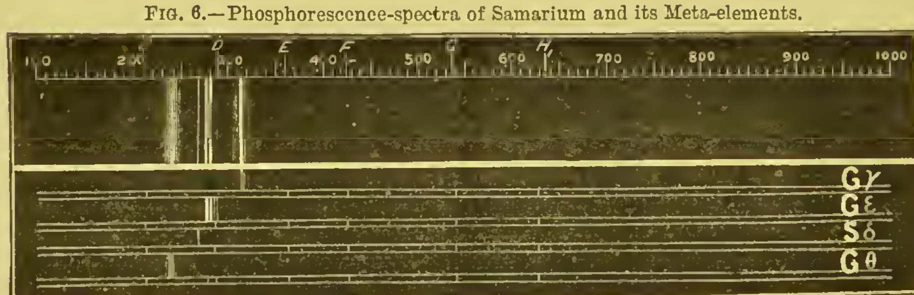
The scale is $\frac{1}{\lambda^2}$.

FIG. 5.—Samarium Spectrum.



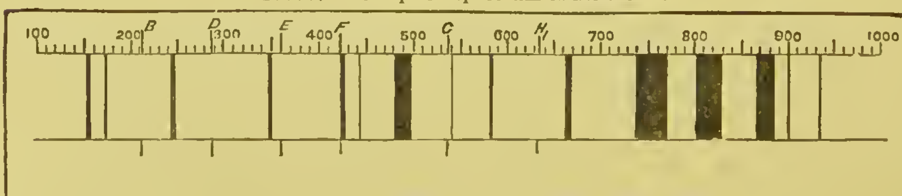
The scale is $\frac{1}{\lambda^2}$.

FIG. 6.—Phosphorescence-spectra of Samarium and its Meta-elements.



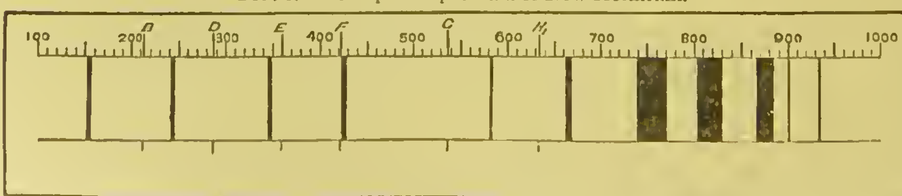
The scale is $\frac{1}{\lambda^2}$.

FIG. 7.—Absorption-spectrum of Holmium.



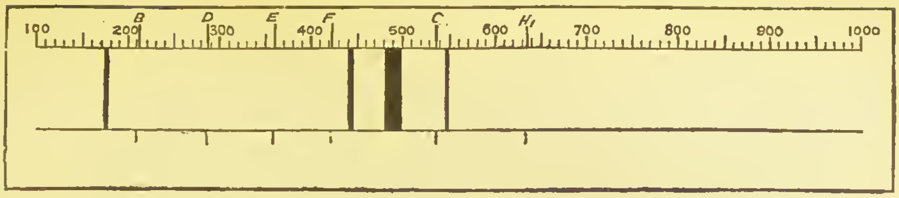
The scale is $\frac{1}{\lambda^2}$.

FIG. 8.—Absorption-spectrum of New Holmium.



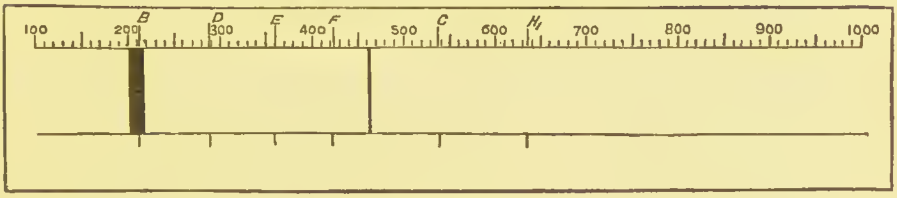
The scale is $\frac{1}{\lambda^2}$.

FIG. 9.—Absorption-spectrum of Dysprosium (De Boisbaudran).



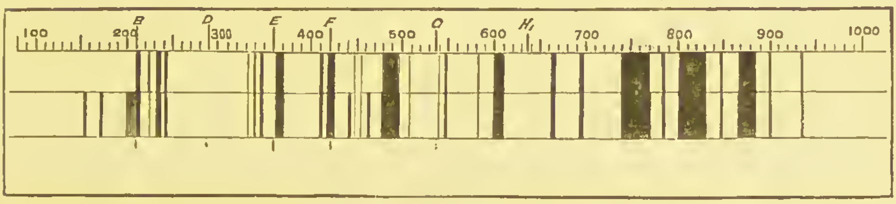
The scale is $\frac{1}{\lambda^2}$.

FIG. 10.—Absorption-spectrum of Thulium.



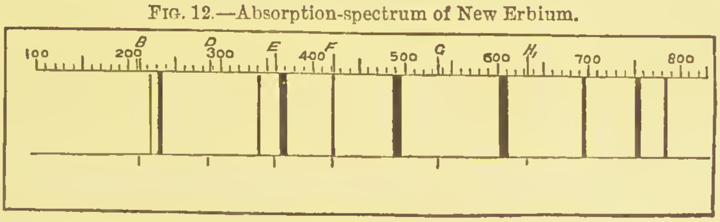
The scale is $\frac{1}{\lambda^2}$.

FIG. 11.—Absorption-spectrum of Erbium (1875).



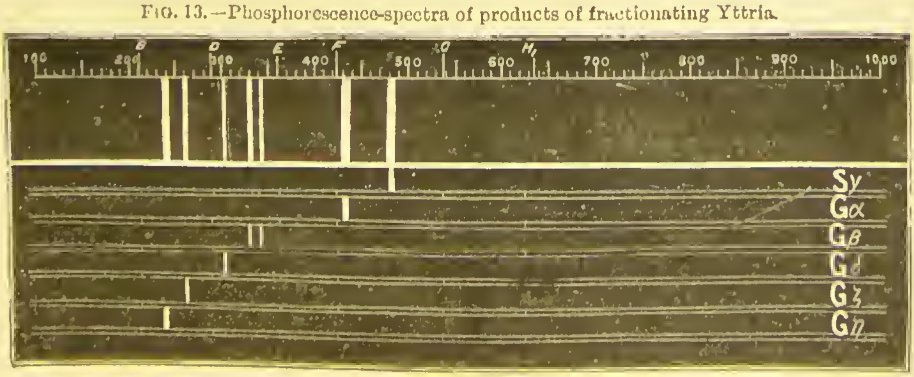
The scale is $\frac{1}{\lambda^2}$.

FIG. 12.—Absorption-spectrum of New Erbium.



The scale is $\frac{1}{\lambda^2}$.

FIG. 13.—Phosphorescence-spectra of products of fractionating Yttria.



The scale is $\frac{1}{\lambda^2}$.

of terbium, yttrium, erbium, didymium, and philippium. In November 1878 and in September 1879 Smith reasserted the elementary character of mosandrum. He states that its compounds are of a deep orange colour, that its double potassium sulphate is not easily soluble, and that its equivalent weight is 51·2. No recent and conclusive investigations on this alleged metal have appeared, and its existence must in the meantime be regarded as exceedingly doubtful.

Decipium has been considered as holding an intermediate position between the didymium and the yttrium groups of rare metals, but its elementary character is very questionable. It has not formed the subject of any recent researches. It is said to show a characteristic absorption band about λ 416.

Gadolinium, otherwise known as the $Y\alpha$ of Marignac, gives no absorption-spectrum. In the writer's investigations its phosphorescence spectrum was found to consist of those of two of the constituents of yttrium, which will be mentioned below.

Yttrium proves to be an exceedingly complex substance. The body to which all chemists would have applied the name yttria as recently as four years ago may be split up into possibly six, but certainly five, bodies, $G\alpha$, $G\beta$, $G\delta$, $G\zeta$, and $G\eta$, two of which, $G\beta$ and $G\zeta$, are also met with as the components of gadolinium. Hence it is convenient to speak of the original substance as 'old yttria' and to remember that such is the substance to which everything written concerning yttria prior to 1885 will be found to refer. Fig. 13 shows the simple phosphorescence spectra of the several components into which yttria may be split up by fractionation. If these components are taken in the order of their apparent basicity—the chemical analogue of refrangibility—the lowest of these constituents gives the deep-blue band $G\alpha$: then follows a strong citron band, $G\delta$, which increases in sharpness as it becomes more separated from its associates until it may be called a line; then a red band, $G\zeta$; then a crimson band, $G\eta$; and, lastly, very close together a pair of greenish-blue bands, $G\beta$.

The diagram, fig. 14, shows a series of nineteen phosphorescence spectra obtained from a prolonged examination of 'old yttria.' The central spectrum, J, is approximately that given by crude 'old yttria,' though this differs slightly according to the mineral from which the old yttria is extracted. After a time fractionation splits up the earth J into two earths here marked I and K, giving slightly different spectra. Fractionating I gives H and J, while K on fractionation yields J and L. It must not be thought that there is so great a difference between any two adjacent spectra as is here shown. To make the diagram accurately represent what is actually seen in the laboratory it would be necessary to place between each of these nineteen spectra about 1,000 intermediate spectra. Beginning at the extreme red it will be seen that a strong band at λ647 [$1/\lambda^2$ 239] is at its maximum intensity from G to K, when it rapidly disappears and is not seen beyond O and N. The component giving this band the writer names provisionally $G\eta$. The next band in the red λ639 [$1/\lambda^2$ 245] reaches its maximum at A or even higher, and fades out between K and L. The band at λ619 [$1/\lambda^2$ 261] has its maximum between I and O, dying out rapidly below but being more persistent above. It is called $G\zeta$. Then comes an extremely sharp band λ609 [$1/\lambda^2$ 269] which appears to belong to an earth absent in gadolinite but present in samarskite and a few other minerals. Its greatest brilliancy is between E and K, and on either side it dies rapidly away. For this the writer proposes the name $S\delta$. Then follows a double orange band, and its two components, though very closely united, are probably capable of separation. The maximum brightness of the first component λ603 [$1/\lambda^2$ 275] extends from O to the top of the figure. The second component λ597 [$1/\lambda^2$ 280] begins to fade about Q, and is at its greatest brilliancy at the highest spectrum shown on the figure. This band occurs almost isolated in a specimen of crude lanthana, and may be provisionally called $G\epsilon$. Next follows the citron, or $G\delta$ band, λ574 [$1/\lambda^2$ 305·5] which is the most prominent feature in the spectrum of old yttrium. This band extends with scarcely diminished sharpness from G to S; above G it fades rapidly and disappears above D. Then follows a double green band separable into two components. The first of these, λ568 [$1/\lambda^2$ 310] is nearly absent in A, reaches a maximum at D, and disappears at K. The second member of this green pair, λ563 [$1/\lambda^2$ 315] has its maximum at A and extends only to H. The substance producing this pair of bands may be called for the present $G\gamma$. Then follows a pair of bright green bands which so far show no signs of dividing. They begin at B, reach a maximum at E, and continue with scarcely diminished brightness to Q. The body giving this double green band is remarkably persistent and may provisionally be called $G\beta$. Next comes a dark interval followed by a broad, hazy, double-blue band, with its centre at λ482 [$1/\lambda^2$ 430·5]; this band appears at F and grows brighter to the last fraction at S. The substance to which it is due is called $G\alpha$. Lastly, at λ456 [$1/\lambda^2$ 481] appears a deep violet band beginning at about Q aud brightening as we proceed lower down. In some samples of ytterbia, supposed to be pure, this band is intensely brilliant, but it is absent in a specimen received from Nilson and considered by him to be perfectly pure. Hence it is probably due to another new body which may be provisionally named $S\gamma$.

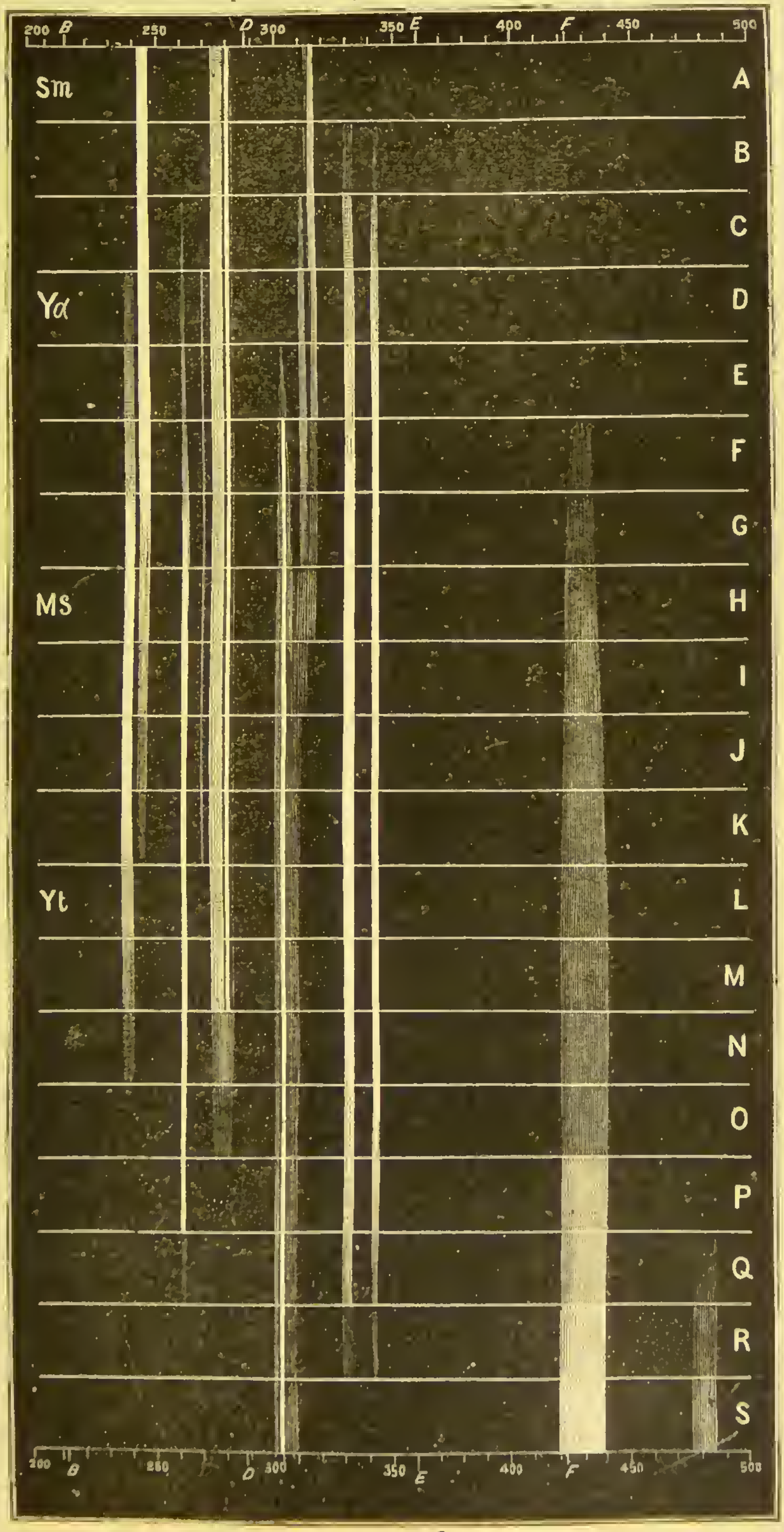
It must be remarked that the writer's fractionations have been carried far beyond the limits shown in the diagram. Fractions above A aud below S afford evidence that the process of differentiation has not yet reached its utmost limit.

On the left side of the diagram will be seen chemical symbols attached to some of the spectra. Thus the top spectrum, A, is the one shown by samarium. At D is the spectrum of Marignac's $Y\alpha$, or gadolinium. H shows the spectrum of mosandrum, and L that which is generally pronounced to be pure yttrium. A careful study of this diagram will lead the observer to conclude that samarium, gadolinium, mosandrum, and yttrium are not true chemical elements but compounds, or perhaps very intimate mixtures, of certain simpler bodies. For these bodies the name 'meta-elements' is proposed (W. Crookes,

B. A. Birmingham Meeting, *C. N.* 54, 155; Krüss a. Nilson, *B.* 20, 2134 and *C. N.* 54, 71, 85, 135, 142, 154, 165, 172; Marignac, *Archives des* *Sciences Physiques*, 16, No. 5 and *C. N.* 57; W. Crookes, *Pr.* Feb. 10, 1887).

De Boisbaudran likewise finds yttrium to be a complex body, and recognises in it three distinct substances which he names Zα, Zβ, and 'new yttria' (*C. R.* 103, 627). It is possible that Zα is Gδ, and that Gβ and Zβ are identical, though de Boisbaudran now regards the latter body as terbia (*C. R.* 102, 395, 902).

FIG. 14.—Phosphorescence-spectra of components of 'Old Yttria.'



The scale is $\frac{1}{\lambda^2}$.

The right of the 'new yttria' to bear this name is in the highest degree questionable. De Boisbaudran assigns to it an atomic weight close upon 89, and states that it has a characteristic spark-spectrum but gives no phosphorescence-spectrum either in the radiant matter tube or by his reversion-process. It evidently cannot be regarded as the old yttrium freed from impurities, since the purest specimens of such yttrium give a phosphorescence-spectrum *in vacuo* of such remarkable intensity that it cannot be due to mere traces of impurities. Gα, Gβ, &c., can no more be spoken of as impurities in old yttrium than can neodymium and praseodymium (assuming them to be elementary) be viewed as impurities in old didymium.

Marignac's Yα is probably a compound. The writer recognises in it two at least of the constituents of yttrium, Gβ and Gζ.

A. E. Nordenskjöld gives the name oxide of gadolinium (a totally different body from Marignac's Yα or gadolinium) to the mixture of earths in gadolinite which are precipitated by ammonia and oxalic acid, but not by sulphate of potash. This mixture consists of yttria, erbia, and ytterbia. A very interesting point is that however different the minerals from which it has been obtained, and however the percentage of the rare earths varies, the equivalent weight of the mixture is always approximately the same, viz. 261·9. This value is determined by transforming a weighed quantity of the oxide into sulphate by digestion with dilute sulphuric acid, and driving off excess of water and acid by heating to incipient redness (Nordenskjöld, *C. R.* 102, 795; W. Crookes, *C. N.* 54, 239).

On the other hand, commenting on this, De Marignac shows that there is sometimes a variation of 15 p.c. in the equivalent weights of these natural mixtures of rare earths (De Marignac, *Arch. des Sci. Phys.* 17, No. 5).

We have therefore some thirty bodies of which the so-called rare metals are composed, or, at least, which they contain; and a variety of facts points to the conclusion that we have by no means come to the end. Several even of the new bodies give signs of a capability of further splitting up, if they are examined with sufficient nicety and persistence. It is far from unlikely that when the various methods of research known as fractionation have been more generally applied we may have to deal, not with thirty, but with nearer sixty, unknown bodies.

But whatever may be the number of these bodies the question must be raised, What are they? Are they each and all independent elements? We have certainly no good *a priori* grounds for asserting that the number of elements now recognised is not capable of considerable extension. But before any body can be accepted as simple it should certainly undergo a very severe scrutiny, more severe than any of these newly-discovered bodies has yet undergone. The case of didymium is here a warning. It had been closely examined by some of the ablest chemists in Europe, it had been freed from several foreign bodies, its atomic weight had been established, when a novel mode of examination proved its compound nature.

Pending therefore the completion of a series of investigations, chemical and optical, which will probably occupy several generations of chemists, it may be safest to call these recently observed bodies not, as yet, elements, but quasi- or meta- elements. Our notions of a chemical element have been enlarged; hitherto the elemental molecule has been regarded as an aggregate of two or more atoms, and no account has been taken of the manner in which these atoms have been agglomerated. The structure of a chemical element is certainly more complicated than has hitherto been supposed. We may reasonably suspect that between the molecules which we are accustomed to deal with in chemical reactions, and the component or ultimate atoms, there may intervene sub-molecules, sub-aggregates of atoms, or meta-elements, differing from each other according to the positions which they occupy in the very complex structures commonly known as didymium, yttrium, and the like. W. C.

METAMERISM. This term is generally applied to those cases of *isomerism* wherein compounds show identity of elementary composition, but belong to different types or classes (*v.* ISOMERISM, pp. 79, 80, 81, 88).

METEORITES. As regards composition, meteorites have been divided into two classes; those which consist for the most part of metals only, and those which are chiefly composed of silicates, sometimes accompanied by unoxidised iron and nickel. Iron and nickel are the principal constituents of those meteorites which are mainly metallic. The quantity of Fe varies from 80 to 95 p.c., and of Ni from 6 to 10 p.c. Co occurs in many meteorites, varying from a mere trace to 2 or 3 p.c.; the other metals found in small quantities are Sn, Mn, Cr, and Cu; small quantities of Fe-Ni phosphide, and also carbide, phosphide, silicide, and sulphide of Fe are also frequently found in metallic meteorites. The silicates which form the chief constituents of meteorites of the second class are silicate of Al, Ca, and Na (*labradorite*), silicate of Ca and Mg (*augite*), and silicate of Fe and Mg (*olivine*). These silicates are often accompanied by nickel and iron, also by iron pyrites, and sometimes by chrome-iron, and magnetic oxide of iron. M. M. P. M.

METHACRYLIC ACID $C_4H_6O_2$ *i.e.* CH_2:CMe.CO_2H. *α-Methyl-acrylic acid.* [16°]. (160·5° i.V.). S.G. $\frac{20}{4}$ 1·0153 (Brühl, *B.* 14, 2800). $\mu_D = 1·4314$. $R_\infty = 35·07$.

Occurrence.—In small quantity in Roman oil of chamomile (Kopp, *A.* 195, 82).

Formation.—1. Obtained as ethyl ether by the action of PCl_3 on oxy-isobutyric ('dimethoxalic') ether CMe_2(OH).CO_2Et (Frankland a. Duppa, *C. J.* 18, 133; *A.* 136, 12; Paul, *A.* 188, 52).—2. By the action of fuming HBr on citraconic acid, mesaconic acid, or citraconic anhydride, the resulting bromo-pyrotartaric acid being boiled with conc. NaOHAq (Fittig, *A.* 188, 95; *B.* 10, 517).—3. By boiling citra- and mesa-chloro-pyrotartaric acid with alkalis (Prehn, *A.* 188, 42).—4. Together with oxy-isobutyric acid, by boiling α-bromo-isobutyric acid (1 pt.) with water (25 pts.) (Thomson, *A.* 200, 86).

Preparation.—Citraconic anhydride is mixed with a saturated solution of HBr (2 vols.) at 0°. In a few days a mass of crystals of citra-bromo-pyrotartaric acid is got. These are collected,

boiled with Na_2CO_3, acidified with HCl, and distilled. The distillate is neutralised by $CaCO_3$, filtered, evaporated to dryness, and mixed with HCl. Methacrylic acid separates as a light oil (Fittig a. C. Kolbe, *J. pr.* [2] 25, 372).

Properties.—Long prisms (from water), with strong but not unpleasant odour. V. sol. water, v. e. sol. alcohol and ether.

Reactions.—1. *Bromine* forms di-bromo-isobutyric acid.—2. *Potash-fusion* gives hydrogen, formic acid, and propionic acid (F. a. D.).—3. *Sodium-amalgam* reduces it to isobutyric acid.—4. Conc. HIAq forms, in the cold, iodo-isobutyric acid crystallising in tufts of prisms.—5. Methacrylic acid dissolves easily in fuming HBr even at 0°, the solution, after some time, depositing a crystalline addition-product and a thick oil (Paul, *B.* 9, 122).—6. *Bromine* forms $CH_2Br.CBrMe.CO_2H$.—7. On contact with cold conc. HClAq or by heating at 130°, it is converted into an amorphous (? polymeric) modification. The ammoniacal solution of this substance gives white pps. with Ba and Ca salts. It is not altered by conc. H_2SO_4 and HNO_3 (Fittig a. Engelhorn, *A.* 200, 70).—8. *Hypochlorous acid* forms chloro-oxy-isobutyric acid [107°] (c. 235°) (Melikoff, *Bl.* [2] 41, 311).

Salts.—CaA'_2: tufts of long needles, v. sol. water. Appears to change on keeping to a salt of the polymeric acid (*v. Reaction* 7).—AgA': needles (from boiling water); scarcely affected by light. Suddenly decomposes at 100°.

Constitution.—Inasmuch as the di-bromo-iso-butyric acid, formed by the addition of bromine, is converted by boiling water into a bromo-oxy-butyric acid that can be reduced to α-oxy-isobutyric acid, $(CH_3)_2C(OH).CO_2H$, it is clear that methacrylic acid is not $CH.CHMe.CO_2H$ but $CH_2:CMe.CO_2H$.

References.—Bromo- and Chloro- methacrylic acids.

METHACYL-BROMIDE *v.* Bromo-acetone.

METHÆMOGLOBIN *v.* Hæmoglobin.

METHAMIDO- *v.* Methyl-amido-.

METHANE CH_4. *Marsh gas. Methyl hydride. Light carburetted hydrogen.* Mol. w. 16. (−155° to −160°). (−131°) at 6·7 atmospheres; −73·5° at 56·8 atmospheres (Wroblewsky, *C. R.* 99, 136). S.G. (air = 1) ·553 (Regnault, *C. R.* 36, 676). S.G. (liquid) ·415 at −164° (Olszewski, *P.* [2] 31, 58). S.H. ·593 (R.). $\mu_D = 1·000412$ (Crouillebois, *C. R.* 67, 692). H.F.p. 21,750. H.F.v. 21,170 (Thomsen, *Th.*). H.C.p. 213,500 (Berthelot, *A. Ch.* [5] 23, 179). S. ·05449 at 0° (Bunsen, *A.* 93, 18). S. (alcohol) ·523 at 0°. *Critical temperature*: −73·5° (Wroblewsky); −99·5° (Dewar, *P. M.* [3] 18). *Critical pressure*: 56·8 atmospheres (Wroblewsky).

Occurrence.—The bubbles of gas given off by decaying vegetable matter in stagnant pools consist of marsh gas, CO_2, and nitrogen. It often escapes into coal mines, where it is known as fire-damp, since it forms an explosive mixture with air. It escapes from the earth in various places, as in Italy, North America, and especially at Baku on the Caspian. It occurs among the products of distillation of wood, peat, coal, and bituminous shale, constituting 35 to 40 p.c. of coal gas. Methane occurs also in the intestinal gases. It occurs also among the products of the passage of ethylene (Norton a. Noyes, *Am.* 8, 362) and other gases through a red-hot tube. The gaseous product obtained by heating ethylene at 400° contains 36 p.c. methane and 40 p.c. ethane (Day, *Am.* 8, 153).

Formation.—1. By the action of potassium-amalgam on CCl_4 in presence of water (Regnault). 2. By passing a mixture of $CHCl_3$ or CCl_4 and hydrogen through a red-hot tube (Berthelot).—3. By the action of powdered zinc on chloroform dissolved in aqueous alcohol (Sabanejeff, *B.* 9, 1810).—4. By exposing a mixture of CO and hydrogen to the action of electricity in an induction-tube (Brodie, *Pr.* 21, 245).—5. By the action of water on zinc methide (Frankland).—6. By the action of sodium on MeI in presence of ether (Wanklyn a. Buckeisen).—7. In small quantity by passing a mixture of CS_2 and H_2S over red-hot copper (Berthelot, *A. Ch.* [3] 53, 69). 8. By heating CS_2 with PH_4I at 130° (Jahn, *B.* 13, 127).—9. Among the products of the dry distillation of barium formate (Berthelot, *J.* 1857, 426).—10. By distilling crystallised sodium acetate (2 pts.) with KOH (2 pts.) and quicklime (3 pts.) (Dumas, *A. Ch.* [2] 73, 92). Von Schlegel (*A.* 226, 140) recommends 1 pt. of sodium acetate and 2 pts. of soda-lime (*cf.* Schorlemmer, *C. N.* 29, 7).—11. When river-mud is added to a solution of calcium acetate a slow evolution of a mixture of methane (2 vols.) and CO_2 (1 vol.) occurs, calcium carbonate being left. Calcium lactate undergoes a similar fermentation, the gases being evolved in the same proportion (Hoppe-Seyler, *H.* 11, 561).

Preparation.—By the action of the copper-zinc couple on an alcoholic solution of MeI, the escaping gas being well washed by a scrubber containing a further quantity of copper-zinc (Gladstone a. Tribe, *C. J.* 45, 154).

Properties. — Colourless gas. V. sl. sol. water. Much less soluble in alcohol than ethane. Its illuminating power is slight (*cf.* L. T. Wright, *C. J.* 47, 200). May be liquefied by combined cold and pressure (Cailletet, *J.* 1877, 221). Methane is not absorbed by aqueous KOH or by ammoniacal cuprous chloride. When compressed with water below 0° under a pressure of 30 atmospheres it forms a crystalline hydrate, the critical temperature of which is 21·5° (Villard, *C. R.* 106, 1602; 107, 395).

Reactions.—1. When passed through a *red-hot tube* it is for the most part unaffected, but a little naphthalene is formed. *Electric sparks* partially convert it into carbon, hydrogen, and acetylene (Berthelot, *C. R.* 67, 1188). When passed over a *red-hot palladium spiral* it is decomposed, if dry, into carbon and hydrogen, and, if moist, into CO and hydrogen (Coquillon, *C. R.* 86, 1197).—2. It is not attacked by *sulphuric acid*, by *nitric acid*, by a mixture of hot conc. H_2SO_4 and HNO_3, by PCl_5 or by chlorine in the dark.—3. A mixture of chlorine (2 vols.) with methane (1 vol.) when exposed to sunlight presently explodes. The explosion may also be brought about by an electric spark. If the mixture be first diluted with CO_2 and then exposed to sunlight, quiet chlorination takes place, and if excess of chlorine is present chloroform and CCl_4 are formed. A mixture of methane (1 vol.) and chlorine (1 vol.) exposed to diffused daylight gives methyl chloride. In presence of moisture, chlorine forms HCl, CO_2, and CO.—

4. A mixture of *air* and methane passed over a red-hot platinum spiral yields formic acid (Coquillon, *C. R.* 77, 444).—5. When mixed with nitric oxide and fired by an electric spark CO_2 and oxygen are among the products (Cooke, *C. N.* 58, 130).

Constitution.—That the four atoms of hydrogen in methane are of equal value may be inferred from the existence of only one set of methyl compounds. The same thing may be shown thus:—

From CHHHI we may obtain, by treatment with KCy, an acetonitrile CHHHCy which we may call 'α.' From this we can obtain $CHHH.CO_2H$, $CHHCl.CO_2H$, $CHHCy.CO_2H$, and 'β' acetonitrile CHHCyH successively. But from $CHHCy.CO_2H$ we can obtain malonic ether $CHH(CO_2Et)(CO_2Et)$, and thence we can get $CHCl(CO_2Et)(CO_2Et)$, $CHCy(CO_2H)(CO_2H)$, and 'γ' acetonitrile CHCyHH successively. The three acetonitriles 'α,' 'β,' and 'γ' are then found to be identical, hence three at least of the atoms of hydrogen in methane are of equal value. The fourth acetonitrile might probably be obtained from $CH(CO_2Et)_3$ *viâ* $CCl(CO_2Et)_3$, and $CCy(CO_2H)_3$ (Henry, *C. R.* 104, 1106). Since $CO{<}^{OC_4H_9}_{OEt}$ the product of the action of $CO{<}^{Cl}_{OEt}$ on isobutyl alcohol, is the same as $CO{<}^{OEt}_{OC_4H_9}$, obtained from $CO{<}^{Cl}_{OC_4H_9}$ and ethyl alcohol, the carbonyl group is united to two atoms of hydrogen of equal value. Now from aldehyde $CO{<}^{H}_{CH_3}$ we may obtain ${}^{Cl}_{AcO}{>}C{<}^{H}_{CH_3}$ whence silver propionate forms ${}^{C_3H_5O.O}_{AcO}{>}C{<}^{H}_{CH_3}$. But from aldehyde we may also obtain ${}^{Cl}_{C_3H_5O.O}{>}C{<}^{H}_{CH_3}$ whence silver acetate yields ${}^{AcO}_{C_3H_5O.O}{>}C{<}^{H}_{CH_3}$. These two acetyl-propionyl derivatives of ortho-aldehyde are found to be identical, hence the two atoms of hydrogen in methane which are displaced by oxygen in forming carbonyl are of equal value. It follows that there are two pairs of equivalent atoms of hydrogen in methane (Geuther, *A.* 205, 203; 225, 290). And since Henry has shown that three of the atoms of hydrogen in methane are equivalent, it follows that the fourth is so also.

References. — TETRA - BROMO-, BROMO - IODO, BROMO-NITRO-, CHLORO-IODO-, CHLORO-NITRO-, and TETRA-IODO-, METHANE, BROMOFORM, CHLOROFORM, IODOFORM, and METHYL, METHYLENE, and METHENYL COMPOUNDS. In fact, all organic compounds may be regarded as derivatives of Methane (Kekulé).

METHANE CARBOXYLIC ACID is ACETIC ACID.

Methane dicarboxylic acid is MALONIC ACID.

Methane tricarboxylic acid $C_4H_4O_6$ *i.e.* $CH(CO_2H)_3$. *Formyl tricarboxylic acid. Methenyl tricarboxylic acid.*

Ethyl ether $CH(CO_2Et)_3$. [29°]. (253°) at 760 mm. (195°-205°) at 140 mm. S.G. $\frac{19}{15}$ 1·100. From sodium malonic ether, benzene and $ClCO_2Et$ (Conrad a. Guthzeit, *A.* 214, 31; *B.* 12, 1236; *cf.* Claisen, *B.* 21, 3397, 3567). Colourless oil. V. sol. alcohol or ether. In a freezing mixture, it solidifies to long needles or prisms. According to Michael (*J. pr.* [2] 37, 473) it dissolves readily in dilute NaOH forming $CNa(CO_2Et)_3$, which may be crystallised.

Reactions.—1. With aqueous KOH at 100° it forms HOEt, K_2CO_3 and potassic malonate.—2. Dilute H_2SO_4 and alcoholic NaOH at 0° also form malonic acid, so that a salt of the acid $CH(CO_2H)_3$ has not been obtained.—3. Chlorine forms $CCl(CO_2Et)_3$ (Conrad, *B.* 14, 618).

Anilide of the *di-ethyl ether* $CH(CO_2Et)_2(CONHPh)$. [124°]. From sodium-malonic ether and an alcoholic solution of phenyl cyanate (Michael, *J. pr.* [2] 35, 452).

Nitrile of the *di-ethyl ether v.* CYANO-MALONIC ETHER.

METHANE PHOSPHONIC ACID *v.* METHYL PHOSPHINE.

METHANE - TRI - QUINOLYL - HYDRO - IODIDE *v.* QUINOLINE-IODOFORM.

METHANE SELINIC ACID *v.* SELENIUM ORGANIC COMPOUNDS.

METHANE SULPHINIC ACID CH_4SO_2 *i.e.* $CH_3.SO_2H$. From $ZnMe_2$ and SO_2 (Hobson, *A.* 106, 287). The aqueous solution of the acid soon decomposes with deposition of sulphur.—CaA'_2 (dried at 100°): amorphous.—BaA'_2 (dried at 100°): cubes, v. sol. water, insol. alcohol.—MgA'_2aq (dried at 100°).—ZnA'_2: amorphous.

Derivative.—TRI-CHLORO-METHANE SULPHINIC ACID.

Methane di-sulphinic ether *v.* METHYLENE DIETHYL DISULPHONE.

METHANE SULPHONIC ACID CH_4SO_3 *i.e.* $CH_3.SO_3H$.

Formation.—1. By the oxidation of di-methyl trisulphide (Cahours, *A. Ch.* [3] 18, 258), or of di-methyl disulphide (Muspratt, *A.* 65, 251).—2. By oxidising methyl sulphocyanide with nitric acid (S.G. 1·25).—3. By treating tri-chloro-methane sulphonic acid with sodium amalgam (Kolbe, *A.* 54, 174).—4. By heating MeI with aqueous K_2SO_3 at 120° (Colman, *A.* 148, 101).

Properties.—Syrup which decomposes above 130°. Potash-fusion forms K_2CO_3, hydrogen, and K_2SO_3 (Berthelot, *J.* 1869, 336).

S a l t s.—NH_4A': thin trimetric plates (from absolute alcohol).—$LiA'aq$.—$(NaA')_4NaI$ (Colman).—KA' (dried at 100°).—KHA'_2 (dried at 100°).—CaA'_2. S. 71 at 20° (Nithack, *A.* 218, 284).—SrA'_2aq. S. 83 at 22°.—BaA'_2aq: v. e. sol. water, insol. alcohol.—MgA'_210aq.—PbA'_2aq.—CuA'_25aq.—AgA'.

Chloride $CH_3.SO_2Cl$. (160°) (N.). S.G. 1·51. From the acid and PCl_5 (Carius, *A.* 114, 142). Not attacked by H_2S, by chlorine, or by KCy (McGowan, *J. pr.* [2] 30, 280). Decomposes aqueous ammonia with evolution of nitrogen.

Amide $CH_3.SO_2NH_2$. Formed by passing NH_3 into a solution of the chloride in ether. Prisms (from benzene containing alcohol).

Anilide $CH_3.SO_2.NHPh$. Large plates (from alcohol) (McGowan).

Derivatives v. CHLORO-, and CHLORO-BROMO-METHANE SULPHONIC ACID.

Methane disulphonic acid $CH_4S_2O_6$ *i.e.* $CH_2(SO_3H)_2$. *Methylene disulphonic acid. Methionic acid.*

Formation.—1. A product of the action of

SO_3 on ether (Liebig, *A.* 13, 35; Wetherill, *A.* 66, 122; Strecker, *A.* 100, 199).—2. From Et_2SO_4 and SO_3 (Hübner, *A.* 223, 208).—3. By the action of hot fuming H_2SO_4 on acetonitrile, acetamide, or sulpho-acetic acid (Buckton a. Hofmann, *A.* 100, 133; *C. J.* 9, 241).—4. Together with sulpho-acetic acid, by the action of $ClSO_3H$ on acetic acid (Baumstark, *A.* 140, 82). 5. By heating lactic acid with fuming H_2SO_4 (Strecker, *A.* 118, 290).—6. From methylene iodide and K_2SO_3 (Strecker, *A.* 148, 90).—7. By heating chloroform with aqueous K_2SO_3 at 180° (Strecker). — 8. From $CCl_3.SO_3K$, water, and K_2SO_3 at 125° (Rathke, *A.* 161, 152).—9. By oxidising $CH_2(SCy)_2$ with HNO_3 (Lermontoff, *B.* 7, 1282).

Properties.—Very deliquescent needles. Not attacked by chlorine or by nitric acid.

Salts.—$(NH_4)_2A''$: trimetric crystals, m. sol. cold water.—K_2A'': needles. S. 7·1 at 22°.—BaA'' 2aq: pearly tables.—PbA'' 2aq: prisms, v. sol. water, insol. alcohol.—CuA'' 5aq.—Ag_2A'': thin plates.

Derivative v. BROMO-METHANE DISULPHONIC ACID.

Methane tri-sulphonic acid $CH_4S_3O_9$ *i.e.* $CH(SO_3H)_3$. Obtained by heating $CH_3O.SO_3K$ (1 pt.) with fuming H_2SO_4 at 100° (Theilkuhl, *A.* 147, 134). Formed also by the action of aqueous K_2SO_3 at 100° on $CH_3.C(NO_2)(SO_3K)_2$ or on $CCl_3(NO_2)$ (Rathke, *A.* 167, 219). Long needles; v. e. sol. water and alcohol.—K_3A'''aq: small prisms.—$Ca_3A'''_2$ 12aq: small prisms, v. sol. water, insol. alcohol.—$Ba_3A'''_2$ 9aq: plates. Not decomposed by HCl.—$Pb_5A'''_2O_2$.

METHANE THIOSULPHONIC ACID. *Methyl ether* $C_2H_6S_2O_2$ *i.e.* $CH_3.SO_2.SCH_3$. *Di-methyl disulphoxide.* Obtained by warming di-methyl disulphide with nitric acid (S.G. 1·2) diluted with four times its volume of water (Lukaschevitch, *Z.* 1868, 641). Oil. Readily oxidised by HNO_3 to methane sulphonic acid.

METHANTHRENE $C_{15}H_{12}$. [117°]. An isomeride of methyl-naphthalene obtained, together with other products, by distilling podocarpic acid with zinc-dust (Oudemans, *B.* 6, 1125). The product is crystallised from alcohol and sublimed. White laminæ with violet fluorescence. It boils above 360°. V. e. sol. boiling alcohol, CS_2 and HOAc.

Picric acid compound $C_{15}H_{12}C_6H_2(NO_2)_3OH$. [117°]. Slender orange needles.

Methanthrene-quinone $C_{15}H_{10}O_2$. [187°]. From methanthrene and CrO_3 in HOAc. Minute trimetric laminæ. May be distilled. Insol. water, sl. sol. ether, v. sol. alcohol. Reduced to a hydride by aqueous SO_2.

METHAZONIC ACID $C_2H_4N_2O_3$ *i.e.* $(NO.CH_2)_2O$? [c. 60°]. The sodium salt is formed by acting on nitro-methane with alcoholic NaOH, the resulting crystalline pulp being heated on the water-bath. The upper (alcoholic) layer is poured off, and the lower layer deposits sodium methazonate on cooling. It is dissolved in water and reppd. by alcohol (Friese, *B.* 9, 304). According to Lecco (*B.* 9, 705) it is best to add dilute H_2SO_4 and shake with ether. If the ether is dried with Na_2SO_4 and evaporated over H_2SO_4, it leaves methazonic acid as large crystals, which may be recrystallised from benzene. It is v. sol. water, alcohol, and ether, m. sol. benzene, insol. petroleum-naphtha. The Na salt crystallises from alcohol in long prisms.

METHENYL-AMIDINE *v.* FORMAMIDINE.

METHENYL-AMIDOXIM *v.* FORMAMIDOXIM.

METHENYL-AMIDO-o-CRESOL C_8H_7NO *i.e.* $C_6H_3(CH_3)\langle{}^{N}_{O}\rangle CH$ $\left[3:\frac{1}{2}\right]$ [39°]. (200°). Colourless crystals. Prepared by the action of formic acid on amido-o-cresol (Hofmann a. Miller, *B.* 14, 570).

Methenyl-amido-*p*-cresol C_8H_7NO *i.e.* $C_6H_3(CH_3)\langle{}^{N}_{O}\rangle CH$ $\left[5:\frac{1}{2}\right]$ [46°]. Formed from amido-*p*-cresol by distillation with formic acid (H. a. M.). Crystals.

METHENYL-(α)-AMIDO-NAPHTHYL-MERCAPTAN $C_{10}H_6\langle{}^{N}_{S}\rangle CH$. [46°]. Formed by heating formyl-(α)-naphthylamine with sulphur. Colourless oily fluid. Insol. water. Volatile with steam. Base.—$B'_2H_2Cl_2PtCl_4$: yellow needles (Hofmann, *B.* 20, 1799, 2265).

METHENYL-AMIDO-PHENOL C_7H_5NO *i.e.* $C_6H_4\langle{}^{N}_{O}\rangle CH$. [30·5°]. (182·5°). V.D. (H=1) 112·5 (calc. 119). Obtained by boiling formic acid with o-amido-phenol (Ladenburg, *B.* 10, 1123). Prisms. Hot conc. HClAq decomposes it, forming o-amido-phenol.

METHENYL-AMIDO-PHENYL MERCAPTAN C_7H_5NS *i.e.* $[1:2]C_6H_4\langle{}^{N}_{S}\rangle CH$ (230°). Colourless fluid. Sparingly soluble in water, easily in alcohol and CS_2. Has decided basic properties. Heavier than water. Volatile with steam. Isomeric with phenyl mustard-oil.

Preparation.—1. By reduction of the chloro-derivative (vol. ii. p. 78) with tin and HCl or with HI.—2. By the action of formic acid on amido-phenyl mercaptan (Hofmann, *B.* 13, 14). 3. Formed together with aniline, methyl-aniline, and a base $C_8H_7NS_2$, by boiling di-methyl-aniline with sulphur (Möhlau a. Krohn, *B.* 21, 59).

Properties.—Oil, smelling like quinoline and having a bitter taste. It is related to thiazole as quinoline is to pyridine. The sulphur cannot be displaced by the action of lead hydrate or even by heating with copper to 250°. On fusion with KOH it gives formic acid and amido-phenyl-mercaptan. PCl_5 at 180° forms the chloro- derivative $C_6H_4(NS)CCl$.

Salts.—$(B'HCl)_2PtCl_4$: sparingly soluble tables, or needles.—$(B'HCl)AuCl_3$.—$B'_2H_4FeCy_6$.

Methylo-iodide C_7H_5NSMeI: [210°]; needles, sl. sol. cold alcohol, v. sol. hot water.

General character.—This base stands in the same relation to quinoline as thiophene stands to benzene. In consequence of this analogy the base and its derivatives exhibit great similarity in properties with the corresponding quinoline compounds: thus the boiling-points of the methenyl- and ethenyl-o-amido-phenyl-mercaptan do not differ much from those of quinoline and methyl-quinoline, and they form crystalline picrates and uncrystallisable chromates. They also form colouring-matters analogous to the cyanines (obtained by the action of alkalis upon a mixture of the alkylo-iodides of quinoline and methyl-quinoline). Thus by boiling an aqueous solution of the amylo-iodides of methenyl- and

ethenyl-amido-phenyl-mercaptans with NH_3, a red colouring-matter $C_{25}H_{31}N_2S_2I$ is obtained which crystallises in four-sided violet-red plates with green reflex, sol. hot alcohol, sl. sol. cold alcohol, insol. water. Neither of the amylo-iodides when treated separately, in the same way, gives any colouring-matter. In a similar manner to the amylo-iodides, the mixed methylo-iodides give a compound crystallising in reddish-golden plates, sol. alcohol with a scarlet-red colour. Similar colouring-matters are also obtained from the corresponding derivatives of amido-naphthyl mercaptan, or from the latter derivatives conjointly with those of amido-phenyl-mercaptan, or from those of amido-phenyl-mercaptan conjointly with those of quinoline and methyl-quinoline. All the above products are stronger colouring-matters than the cyanines (Hofmann, *B.* 20, 2262).

Derivatives v. AMIDO-, CHLORO-, and NITRO-METHENYL-AMIDO-PHENYL-MERCAPTAN.

METHENYL-o-AMIDO-PHENYL-MERCAPTAN ω-CARBOXYLIC ACID $C_6H_4<{N \atop S}>C.CO_2H$. [108°].

Formation.—1. By the action of cold alcoholic caustic potash upon amido-imido-ethenyl-o-amido-phenyl-mercaptan

$C_6H_4<{N \atop S}>C.C(NH_2)NH$, ammonia being eliminated.—2. In small quantity by oxidation of ethenyl-o-amido-phenyl mercaptan

$C_6H_4<{N \atop S}>C.CH_3$ with cold aqueous $KMnO_4$.

Properties.—White needles. Sol. water and alcohol. It very readily splits off CO_2 giving methenyl-amido-phenyl mercaptan (Hofmann, *B.* 20, 2256).

METHENYL-AMIDO-TOLYL MERCAPTAN $C_6H_3(CH_3)<{N \atop S}>CH$ $\left[1:{4 \atop 3}\right]$. [15°]. (255°). Prepared by boiling *p*-amido-*m*-tolyl-mercaptan with formic acid (Hess, *B.* 14, 492). Sol. alcohol and ether. Weak base forming unstable salts.—$(B'HCl)_2PtCl_4$: needles.

METHENYL-AMIDOXIM *v.* FORMAMIDOXIM.

METHENYL-AMIDO-XYLYL MERCAPTAN $C_6H_2(CH_3)_2<{N \atop S}>CH$. From the thio-formyl derivative of *u*-*m*-xylidine $C_6H_3Me_2(NH.CSH)$ by oxidising with alkaline K_3FeCy_6 (Gudeman, *B.* 21, 2549). Heavy oil.

METHENYL-BROMO-TOLYLENE-o-DIAMINE. $\left[1:4:{2 \atop 3}\right]$ $C_6H_2(CH_3)(Br)<{NH \atop N}>CH$. [187°]. Obtained by heating bromo-tolylene-diamine with formic acid (Hübner a. Schüpphaus, *B.* 17, 776). Fine colourless needles. Sol. alcohol, ether, and acetone, sl. sol. water and benzene.

Salts.—B'HCl: colourless soluble needles.—$B'H_2SO_4aq$: long needles.—$B'HNO_3$: sparingly soluble colourless needles. — $B'_2H_2Cl_2HgCl_2$: needles.—$B'_2H_2Cl_2PtCl_4$: orange crystalline pp. —$B'_2H_2Cr_2O_7$: glistening red needles. — $B'C_6H_2(NO_2)_3OH$: this picrate forms yellow needles [229°].

METHENYL-TRICARBOXYLIC ACID *v.* METHANE-TRICARBOXYLIC ACID.

METHENYL FLUORIDE CHF_3. *Fluoroform.* V.D. 2·50 (calc. 2·44). S. (alcohol) 5. Formed by warming a mixture of iodoform (2 pts.), chloroform (1 pt.), and silver fluoride (2 pts.) (Meslans, *C. R.* 110, 717). Colourless gas, condensing at 20° under 40 atmospheres' pressure. Smells like chloroform, and burns with blue flame forming HF. Sl. sol. water, chloroform, and benzene. Alcoholic KOH yields KF and potassium formate.

METHENYL DI-PHENYL-DIAMINE *v.* DI-PHENYL-FORMAMIDINE.

METHENYL-o-PHENYLENE-DIAMINE $C_6H_4<{NH \atop N}>CH$. *Anhydro-formyl-phenylene diamine.* [167°]. (above 360°). Prepared by heating *ortho*-phenylene diamine for 5 or 6 hrs. with formic acid. The yield is nearly theoretical (Wundt, *B.* 11, 826). Large crystals. Monacidic base.—$(B'HCl)_2PtCl_4$.—$(B'HCl)AuCl_3$.

METHENYL TRI-PHENYL TRI-KETONE *v.* TRI-BENZOYL-METHANE.

METHENYL-DI-TOLYL-AMIDINE *v.* DI-TOLYL-FORMAMIDINE.

METHENYL-TOLYLENE-o-DIAMINE $C_6H_3(CH_3)<{NH \atop N}>CH$ [1:2:3]. [143°]. Obtained by reduction of methenyl-bromo-tolylene-o-diamine (Hübner a. Schüpphaus, *B.* 17, 777). Colourless glistening needles (from benzene). V. e. sol. water and alcohol.

Salts.—$B'HNO_3$: long soluble needles.—$B'_2H_2Cl_2PtCl_4$ 3aq: sparingly soluble orange needles.

Methenyl-tolylene-diamine $C_6H_3(CH_3)<{NH \atop N}>CH$ [1:3:4]. [c. 101°]. From the diamine and formic acid (Ladenburg, *B.* 10, 1123).—$B'_2H_2PtCl_6$: yellow prisms.

METHIONIC ACID *v.* METHANE DISULPHONIC ACID.

METHOXY- compounds *v. Methyl derivatives* of OXY- compounds.

METHRONIC ACID $C_8H_8O_5$ *i.e.* $C_6H_6O(CO_2H)_2$

$$\begin{array}{l} \quad C(CO_2H).CH \\ \text{or} \;\; \| \qquad\qquad \| \\ \quad CMe.\;O.\;C.CH_2.CO_2H \end{array}$$ (Knorr, *B.* 22, 152).

Di-methyl-furfurane dicarboxylic acid. Sylvane carboxyacetic acid. Pyrotritaric carboxylic acid. [205°] (F.); [207°] (P.).

Formation.—1. By heating equimolecular weights of aceto-acetic ether, Ac_2O, and sodium succinate, and saponifying the resulting mono-ethyl methronate $C_6H_6O(CO_2Et)(CO_2H)$ with baryta (Fittig, *A.* 250, 173, 182).—2. By treating a mixture of glyoxal and aceto-acetic ether with a concentrated aqueous solution of $ZnCl_2$, and extracting the product with aqueous KOH (Polonowsky, *A.* 246, 6; Fittig a. Hantzsch, *B.* 21, 2135, 3189).

Properties.—Needles (from water); v. e. sol. alcohol, m. sol. ether and HOAc, m. sol. hot, v. sl. sol. cold, water, almost insol. $CHCl_3$ and CS_2. The aqueous solution gives no colour with $FeCl_3$. It is not attacked by reducing agents.

Reactions.—1. On *heating* it gives off carbonic acid gas leaving methyl-furfuryl-acetic

$$\begin{array}{l} \quad CH \quad CH \\ \text{acid} \;\; \| \qquad \| \\ \quad CMe.O.C.CH_2.CO_2H \end{array}$$ [138°]. — 2. Dilute HClAq at 200° gives CO_2 and acetonyl-acetone.

Salts.—$(NH_4)_2A''\frac{1}{2}aq$: small needles.—$CaH_2A''_2$: heavy crystalline pp. nearly insol.

hot water.—CaA″ 2aq.—BaA″ 2aq: needles (P.).—BaA″: amorphous (F.).—$BaH_2A''_2$: needles, more soluble than the Ca salt (F.).—$Ag_2A''aq$: bulky white pp.

Mono-methyl ether MeHA″: [98°]; needles.—AgMeA″: white pp. (P.).

Di-methyl ether Me_2A''. Oil.

Mono-ethyl ether EtHA″. [76°]. Prepared as above. Long pointed needles, v. sol. alcohol, ether, chloroform, and benzene; m. sol. CS_2; sl. sol. water.—$Ca(EtA'')_2$ 2aq: needles or prisms.—$Ba(EtA'')_2$ 2aq: needles, v. sol. hot, sl. sol. cold, water.—AgEtA″: white matted needles.

Di-ethyl ether Et_2A''. (300°–305°) (F.).

Phenyl hydrazide $C_{14}H_{14}N_2O_4$ *i.e.* $C_8H_3O_4{:}N_2HC_6H_5$. [212°] (F.).

Phenyl hydrazide of the mono-ethyl ether $C_{16}H_{18}N_2O_4$: [134°]; crystalline. Insol. cold aqueous alkalis.

METHRONOL $C_{18}H_{20}$ *i.e.*

CH:CH.C.CHPh.CHMe
| || | ?
CH:CH.C. CH_2 .CHMe

Phenyl-di-methyl-naphthalene tetrahydride. (323°). V.D. 8·0 (calc. 8·2). Formed from phenyl-methacrylic acid by heating with H_2SO_4 (40 c.c.) and water (60 c.c.) (H. Erdmann, *A.* 227, 250). Oil. Chromic mixture oxidises it to o-benzoyl-benzoic acid, acetic acid, benzoic acid, anthraquinone, and CO_2.

METHYL. The radicle CH_3. The name methyl was also given by Frankland and Kolbe (*C. J.* 1, 60) to dimethyl C_2H_6, now called ethane. The methyl derivatives of hydroxylic compounds are described under the compounds of which they are the ethers: *e.g.* $CH_3O.C_6H_4.CO_2H$, the methyl derivative of oxy-benzoic acid is described under Oxy-benzoic acid.

DI-METHYL-ACETAL so-called. *V.* vol. i. p. 105.

METHYL-ACETAMIDE *v. Acetyl derivative* of Methylamine.

METHYL-ACETANILIDE *v. Acetyl derivative* of Methyl-aniline.

METHYL ACETATE *v.* Acetic acid.

METHYL-ACETIC ACID is Propionic acid.

Di-methyl-acetic acid is *Iso*-butyric acid.

Tri-methyl-acetic acid *v.* Valeric acid.

METHYL-ACETO-ACETIC ACID *v.* vol. i. p. 22; vol. ii. p. 78.

METHYL ACETO-ACETATE *v.* Aceto-acetic acid.

METHYL-DI-ACETONAMINE *v.* Aceton-amine.

METHYL-ACETONE *v.* Methyl ethyl ketone.

Di-methyl-acetone *v.* Methyl isopropyl ketone and Di-ethyl ketone.

METHYL-TRI-ACETONE-ALCAMINE *v.* Acetone-alcamine.

METHYL-TRI-ACETONINE *v.* Acetonines.

METHYL-ACETO-PROPIONIC ACID *v.* Acetyl-butyric acid.

METHYL ACETO-SUCCINIC ETHER *v.* Acetyl-methyl-succinic ether.

METHYL-ACETOTHIENONE *v.* Methyl-thienyl methyl ketone.

METHYL-ACETYL-BENZENE *v.* Tolyl methyl ketone.

Di-methyl-acetyl-benzene *v.* Xylyl methyl ketone.

METHYL-ACETYLENE *v.* Allylene.

Di-methyl-acetylene *v.* Butinene.

Di-methyl-di-acetylene C_6H_6 *i.e.* $CH_3.C{:}C.C{:}C.CH_3$. *Hexinene.* [64°]. (130°). Formed by oxidising the copper derivative of allylene with alkaline K_3FeCy_6 (Griner, *C. R.* 105, 283). Solid; volatile with steam. Does not react with ammoniacal cuprous chloride. Combines with bromine in the cold, forming $C_6H_6Br_4$ [44°].

METHYL-ACETYLENE-DI-QUINOLINE $C_{21}H_{16}N_2$ *i.e.*

$C_6H_4<$ CH:CH ... N:C.CH:CH.C ; CH:CH.C. N : CMe ... : CH.C.CH:CH

Ethyl-ene-quinoline-methyl-quinoline. [157·5°]. Formed on heating *p*-amido-(*Py.* 3)-styryl-quinoline with HCl at 150°, and then gradually adding paraldehyde (Bulach, *B.* 22, 289).

DI-ν-METHYL-ACETYLENE-DI-UREA

$C_6H_{10}N_4O_2$ *i.e.* CO<(NMe.CH.NMe / NH. CH.NH)>CO or CO<(NMe.CH.NH / NH. CH.NMe)>CO. *Glycol-di-methyl-uril.* [210°]. Formed by adding HCl to a mixture of glyoxal and methyl-urea (Franchimont a. Klobbie, *R. T. C.* 7, 19). Needles, v. sol. water; insol. ether and ligroïn. Forms with HNO_3 a di-nitro-compound, which is not decomposed by boiling with water.

Di-methyl-acetylene-di-urea $C_6H_{10}N_4O_2$ *i.e.* CO<(NH.CMe.NH / NH.CMe.NH)>CO. Formed by heating di-methyl-diketone with urea in aqueous solution (Franchimont a. Klobbie, *R. T. C.* 7, 251). Prisms or needles; insol. ether and $CHCl_3$, sl. sol. alcohol. Does not melt below 290°. Nitric acid converts it into a nitramine CO<(NH.CMe.N(NO_2) / NH.CMe.N(NO_2))>CO, which crystallises from alcohol in plates, and is decomposed by boiling water into CO_2, N_2O, di-methyl-diketone, and urea.

α-DI-METHYL-β-ACETYL-PROPIONIC ACID *v.* Mesitonic acid.

METHYL-ACETYL-PYRROLE *v.* Methyl-pyrryl methyl ketone.

ν-Methyl-di-acetyl-pyrrole *v.* Methyl-pyrrylene di-methyl-di-ketone.

METHYL-ACETYL-UREA *v. Acetyl derivative* of Methyl-urea.

METHYL-ACRIDINE $C_{14}H_{11}N$ *i.e.* $C_6H_4<$(CMe / N)$>C_6H_4$. [114°]. Formed by heating diphenylamine (50 g.), glacial acetic acid (30 c.c.), and $ZnCl_2$ (85 g.) at 220° for 14 hours. The yield is good (32 g.) (Bernthsen, *A.* 224, 35). Formed also by heating diphenylamine with acetonitrile at 200° (Bernthsen, *A.* 192, 29). Dimetric crystals; $a{:}c = 1{:}\cdot2397$ (Bernthsen a. Osann, *B.* 19, 427). Aqueous $KMnO_4$ at 100° oxidises it very slowly, a product being perhaps quinoline tri-carboxylic acid. HNO_3 (S.G. 1·33) boiled for 6 hours with methyl-acridine (6 g.) gives tri-nitro-acridine carboxylic acid, which forms glittering

prisms, sparingly soluble in the usual menstrua. —B'HCl.—$B'_2H_2PtCl_6$.

Methylo-iodide B'MeI: [185°]; red needles (from water). Sol. hot water, less sol. hot alcohol, least sol. ether.

Methylo-chloride B'MeCl. Decomposes at 130°–135°.

Methylo-hydroxide B'Me(OH). From the methylo-iodide by treatment with aqueous NaOH. Grey powder, turning green in air. Sol. alcohol, but soon decomposes.

Methyl-acridine $C_6H_4\left\langle\begin{matrix}CH\\ |\\ N\end{matrix}\right\rangle C_6H_3Me \left[\begin{matrix}2\\1\end{matrix}\ 4\right]$.

[132°]. Formed by distilling diamido-di-*p*-tolyl-phenyl-methane $PhCH(C_6H_3MeNH_2)_2$ with zinc-dust (Ullmann, *J. pr.* [2] 36, 265). Yellow matted needles. Smells aromatic, and causes sneezing. V. sl. sol. water, v. sol. alcohol, ether, benzene, and hot petroleum-ether. Its solution in dilute H_2SO_4 exhibits bluish-green fluorescence.

Di-methyl-acridine $C_{15}H_{13}N$ *i.e.*

$C_6H_4\left\langle\begin{matrix}CMe\\ |\\ N\end{matrix}\right\rangle C_6H_3Me \left[\begin{matrix}2\\1\end{matrix}\ 4\right]$. [123°]. Formed by heating phenyl-*p*-toluidine (12 g.) with HOAc (6·6 g.) and $ZnCl_2$ (18 g.) at 230° (Bonna, *A.* 239, 64). Needles or prisms (from alcohol). Volatile with steam. V. sol. alcohol and benzene.—B'HCl: yellow needles.—B'HI: orange-red needles.—$B'C_6H_2(NO_2)_3OH$: brown crystals.—The sulphate is reddish-brown.

Methyl-acridine chloral *v.* Tri-chloro-oxy-propyl-acridine.

DI-METHYL-ACRYLIC ACID *v.* Pentenoic acid.

TETRA-METHYL-ADIPIC ACID $C_{10}H_{18}O_4$ *i.e.* $CO_2H.CH_2.CMe_2.CMe_2.CH_2.CO_2H$? [210°]. A product of the action of finely-divided silver on α-bromo-isovaleric ether $CHMe_2.CHBr.CO_2Et$ (C. Hell a. W. Mayer, *B.* 22, 52). Snowy-white granules (from benzene); v. sol. alcohol and chloroform. Forms no anhydride on heating (difference from di-isopropyl-succinic acid which accompanies it in its preparation). May be sublimed.—BaA″ 2aq.—SrA″ 4aq. S. 16·6 at 19°.—MgA″ 5aq. S. 12·5 at 15°.—MnA″ 3aq. S. 5·9 at 25°.—NiA″ 4aq. S. (of NiA″) 4·7 at 25°.—CoA″ 3aq. S. (of CoA″) 6·65 at 23°.—ZnA″. S. ·195 at 13°.—CdA″ 3aq. S. 2·29 at 31°.—CuA″. S. ·024.—PbA″. S. ·045 at 13°.—Ag_2A''. S. ·046 at 13°.

METHYL-ÆSCULETIN *v.* Æsculetin.

METHYLAL *v.* Formic aldehyde.

METHYLALACREATINE *v.* Alacreatine.

METHYL ALCOHOL CH_4O *i.e.* $CH_3.OH$. *Oxy-methane. Methyl hydroxide. Wood spirit. Wood naphtha.* Mol. w. 32. (64·8°) (R. Schiff, *A.* 220, 99); (65·9°) (Perkin, *C. J.* 45, 465); (66·2°) (Zander). S.G. $\frac{20}{4}$ ·7953 (Brühl); $\frac{15}{15}$ ·79726; $\frac{25}{25}$ ·78941 (Perkin); $\frac{0}{0}$ ·8111 (Zander). S.V. 42·7 (S.); 42·6 (Lossen, *A.* 254, 55). $\mu_\beta = 1·3332$. $R_\infty = 12·93$ (Brühl). H.F.p. 51,450 (Thomsen); 61,400 (Stohmann, *J. pr.* [2] 40, 353). H.F.v. 50,580 (Thomsen, *Th.*). H.C. 170,600 (Stohmann). M.M. 1·640 at 18·7°. *Compressibility*: ·00010879 at 15° (Dupré, *Pr.* 20, 336).

Occurrence.—Free in the juices of plants (Guthzeit, *J.* 1879, 905; Maquenne, *C. R.* 101, 1067) and in the aqueous distillate in the fruits of *Heracleum* (Guthzeit, *A.* 177, 344; 240, 243). Methyl alcohol occurs also in the product of the distillation of wood (Taylor [A.D. 1812], *Tilloch's Phil. Mag.* 60, 315; Dumas a. Peligot, *A.* 15, 1; *A. Ch.* 58, 5; 61, 193) and of colophony (Kelbe a. Lwow, *B.* 16, 351). It occurs as methyl salicylate in oil of winter-green (*Gautheria procumbens*).

Formation.—1. From methane by chlorinating, and heating the resulting methyl chloride with aqueous KOH for 7 days at 100° (Berthelot, *A.* 105, 241). The MeCl may also be treated with HOAc and NaOAc at 200°, and the resulting MeOAc saponified. MeCl treated with Ag_2SO_4 and H_2SO_4 at 100° gives $HMeSO_4$, whence methyl alcohol can be readily obtained.—2. From hydrogen cyanide by reduction with zinc and H_2SO_4, and treating the resulting methylamine with nitrous acid (Linnemann, *Z.* [2] 4, 284).—3. By distilling calcium formate (Lieben a. Paternò, *G.* 3, 290; *A.* 167, 293; Friedel a. Silva, *C. R.* 76, 1545).

Preparation.—The crude watery liquid obtained by the distillation of wood contains methyl alcohol, acetone, acetic acid, methyl acetate, and ammonium acetate. It is separated from the tarry products and redistilled; the first tenth of the distillate is mixed with slaked lime and redistilled; a little sulphuric acid is then added, and the liquid redistilled and rectified over quick-lime. The crude wood spirit thus obtained has a strong aromatic odour and turns brown on keeping. It contains methyl acetate, acetone, di-methyl acetic orthaldehyde $CH_3.CH(OMe)_2$ (Dancer, *C. J.* 17, 222), allyl alcohol, methyl ethyl ketone, and other ketones (Grodzky a. Krämer, *B.* 9, 1920). Methyl alcohol may be obtained from wood spirit by saturating with fused $CaCl_2$ and heating on a water-bath. The residue is a compound of methyl alcohol with $CaCl_2$, which when distilled with water is decomposed, giving off the methyl alcohol. The distillate is then rectified over quick-lime (Kane, *A.* 19, 164). According to Gould (*C. J.* 7, 311) it is best to distil the wood spirit with conc. NaOHAq (to saponify MeOAc) and then to dehydrate with K_2CO_3 before saturating with $CaCl_2$. A better method for obtaining methyl alcohol from wood spirit is to distil the spirit (1 pt.) with H_2SO_4 (1 pt.) and potassium oxalate (2 pts.); the crystalline di-methyl oxalate is then decomposed by distillation with water, and the MeOH dried over lime (Wöhler, *A.* 81, 376). The oxalate may also be obtained by dissolving oxalic acid, dehydrated at 100°, in boiling MeOH, leaving the solution to cool, and washing the crystals with cold water as long as the filtrate exhibits the iodoform reaction (Erlenmeyer, *N. Rep. Pharm.* 23, 624). An alternative method consists in passing HCl into a solution of benzoic acid in wood spirit, distilling, ppg. with water the portion collected above 100°, decomposing by boiling for several hours with aqueous NaOH, distilling, and rectifying over quick-lime (Carius, *A.* 110, 210). The following modification of Wöhler's process is recommended by Dittmar a. Fawsitt (*Tr. E.* 33, 509): 100 c.c. of wood spirit are digested with 150 g. of powdered NaOH, and then distilled on a water-bath; 500 g. of oxalic acid crystals are mixed with 200 c.c. of sulphuric acid, and then 400 c.c. of the alcohol, purified as above, is added, and the whole cautiously heated on a

water-bath. The methyl oxalate thus obtained is thoroughly dried by pressure, and the alcohol regenerated by digestion with water at 70°. To dehydrate the alcohol thus obtained, digestion with baryta, lime, and dried copper sulphate is necessary. Even when prepared from the oxalate methyl alcohol is not quite pure, as it contains bodies which exhibit Lieben's iodoform reaction. It may be freed from these by dissolving in it one-tenth of its weight of iodine, gradually adding NaOH until the liquid is distinctly alkaline, and distilling. The product, rectified over CaO, has a specific gravity of ·81 at 15° (Regnault a. Villejean, *A. Ch.* [6] 4, 430; *C. R.* 99, 82). Methyl alcohol may also be prepared by saponifying methyl formate (3 pts.) with NaOH (2 pts.) and water (6 pts.) (Grodski a. Krämer, *B.* 9, 1928; Bardy a. Bordet, *A. Ch.* [5] 16, 564). Methyl alcohol may be obtained very nearly pure by distilling oil of winter-green with potash, and rectifying the distillate over lime.

Properties.—Colourless mobile liquid, with purely spirituous odour. Burns with a pale flame. Mixes with water, alcohol, and ether; dissolves fixed and volatile oils and most resins. Hence it is much used as a solvent. In aqueous solution it produces intoxication, in concentrated solution it is poisonous. When perfectly dry it dissolves a little $CuSO_4$, acquiring a bluish-green colour; but it does not dissolve crystallised $CuSO_4 7aq$ (Klepl, *J. pr.* [2] 25, 526). Methyl alcohol is etherified by acetic acid more rapidly and completely than any other alcohol (Menschutkin, *Z. P. C.* 1, 611). Dittmar a. Fawsitt give the specific gravity of mixtures of methyl alcohol and water as follows:

P.c. of $CH_3.OH$	S.G. at 0°	S.G. at 15·56°
0	·99987	·99907
10	·98429	·98262
20	·97233	·96808
30	·96057	·95367
40	·9457	·93697
50	·92873	·91855
60	·90917	·89798
70	·88687	·87487
80	·86314	·85035
90	·83751	·82396
100	·81015	·79589

Older determinations are by Ure (*P. M.* [3] 19, 51), Dupré (*Pr.* 20, 336), and Duclaux (*A. Ch.* [5] 13, 87). The same observers find the vapour tension of methyl alcohol, measured in millimetres of mercury at 0°, to be:

Temp.	Tension	Temp.	Tension
0°	29·7	40°	259·4
10	53·8	50	409·4
20	94·0	60	624·3
30	158·9	64·96	760·0

(*cf.* Konovaloff, *P.* [2] 14, 40). The following vapour-tensions are given by Richardson (*C. J.* 49, 762):

Temp.	Tension	Temp.	Tension
−8·3°	17·3	39·2°	235·13
+0·7	32·06	49·2	370·26
11·2	55·82	59·9	584·24
22·7	108·96	65·7	753·05
30·2	155·32		

The specific heat of aqueous methyl alcohol was found by Dupré to be as follows:—

Weight p.c. of methyl alcohol	Specific heat	Weight p.c. of methyl alcohol	Specific heat
10	·98582	60	·80177
20	·95914	70	·75500
30	·92658	80	·69999
40	·89219	90	·64282
50	·84645	100	·54325

Estimation.—Pure methyl alcohol does not give Lieben's iodoform reaction with iodine and potash.

The amount of methyl alcohol in commercial wood spirit may be estimated by adding 5 c.c. of the spirit, drop by drop, to 30 g. of PI_2 in a flask provided with inverted condenser. The flask is then heated for 5 minutes in boiling water, and the MeI then distilled off by inclining the condenser. The volume of MeI is read off in a graduated receiver 5 c.c. of methyl alcohol yield 7·19 c.c. of methyl iodide (Krell, *B.* 6, 1310; *cf.* Grodzky a. Krämer, *B.* 7, 1495; 9, 1928). If it is desired to determine how much of the methyl alcohol is in the form of MeOAc, the spirit may be boiled with standard alkali, and the amount used up in the saponification determined.

Bardy and Bordet (*A. Ch.* [5] 16, 565) modify Krell's process, using only 15 g. of PI_2 to 5 c.c. of wood spirit, but adding 5 c.c. of aqueous HI subsequently. They distil the liquid at 80°–90°, and at the end of the distillation add 5 c.c. of water and quickly distil. The methyl iodide is washed once or twice with water and measured.

Di-methyl ortho-acetic aldehyde or methyl-acetal $CH_3.CH(OMe)_2$ boils at 64° and gives MeI on treatment with PI_2, but it does not react with aniline, so that when the wood-spirit is to be used in preparing di-methyl-aniline, by heating with aniline hydrochloride, the estimation by PI_2 will give too high results.

The presence of *acetone* is objectionable in methyl alcohol that is to be used for preparing di-methyl-aniline. Its amount can be determined by shaking 1 or 2 c.c. of the alcohol with 20 or 30 c.c. of normal aqueous KOH, adding 20 or 30 c.c. of a decinormal solution of iodine, until the solution is clear. The liquid is then acidified with HCl (S.G. 1·025), excess of decinormal sodium thiosulphate added, and the excess determined by titrating back with iodine solution. If 1 c.c. of methyl alcohol be taken, the weight of acetone in 100 c.c. will be found by multiplying the amount of iodine used up by 7·612 (Messinger, *B.* 21, 3366; *cf.* Krämer, *B.* 13, 1002; Hintz, *Fr.* 27, 182).

The estimation of methyl alcohol in ethyl alcohol can be effected by oxidation with a standard solution of $K_2Cr_2O_7$, for 1 pt. of ethyl alcohol reduces 4·278 pts. of the dichromate in becoming oxidised to acetic acid, while 1 pt. of methyl alcohol, in being oxidised to CO_2 and water, reduces 9·224 pts. of $K_2Cr_2O_7$. A solution of 80 g. $K_2Cr_2O_7$ and 150 c.c. H_2SO_4 per litre is employed, and the unreduced chromate estimated volumetrically (O. Hehner, *An.* 12, 25).

When 10 c.c. of pure ethyl alcohol are shaken with 1 c.c. of a ·1 p.c. solution of $KMnO_4$ at 20°, no reduction takes place for 20 minutes, but if the ethyl alcohol contains crude wood

spirit, decolourisation takes place at once (Habermann, *Fr.* 27, 663).

Reactions.—1. Passage through a *red-hot tube* yields acetylene and other products (Berthelot, *C. R.* 50, 805).—2. In contact with *platinum-black* and air it is oxidised to formic aldehyde and formic acid.—3. Heated with *ammonium chloride* in a sealed tube at 300° it yields mono-, di-, and tri-methylamine (Berthelot).—4. *Bleaching-powder* does not yield chloroform (Goldberg, *J. pr.* [2] 24, 115).—5. *Potassium* gives off hydrogen, forming KOMe.—6. When its vapour is passed over heated *potash*, hydrogen is given off, and potassium formate, oxalate, and carbonate are successively formed.—7. Conc. H_2SO_4 forms $HMeSO_4$, which, when heated with excess of methyl alcohol, yields di-methyl oxide. When distilled with excess of H_2SO_4 di-methyl sulphate passes over.—8. Converted into methyl chloride by treatment with HCl, with PCl_5, or with S_2Cl_2. The joint action of H_2SO_4 and HBr gives rise to methyl bromide and ethyl bromide (Niemilovitch, *M.* 10, 820).—9. $SOCl_2$ forms MeSH, Me_2SO_4, MeCl, and other products (Carius, *A.* 111, 93).—10. SO_3 forms $CH(OH)(SO_3H)_2$ (Max Müller, *B.* 6, 1031).—11. When acidulated with 5 p.c. sulphuric acid and submitted to electrolysis it forms CO_2, CO, methyl formate, methyl sulphate, and methylal (Renard, *C. R.* 80, 236).—12. Distillation over *heated zinc-dust* splits it up into CO and hydrogen, a very little methane being also formed (Jahn, *B.* 13, 983; *M.* 1, 378).—13. *Zinc chloride* forms CH_4, water, Me_2O, hexa-methyl-benzene, and traces of propylene, butylene, and other hydrocarbons (Le Bel a. Greene, *C. R.* 87, 260; 89, 413).—14. *Aldehyde* (1 vol.), MeOH (2 vols.), and HCl form $CH_3.CH(OMe)_2$ (Claus a. Trainer, *B.* 19, 3004).—15. Not affected by *B. aceti* growing in solutions containing it (Brown, *C. J.* 49, 177).—16. Converts *m-* and *p-diazo-benzoic acid* into $C_6H_4(OMe).CO_2H$, while o-diazo-benzoic acid only gives benzoic acid (Griess, *B.* 21, 978).—17. When heated with hydrochlorides of aromatic bases (*e.g.* aniline, xylidine, piperidine) it often displaces hydrogen in the nucleus by methyl (Hofmann, *B.* 15, 2895; Ladenburg, *B.* 16, 2057).—18. Unlike EtOH, it hardly reacts when heated with phenol and $ZnCl_2$ (Auer, *B.* 17, 669).—19. Unlike butyl and amyl alcohols, it does not form a homologue of benzene when heated with benzene and $ZnCl_2$ at 270° (Goldschmidt, *B.* 15, 1066).—20. $ClCONH_2$ forms methyl allophanate $NH_2.CO.NH.CO_2Me$ [208°] (Gattermann, *A.* 244, 40).

Metallic derivatives.—KOMe. Obtained by dissolving K in methyl alcohol.—$(KOH)_3(MeOH)_5$ or $(KOMe)_3(MeOH)_2$ 3aq. [c. 110°]. Obtained by evaporating a solution of KOH in methyl alcohol (Göttig, *B.* 21, 1832). Large elastic plates, somewhat heavier than water, on which they move about rapidly, being decomposed.—$(NaOH)_5(MeOH)_6$ or $(NaOMe)_5MeOH$ aq. Obtained by dissolving NaOH in dry MeOH and evaporating. Crystalline mass, which moves about on the surface of water while decomposing and dissolving.—NaOMe $1\frac{1}{2}$aq. Obtained by evaporating a solution of NaOH in not quite dry methyl alcohol (Göttig, *B.* 21, 561).—$NaOMe(MeOH)_2$ (Fröhlich, *A.* 202, 295). CO passed over NaOMe at 160° forms acetic acid. CO passed into a hot mixture of NaOMe and NaOAc forms propionic acid (Geuther a. Fröhlich, *A.* 202, 312). When distilled with the Ba salt of a carboxylic acid it displaces the carboxyl by hydrogen. Thus succinic acid may be converted into propionic acid (Mai, *B.* 22, 2135).—TlOMe. From TlOEt and excess of MeOH (Lamy, *J.* 1864, 466).—$(Ba(OMe)_2)_2BaO_2H_2$ aq. White nacreous plates, obtained by evaporating at 135° a solution of BaO in MeOH (De Forcrand, *C. R.* 102, 1397, 1557). Perhaps identical with $Ba(OMe)_2$ aq described by Dumas and Péligot (*A. Ch.* 58, 17). 1 litre of MeOH dissolves 200 g. of BaO. The heat of formation of the compound from solid 3BaO and liquid 4MeOH is 62,500. If a considerable quantity of water is added to the solution of BaO in MeOH the hydrate BaO 10aq is precipitated. The compound $BaO2Ba(OMe)_2$ 2aq is readily formed, even if as much as 3 p.c. water be present in the methyl alcohol, but by evaporating in the cold over H_2SO_4 crystals of $Ba(OMe)_2$ 3aq are formed. These are sol. water and alcohol. By passing HCN into a solution of baryta in methyl alcohol there is formed barium cyano-methylate Ba(OMe)CN,MeOH. This is a crystalline powder, sol. water, less sol. methyl alcohol. It loses at 100° the methyl alcohol of crystallisation.

Combinations.—$CaCl_2$4MeOH. Methyl alcohol dissolves $CaCl_2$ with great rise of temperature, and on cooling this compound separates in large six-sided tables (Kane, *A.* 19, 168). It is not decomposed at 100°, but water readily liberates the MeOH.—LiCl3MeOH.—$MgCl_2$6MeOH (Simon, *J. pr.* [2] 20, 377).—$SbCl_5$MeOH. [81°]. Slightly yellow crystals (from hot alcohol); decomposes at 130°, giving off MeCl and HCl (W. C. Williams, *C. J.* 30, 463).—$CuSO_4$2MeOH. Minute bluish-green crystals, obtained by shaking anhydrous $CuSO_4$ with methyl alcohol (Forcrand, *C. R.* 102, 551).

METHYL ALDEHYDE is FORMIC ALDEHYDE.

METHYL-ALIZARIN *v.* DI-OXY-METHYL-ANTHRAQUINONE.

METHYL-ALLANTOÏN $C_5H_8N_4O_3$. [225°]. Formed by oxidising methyl-uric acid with cold aqueous $KMnO_4$ (Hill, *B.* 9, 1090). Monoclinic prisms; decomposed by fusion. V. sol. hot water, sl. sol. alcohol, insol. ether. Conc. HIAq splits it up into urea and methyl-hydantoïn.—$AgC_5H_7N_4O_3$: prisms, sl. sol. cold water.

METHYL-ALLOXAN $C_5H_4N_2O_4$ *i.e.* $CO<\begin{smallmatrix}NH.CO\\NMe.CO\end{smallmatrix}>CO$. Formed by oxidising methyl-uric acid with HNO_3 or with $KClO_3$ and HCl (Hill, *B.* 9, 1092). Formed also by treating theobromine (2 pts.) with $KClO_3$ (·9 pts.) and HCl (S.G. 1·06) at 50° (Maly a. Andreasch, *M.* 3, 108; *cf.* Fischer, *A.* 215, 304). It is converted by alkalis into methyl-alloxanic acid, and by boiling HNO_3 into methyl-parabanic acid. H_2S forms di-methyl-alloxantin. $KHSO_3$ forms a compound $B'KHSO_3$aq, which crystallises in large monoclinic prisms.

Di-methyl-alloxan $C_6H_6N_2O_4$ *i.e.* $CO<\begin{smallmatrix}NMe.CO\\NMe.CO\end{smallmatrix}>CO$. A product of the action of $KClO_3$ and HCl on caffeïne at 50°. It is extracted by ether (E. Fischer, *A.* 215, 257; Maly a. Andreasch, *M.* 3, 92). Colourless six-sided

tables (containing 2aq), which slowly turn red in air. V. sol. water, almost insol. alcohol, insol. ether. Dyes the skin red. With $FeSO_4$ and ammonia it gives a characteristic indigo colouration. After drying over H_2SO_4 it is left as an amorphous powder (containing aq), sol. alcohol and ether. Di-methyl-alloxan decomposes at 100°. It prevents the ppn. of cupric and ferric salts by potash. Hydrogen sulphide converts it into amalic acid. $KHSO_3$ forms the compound $C_6H_6N_2O_4KHSO_3$ which crystallises in long tablets, S. 7·2 at 20°, almost insol. alcohol, insol. ether. This compound may be crystallised from warm water, and does not give the indigo colouration with $FeSO_4$ and ammonia.

METHYL-ALLOXANIC ACID $C_5H_6N_2O_5$. Formed by the action of alkalis on methyl-alloxan. When the product of the action of HNO_3 on methyl-uric acid is neutralised with $CaCO_3$, and then mixed with alcohol and ammonia the salt $CaC_5H_4N_2O_5$ is ppd. (Hill, *B.* 9, 1092). This salt is gelatinous, and when boiled with water it gives off methylamine.

METHYL-ALLOXANTIN $C_9H_8N_4O_8$. Obtained by mixing solutions of dialuric acid and methyl-alloxan (Andreasch, *M.* 3, 431). Crystallises from water in minute thin tables (containing 3aq).

s-**Di-methyl-alloxantin** $C_{10}H_{10}N_4O_8$ *i.e.*

$$CO{<}{NMe.CO \atop NH\ .CO}{>}C(OH).C(OH){<}{CO.NMe \atop CO.NH}{>}CO.$$

Formed by passing H_2S into an aqueous solution of methyl-alloxan (Maly a. Andreasch, *M.* 3, 109). Thin plates (containing 4aq); almost insol. alcohol and ether, sl. sol. cold water. Turns red in air. Gives a red colouration with ammonia, and a violet colouration with potash or baryta (Andreasch, *M.* 3, 109).

u-**Di-methyl-alloxantin**

$$CO{<}{NMe.CO \atop NMe.CO}{>}C(OH).C(OH){<}{CO.NH \atop CO.NH}{>}CO.$$

Formed by reducing di-methyl-alloxan to di-methyl-dialuric acid, and ppg. the aqueous solution of this acid with alloxan (Andreasch, *M.* 3, 428). Crystallises from hot water in minute four-sided pyramids (containing aq); insol. alcohol and ether.

Tetra-methyl-alloxantin *v.* AMALIC ACID.

METHYL-ALLYL *v.* BUTYLENE.

METHYL-ALLYL-ACETO-ACETIC ACID *v.* ACETO-ACETIC ACID.

DI-METHYL-ALLYL-AMINE. *Methylo-iodide* $C_3H_5NMe_3I$. From allylamine and MeI (Bono, *B.* 20, Ref. 137). When distilled with KOH it yields NMe_3 and an aldehyde $C_6H_{10}O$ (130°–135°).

p-**METHYL-ALLYL-BENZENE** $C_{10}H_{12}$ *i.e.* $CH_3.C_6H_4.C_3H_5$. *p-Allyl-toluene.* (192°). Formed from cymene by chlorinating and heating the resulting $CH_3.C_6H_4.C_3H_6Cl$ with alcoholic KOH (Errera, *G.* 14, 283, 505). Liquid. Combines with bromine. $KMnO_4$ oxidises it to *p*-toluic acid. HBrAq (S.G. 1·59) at 200° forms a polymeride $(C_{10}H_{12})_x$ (350°), and this on keeping changes to an amorphous solid, which by distillation is re-converted into *p*-methyl-allyl-benzene.

METHYL-DI-ALLYL-CARBINOL *v.* OCTINYL ALCOHOL.

Di-methyl-allyl-carbinol *v.* HEXENYL ALCOHOL.

METHYL-ALLYL-CHLORACETOL *v.* DI-CHLORO-HEXYLENE.

METHYL ALLYL ETHER *v.* METHYL ALLYL OXIDE.

METHYL ALLYL DIKETONE $C_6H_8O_2$ *i.e.* $CH_3.CO.CO.C_3H_5$. *Acetyl-crotonyl.* (c. 130°). Obtained by distilling its mono-oxim with dilute H_2SO_4 (Otte a. Von Pechmann, *B.* 22, 2124). Yellow oil with irritating odour. Not obtained pure.

Mono-oxim $CH_3.CO.C(NOH).C_3H_5$. *Nitroso-allylacetone. Methyl nitroso-butenyl ketone.* [46°]. From allyl-aceto-acetic acid and nitrous acid. White plates (from ligroïn), v. sol. usual menstrua. Its solution in NaOHAq is yellow.

Di-oxim $CH_3.C(NOH).C(NOH).C_3H_5$. [135°]. Formed from the mono-oxim by warming with hydroxylamine. Small plates.

Phenyl-hydrazide oxim $CH_3.C(N_2HPh).C(NOH).C_3H_5$. [137°]. Brownish-red needles (from benzene and ligroïn).

METHYL ALLYL OXIDE C_4H_8O *i.e.* $CH_3.O.C_3H_5$. *Allyl methyl ether.* (46°). S.G. $\frac{11}{}$ ·77. H.F.p. 34,080. H.F.v. 32,050. From allyl bromide and NaOMe (Henry, *B.* 5, 455). With bromine it forms $CH_3.O.CH_2.CHBr.CH_2Br$ (185°). ICl gives $CH_3.O.C_3H_5ClI$ (196°) (Silva, *B.* 8, 1469).

METHYL-ALLYL-PROPYL-CARBINOL *v.* OCTENYL ALCOHOL.

METHYL ALLYL SULPHIDE C_4H_8S *i.e.* $CH_3.S.C_3H_5$. (c. 92°). V.D. 43·36. Formed by heating lead methyl mercaptide $(CH_3S)_2Pb$ with allyl bromide and ether at 100° (Obermeyer, *B.* 20, 2925).

METHYL ALLYL THIO-UREA $CH_3.NH.CS.NH.C_3H_5$. [50·5°]. Formed from allylamine and methyl thio-carbimide or from methylamine and allyl thio-carbimide (O. Hecht, *B.* 23, 286). White mass.

METHYL-AMIDO-ACETIC ACID $C_3H_7NO_2$ *i.e.* $CH_3NH.CH_2.CO_2H$. *Methyl-glycocoll. Sarcosine.* Mol. w. 89. [210°–215°]. Formed by the action of boiling baryta-water on creatine or caffeïne (Liebig, *A.* 62, 310; Rosengarten a. Strecker, *A.* 157, 1; Schilling, *C. C.* 1884, 811). Formed also by heating chloro-acetic ether with aqueous methylamine at 125° (Volhard, *A.* 123, 261).

Properties.—Trimetric prisms, v. e. sol. water, sl. sol. alcohol. Has a somewhat sweet taste. Heated to 210°–220° the greater part evolves H_2O giving the anhydride $C_6H_{10}N_2O_2$, whilst a smaller portion splits up into di-methyl-amine and CO_2 (Mylius, *B.* 17, 286). Chloride of cyanogen passed into the fused substance gives methyl-hydantoïn and sarcosine-anhydride (Traube, *B.* 15, 2110). When taken internally, the greater part passes as such into the urine (Baumann a. Mering, *B.* 8, 587; Salkowski, *H.* 4, 107; Schiffer, *H.* 5, 266). Nitrous acid passed into its hot aqueous solution forms a nitroso-derivative $CH_3.N(NO).CH_2.CO_2H$, which is a thick liquid, forming the salt CaA'_2 aq crystallising in needles (Schultzen, *Z.* 1867, 616). Gives methyl-uric acid when heated with urea (Horbaczewski, *M.* 6, 356).

Salts.—$(C_3H_6NO_2)_2Cu$ 2aq: ultramarine blue crystals (E. Schmidt, *A.* 217, 273).—$C_3H_7NO_2HCl$: needles (from alcohol).—$(C_3H_6NO_2)_2ZnH_2Cl_2$: S. (alcohol) ·038. V. e. sol. water (Bulginsky, *J.*

1867, 495).—$(C_3H_7NO_2)_2H_2PtCl_6$ 2aq : monoclinic tables, $a:b:c$ = 1·0331 : 1 : ·6747 ; β = 75°27′. — $C_3H_7NO_2HAuCl_4$: yellow needles, sl. sol. cold water.—$C_3H_7NO_2HNO_3$. [c. 70°]. Very hygroscopic, v. sol. cold alcohol (Franchimont, *R. T. C.* 2, 339).—$(C_3H_7NO_2)_2H_2SO_4$ aq : four-sided tables, v. e. sol. water. S. (boiling alcohol) 10.

Guanidine hydrochloride $C_3H_7NO_2HClCH_5N_3$. Formed by heating methyl-amido-acetic acid with guanidine hydrochloride (Baumann, *B.* 7, 1151). Tables (from alcohol).

Anhydride $C_6H_{10}N_2O_2$ *i.e.*

$$\begin{array}{l} CH_3.N.CH_2.CO \\ \;\;\;\;| \;\;\;\;\;\;\;\;\;\;\;\;\;\;\;\; | \\ OC.CH_2.N.CH_3 \end{array}$$

(?). *Sarcosine anhydride.* [150°]. Formed by the action of cyanogen chloride on melted sarcosine. Prepared by heating sarcosine to 210°–220° and distilling the residue (Traube, *B.* 15, 2112 ; Mylius, *B.* 17, 286). Colourless prisms. V. sol. water, alcohol, and ether. Bitter taste. Weak base. By boiling with water it again gives sarcosine. On oxidation with $KMnO_4$ it yields *s*-di-methyl-oxamide.

Salts. — $B'_2H_2Cl_2PtCl_4$ 2aq : prisms. — $B'_2H_2Cl_2PtCl_4$ 4aq : large six-sided tables. — $B'_2HClAuCl_3$ 2aq : prisms.

Sarcosine-uric acid $C_8H_9O_4N_5$. Obtained by heating a mixture of sarcosine (3 pts.) and uric acid (2 pts.) at 210° ; a good yield is obtained.

Properties.—Colourless prismatic crystals (containing 2aq). Sol. hot water. It shows the murexide reaction. It slowly reduces alkaline solutions of copper. It has weak acid and basic properties, dissolving in aqueous acids and alkalis. By fusion with KOH at 110° it is resolved into uric acid and sarcosine. Heated with bromine water it is converted into bromo-sarcosine-mesouric acid $C_8H_7N_4O_5Br$.

Salts.—The acetate forms microscopic crystals, sl. sol. hot acetic acid, insol. cold HOAc, v. sol. water. The formate is very analogous to the acetate. The ammonium salt is crystalline.—$A''Ag_2$: insol. white amorphous pp. (Mylius, *B.* 17, 518).

Bromo-sarcosine-mesouric acid $C_8H_7N_4O_5Br$. Formed by digesting a warm aqueous solution of sarcosine-uric acid with bromine, which gives a nearly theoretical yield (Mylius, *B.* 17, 521). Heavy colourless tables. Sl. sol. water. By H_2S it is reduced to sarcosine-mesouric acid. It is readily decomposed by alkalis, but is stable towards acids.

Sarcosine-mesouric acid $C_8H_8O_5N_4$. Obtained by reducing a hot aqueous solution of bromo-sarcosine-mesouric acid with H_2S (Mylius, *B.* 17, 524). Trimetric tables or needles. V. sol. water, insol. alcohol. It is a strong acid, but also possesses weak basic properties. By bromine water it is reconverted into the bromo-derivative ; similarly chlorine-water gives the chloro-derivative. It is very oxidisable, reducing $AuCl_3$, alkaline, copper solution, $KMnO_4$, &c., very readily.

Salts.—The acetate forms an unstable crystalline pp., sl. sol. acetic acid.—$A''HNH_4$: fine needles, v. sol. water.—$A''Ag_2$: white amorphous pp.

Tri-methyl-amido-acetic acid internal anhydride *v.* Betaïne.

DI-METHYL-AMIDO-ACETIC ORTHALDEHYDE. *Methylo-hydroxide* $C_5H_{15}NO_3$ *i.e.* $CH_2(NMe_3OH).CH(OH)_2$. *Muscarine.* Occurs, together with neurine, in the fly agaric (Schmiedeberg a. Koppe, *J.* 1870, 875). Formed from neurine by oxidation with conc. HNO_3 (Schmiedeberg a. Harnack, *J.* 1876, 804). Deliquescent crystalline mass, sol. alcohol. Alkaline in reaction. Active narcotic poison. Separated from neurine by placing the mixed hydrochlorides on filter-paper, when the muscarine salt deliquesces and is absorbed by the paper (Harnack, *J.* 1876, 803).—$B'(C_5H_{14}NO_2Cl)_2PtCl_4$ 2aq.—$C_5H_{14}NO_2AuCl_4$.

Di-ethyl derivative of the methylo-hydroxide $C_9H_{23}NO_3$ *i.e.* $CH_2(NMe_3OH).CH(OEt)_2$. *Hydroxide of tri-methyl-amido-acetal.* When chloro-acetal $CH_2Cl.CH(OEt)_2$ is treated with tri-methyl-amine there is formed $CH_2(NMe_3Cl).CH(OEt)_2$ and $C_5H_{12}NOCl$, which is probably $CH_2(NMe_3Cl).CHO$. The two salts are separated by fractional ppn. by platinic chloride.—$(C_9H_{22}NO_2Cl)_2PtCl_4$: orange crystals, sl. sol. cold water. — $C_9H_{22}NO_2AuCl_4$: lemon-yellow needles.

Di-methyl-amido-acetic aldehyde. *Methylo-hydroxide* $C_5H_{13}NO_2$ *i.e.* $CH_2(NMe_3OH).CHO$. Formed by saponifying $CH_2(NMe_3OH).CH(OEt)_2$ with baryta (Berlinerblau, *B.* 17, 1142). The hydrochloride $C_5H_{12}NOCl$ is also formed as above. Gives the aldehyde reactions.—Platinochloride $(C_5H_{12}NOCl)_2PtCl_4$: octahedra (from dilute alcohol).

DI-METHYL-AMIDO-ACETONE. *Methylo-chloride.* $C_6H_{14}NOCl$ *i.e.* $CH_3.CO.CH_2NMe_3Cl$. *Caprine chloride.* Formed by the action of dry NMe_3 upon chloro-acetone in the cold (Niemitowitch, *M.* 7, 241). Very deliquescent shining needles ; sol. alcohol. Gives the alkaloidal reactions. Acts physiologically like curare.—$C_6H_{14}NOClAuCl_3$ [139°].

p-**DI-METHYL-AMIDO-ACETOPHENONE** $C_6H_4(NMe_2).CO.CH_3$ [59°]. Formed by methylation of *p*-amido-acetophenone (Klingel, *B.* 18, 2694). Yellowish plates (from hot water). V. sol. alcohol, ether, and hot water.

o-**DIMETHYL-AMIDO-ANISOL** *v.* o-Di-methyl-amido-phenol *methyl ether.*

METHYL-AMIDO-AZO- COMPOUNDS *v.* Azo-compounds.

METHYL-AMIDO-BENZAMIDE *v. Amide* of Methyl-amido-benzoic acid.

METHYL-AMIDO-BENZENE *v.* Methyl-aniline and Toluidine.

Di-methyl-amido-benzene *v.* Xylidine, Methyl-toluidine, and Di-methyl-aniline.

Tri-methyl-amido-benzene *v.* Mesidine and ψ-Cumidine.

Tetra-methyl-amido-benzene *v.* Tetra-methyl-phenyl-amine.

Tetra-methyl-di-amido-benzene *v.* Tetra-methyl-phenylene diamine.

Di-methyl-tri-amido-benzene $C_6H_3(NMe_2)(NH_2)_2$ [1:3:4]. [44°] (298°). Needles. Readily turned blue in the air. Prepared by reduction of dinitro-dimethyl-aniline [87°]. Formed also by reduction of nitro-*p*-dimethyl-amido-phenyl-oxamic ether.

Acetyl derivative $C_6H_3(NMe_2)(NH_2)(NHAc)$. [153°]. Prisms (containing aq) (Wurster a. Sendtner, *B.* 12, 1805).

u-Tri-methyl-tri-amido-benzene $C_6H_3(NMe_2)(NH_2)(NHMe)$ [1:*x*:4]. [90°]. (294°). Prepared by reduction of the nitrosamine derived from nitro-trimethyl-*p*-phenylene-diamine (Wurster a. Schobig, *B.* 12, 1812). White needles. Sol. water. Gives a blue colouration with HNO_2.

Diacetyl derivative [184°]. Leaflets.

METHYL-AMIDO-BENZENE-AZO- COMPOUNDS *v.* AZO- COMPOUNDS and *Dis*-AZO- COMPOUNDS.

DI-METHYL-AMIDO-BENZENE PHOSPHINIC ACID $NMe_2.C_6H_4.P(OH)_2$. [162°]. Formed by decomposing its chloride with water (Schenk a. Michaelis, *B.* 21, 1498). White needles; v. sol. hot water and alcohol. On boiling its aqueous solution it is split up into di-methyl-aniline and phosphorous acid. When heated alone it gives phosphorus, PH_3, and di-methyl-aniline.

Salt.—NaHA″ 2aq: large crystals (from alcohol).

Chloride $NMe_2.C_6H_4.PCl_2$. [66°]. (250° at 120 mm.). Formed by the action of PCl_3 (100 g.) on di-methyl-aniline (70 g.) in presence of $AlCl_3$ (20 g.). The mixture is boiled for eight hours with inverted condenser, and the product extracted with petroleum ether and distilled *in vacuo*. Thin plates; v. sol. benzene, m. sol. ether, sl. sol. petroleum ether. Converted by the action of chloro-benzene and sodium into di-methyl-amido-tri-phenyl-phosphine.

DI-METHYL-AMIDO-BENZENE PHOSPHONIC ACID. $NMe_2.C_6H_4.PO(OH)_2$. [133°]. Formed by oxidising $NMe_2.C_6H_4.P(OH)_2$ with $HgCl_2$ (Schenk a. Michaelis, *B.* 21, 1500). Crystals; v. e. sol. water and alcohol.

METHYL-AMIDO-BENZENE SULPHONIC ACID $C_7H_9NSO_3$ *i.e.* $NHMe.C_6H_4.SO_3H$. Formed, together with methane disulphonic acid, by heating the acetyl derivative of methyl-aniline with H_2SO_4 at 145° (Smyth, *B.* 7, 1240). Crystals, which decompose at 182° without previous fusion. —BaA'_2aq : crystalline powder.

Methyl-amido-benzene sulphonic acid $NHMe.C_6H_4.SO_3H$. Formed by heating methyl-aniline ethyl sulphate at 210° (Mundelius, *B.* 7, 1350). Plates (containing aq); insol. alcohol and ether. — BaA'_2 $3\frac{1}{2}$aq: small prisms. — CaA'_2 4aq.—PbA'_2 8aq.

Di-methyl-amido-benzene *p*-sulphonic acid $NMe_2.C_6H_4.SO_3H$. [150°] (S.); [257°] (M. a. G.).

Formation.—1. By heating di-methyl-aniline with rather more than the equivalent quantity of sulphuric acid at 185° (Smyth, *B.* 6, 344; 7, 1237; Armstrong, *B.* 6, 663; Vignon, *C. R.* 107, 263).—2. From di-methyl-aniline and $ClSO_3Et$ (Wenghöffer, *J. pr.* [2] 16, 448).—3. From bromo-di-methyl-aniline and H_2SO_4 at 180° (Michler a. Walder, *B.* 14, 2177).—4. From di-methyl-aniline and $SOCl_2$ followed by water (Michaelis a. Godchaux, *B.* 23, 555).

Properties.—8-sided prisms (containing aq). Decomposes at 230°.

Salts.—BaA'_2 3aq : needles or plates.— BaA'_2 5aq (Vignon).— BaA'_2 11aq : efflorescent triclinic crystals (Laar, *J. pr.* [2] 20, 262).— NaA' 2aq. Long needles, m. sol. water, sl. sol. aqueous NaOH, insol. water (M. a. G.)

Chloride $C_6H_4(NMe_2)SO_2Cl$.

Ethyl ether EtA′. [85°]. Formed from alcohol and the chloride.

Di-methyl-amido-benzene *p*-sulphonic acid.

Anhydride of the *methylo-hydroxide* $C_9H_{13}NSO_3$ *i.e.* $C_6H_4<\begin{matrix}NMe_3\\SO_2\end{matrix}>O$. Formed by allowing a mixture of amido-benzene *p*-sulphonic acid, MeI, conc. KOHAq, and MeOH to stand for some time in the cold (Griess, *B.* 12, 2116). Four-sided plates; v. sol. cold water, almost insol. alcohol, insol. ether. Decomposes before fusion. Ppd. as periodide by a solution of iodine in HIAq.— $(SO_3H.C_6H_4.NMe_3Cl)_2PtCl_4$ 8aq : orange tables, v. e. sol. cold water.

METHYL-o-AMIDO-BENZOIC ACID.

Amide $NHMe.C_6H_4.CONH_2$. [160°]. Formed by heating o-amido-benzamide with MeI at 100° (Weddige, *J. pr.* [2] 36, 152). Plates; v. sol. hot alcohol, sol. water. In dilute solutions it shows blue fluorescence.

Acetyl derivative $NHMe.C_6H_4.CO.NHAc$. [155°]. Long needles; v. sol. hot alcohol, sl. sol. benzene and ether. When heated above 155° it forms the anhydro-derivative $C_6H_4<\begin{matrix}CO.N\\NMe\end{matrix}>CMe$ [199°] which is an oxy-di-methyl-quinazoline.

Nitroso-derivative of the *amide* $NO.NMe.C_6H_4.CO.NH_2$. [149°]. Pale yellow prisms (from hot alcohol) (Finger, *J. pr.* [2] 37, 431).

Methyl-*m*-amido-benzoic acid $C_8H_9NO_2$ *i.e.* $NHMe.C_6H_4.CO_2H$. Formed by boiling (α)-benzcreatin $NH_2.C(NH).NMe.C_6H_4.CO_2H$ with baryta-water (Griess, *B.* 8, 325). Nodular groups of plates; v. sol. hot water. Nitrous acid ppts. a nitroso- derivative. Salt.—$C_8H_9NO_2HCl$: six-sided plates.

Di-methyl-*m*-amido-benzoic acid $C_9H_{11}NO_2$ *i.e.* $NMe_2.C_6H_4.CO_2H$. [151°]. Obtained by saponifying its methyl ether. Needles, sl. sol. hot water.

Methyl ether $NMe_2.C_6H_4.CO_2Me$. (270° uncor.). Obtained by fusing the isomeric anhydride of the methylo-hydroxide (*v. infra*) (Griess, *B.* 6, 587). Heavy yellowish oil, sol. acids.—$C_9H_{10}MeNO_2H_2SO_4$: very small prisms, sl. sol. dilute sulphuric acid, v. sol. water.— $(C_9H_{10}MeNO_2)_2H_2PtCl_6$: spindle-shaped laminæ, v. sl. sol. cold water.

Anhydride of the *methylo-hydroxide* $C_{10}H_{13}NO_2$ *i.e.* $C_6H_4<\begin{matrix}NMe_3\\CO\end{matrix}>O$. *Benzbetaïne.* Formed by allowing a mixture of *m*-amido-benzoic acid with MeOH (1 mol.), aqueous KOH (3 mols.), and MeI (3 mols.) to stand in the cold; the product, after freeing from MeOH by distillation, being saturated with HI, whereupon the iodide $NMe_3I.C_6H_4.CO_2H$ is ppd. This iodide is then boiled with water and lead hydroxide (Griess). Small deliquescent needles (containing aq), which give up their water of crystallisation at 105°. V. e. sol. cold alcohol, insol. ether. Tastes bitter and is neutral in reaction. Forms $(NMe_3Cl.C_6H_4.CO_2H)_2PtCl_6$ 4aq crystallising in large prisms, sl. sol. hot water.

Methylo-iodide $NMe_3I.C_6H_4.CO_2H$. Formed as above. Small short prisms (containing aq); sl. sol. cold water.

Methylo-chloride $NMe_3Cl.C_6H_4.CO_2H$.

Monoclinic crystals; $a:b:c = 1\cdot939:1:0\cdot876$; $\beta = 88° 49'$ (Zingel, *Z. K.* 10, 414).

Di-methyl-*p*-amido-benzoic acid $NMe_2.C_6H_4.CO_2H$. [235°]. Formed by boiling its chloride with water. Prepared by boiling for three hours a mixture of *p*-amido-benzoic acid (1 mol.), MeI (2 mols.), and aqueous KOH (3 mols.) dissolved in methyl alcohol (Michler, *B.* 9, 400). Obtained also by heating tetra-methyl-di-amido-benzophenone with soda-lime at 340°, extracting the product with hot water, and ppg. by acetic acid (E. Bischoff, *B.* 22, 341). Short needles (from alcohol); sol. aqueous KOH and HClAq, insol. dilute acetic acid. Nitrous acid forms $NMe_2.C_6H_3(NO).CO_2H$ [224°]. The Ca salt forms yellowish plates.

Methyl ether $NMe_2.C_6H_4.CO_2Me$. [102°]. Silvery plates (from alcohol); v. sol. benzene, ether, and chloroform, m. sol. dilute alcohol. Nitrous acid forms $NMe_2.C_6H_3(NO).CO_2Me\,6\frac{1}{2}aq$ [101°].

Chloride $NMe_2.C_6H_4.COCl$. Obtained by heating di-methyl-aniline with $COCl_2$ at 50° in a sealed tube (Michler). Crystalline.

Nitrile $NMe_2.C_6H_4.CN$. From di-methyl-*p*-phenylene-diamine by Sandmeyer's reaction (Ahrens, *B.* 20, 2958).

Anhydride of the *methylo-hydroxide* $C_{10}H_{13}NO_2$ *i.e.* $C_6H_4{<}\begin{smallmatrix}NMe_3\\CO\end{smallmatrix}{>}O$. [c. 255°]. When *p*-amido-benzoic acid is mixed with MeI, KOH, and methyl alcohol, there is formed, even in the cold, di-methyl-*p*-amido-benzoic acid and the iodide $NMe_3I.C_6H_4.CO_2H$ which crystallises in short yellow plates [233°] (Michael a. Wing, *Am.* 7, 195). The corresponding anhydride crystallises from alcohol in colourless plates (containing aq); v. sol. water. It loses its water of crystallisation at 100°. The periodide forms long dark prisms [200°]. The platinochloride $(NMe_3Cl.C_6H_4.CO_2H)_2PtCl_4$ forms large red prisms.

Tetra-methyl-di-amido-benzoic acid. *Di-methylo-di-hydroxide* $(HO.NMe_3)_2C_6H_3CO_2H$ [1:3:5]. The iodide $(INMe_3)_2C_6H_3.CO_2H$ aq is formed when di-amido-benzoic acid (1 pt.) is mixed with MeI (6 pts.), methyl alcohol (10 pts.), and twice as much of a concentrated solution of KOH as is required to neutralise the acid. The mixture should stand for some time, being kept alkaline by further additions of potash. The alcohol is then distilled off, and the iodide ppd. by HIAq (Griess, *B.* 7, 39). This iodide crystallises from hot water in six-sided tables or plates, v. sol. hot water. With moist Ag_2O it yields a caustic alkaline liquid which, on evaporation, leaves the hydroxide as a hygroscopic mass of soft white plates. It rapidly absorbs CO_2, and ppts. metallic oxides from their salts. The corresponding chloride $(NMe_3Cl)_2C_6H_3.CO_2H\,4aq$, obtained by neutralising the hydroxide by HCl, crystallises in small six-sided plates, v. sol. water, sl. sol. hot alcohol. The periodide forms brownish-yellow needles. The carbonate $CO{<}\begin{smallmatrix}O.NMe_3\\O.NMe_3\end{smallmatrix}{>}C_6H_3.CO_2H\,3aq$, obtained from the iodide and Ag_2CO_3, crystallises from water in very small soluble plates, having an alkaline reaction. The platinochloride $(ClNMe_3)_2C_6H_3.CO_2HPtCl_4aq$ is a pp. composed of very small pale-yellow plates, usually grouped in stars.

Derivative v. CHLORO-METHYL-AMIDO-BENZOIC ACID.

DI-METHYL-*p*-AMIDO-BENZOIC ALDEHYDE, $C_9H_{11}NO$ *i.e.* $NMe_2.C_6H_4.CHO$. [73°]. Formed, together with $CHCl_3$, by heating $NMe_2.C_6H_4.CH(OH).CCl_3$ with alcoholic KOH (Bössneck, *B.* 18, 1520; 19, 366). With di-methyl-aniline and hydrochloric acid it forms $(NMe_2.C_6H_4)_3CH$.

Oxim $NMe_2.C_6H_4.CH{:}NOH$. [144°]. Yellowish-brown plates (Knöfler a. Bössneck, *B.* 20, 3195).

Phenyl hydrazide $NMe_2.C_6H_4CH{:}N_2HPh$. [148°]. Needles (from alcohol).

DIMETHYL-AMIDO-BENZOPHENONE $C_6H_5.CO.C_6H_4.NMe_2$. *Benzodimethylaniline. Benzoyl-di-methyl-aniline. Benzoyl-phenyl-di-methyl-amine.* [90°]. Formed by heating the methylo-iodide to 181°. Formed also by heating malachite green $(NMe_2.C_6H_4)_2C(OH).C_6H_5$ with conc. HClAq at 180°. Colourless plates (from alcohol). Insol. water, sl. sol. cold alcohol, v. e. sol. hot alcohol or ether. It is a feeble base, its solution in concentrated acids being ppd. by water.

Methylo-iodide $C_6H_5.CO.C_6H_4.NMe_3I$. Large tables, sl. sol. cold water. Formed by heating *p*-amido-benzophenone with MeI at 100°. It decomposes at 181° (Doebner a. Weiss, *B.* 14, 1836; *A.* 210, 270; 217, 257).

Di-methyl-amido-benzophenone $C_6H_5.CO.C_6H_4NMe_2$. [39°]. (330°–340°). Obtained by heating benzoic acid with di-methyl-aniline and P_2O_5 at 185° (O. Fischer, *A.* 206, 88). Needles (from ligroïn). Forms unstable salts. With nitrous acid it yields the oily nitroso- derivative $C_6H_5.CO.C_6H_3(NO)NMe_2$ (E. Bischoff, *B.* 22, 340).

Di-methyl-di-*p*-amido-benzophenone. *Dibenzoyl derivative* $C_{29}H_{24}N_2O_3$ *i.e.* $(NMeBz.C_6H_4)_2CO$. [102°]. Formed by heating tetra-methyl-di-amido-benzophenone with BzCl at 190° (Nathansohn a. Müller, *B.* 22, 1877). Small light-brown plates, sl. sol. cold, v. sol. hot, alcohol; sl. sol. benzene, almost insol. water and ether. Acids and alkalis at 100° do not saponify it.

Tri-methyl-di-amido-benzophenone $NHMe.C_6H_4.CO.C_6H_4.NMe_2$. [156°]. Formed, together with di-methyl-aniline, by boiling penta-methyl-tri-amido-tri-phenyl-carbinol with HClAq (Wichelhaus, *B.* 19, 109). Nodular groups of needles (from alcohol).

Tetra-methyl-di-amido-benzophenone $NMe_2.C_6H_4.CO.C_6H_4.NMe_2$. [172°]. (above 360°) (Græbe, *B.* 20, 3262).

Formation.—1. By passing $COCl_2$ into di-methyl-aniline (Michler, *B.* 9, 716, 1900).—2. By boiling hexa-methyl-tri-amido-tri-phenol-carbinol with HClAq (Wichelhaus, *B.* 19, 109).—3. From $CCl_3.SO_2Cl$ and di-methyl-aniline (Michler a. Moro, *B.* 12, 1168).

Preparation.—By boiling auramine with aqueous HCl till decolourised, and ppg. with NH_3.

Properties.—White plates (from dilute alcohol); insol. water, m. sol. alcohol, v. e. sol. warm benzene, v. sl. sol. ether.

Reactions.—1. Heating with $ZnCl_2$ and

NH_4Cl at 160° produces auramine (Fehrmann, *B.* 20, 2844).—2. Boiling HNO_3 (S.G. 1·48) gives insoluble yellow crystals of tetra-nitro-di-methyl-di-nitramido-benzophenone and tri-nitro-phenyl-methyl-nitramine [127°], soluble in alcohol (Romburgh, *R. T. C.* 6, 367).—3. Excess of *bromine* added to a solution of the base in glacial acetic acid gives the tetra-bromo- derivative $(C_6H_2Br_2NMe_2)_2CO$ [172°] which crystallises in slender yellow needles from alcohol (Nathansohn a. Müller, *B.* 22, 1883).—4. Heating with *aniline hydrochloride* yields phenyl-auramine.—5. Combines with *tri-nitro-benzene* (2 mols.) forming a compound which crystallises in long reddish-violet needles [c. 100°]. With half the quantity of tri-nitro-benzene (1 mol.) it forms small deep-violet plates [123°].—6. Combines with *m-di-nitro- benzene* (2 mols.) forming a red crystalline compound.—7. *Nitrous acid* in the cold forms the nitroso- derivative $NMe_2.C_6H_4.CO.C_6H_2(NOH).NMe_2$ [159°] crystallising from alcohol in golden plates. This substance is a weak base, its solution in HClAq being ppd. by water. It gives Liebermann's reaction. Stannous chloride reduces it to the original tetra-methyl-di-amido-benzophenone. The nitroso- derivative forms the following salts: $B''H_2Cl_2$. Obtained by passing HCl into a solution of the nitroso- ketone in benzene.—$B''C_6H_2(NO_2)_3OH$. [152°]. Orange needles (from alcohol). The nitroso- ketone gives also a phenyl-hydrazide $C_{23}H_{25}N_5O_3$ [148°] (E. Bischoff, *B.* 21, 2452; 22, 337).—8. In presence of dehydrating agents, such as PCl_5 or $AlCl_3$, it condenses with *secondary* and *tertiary bases.* Thus with di-methyl-aniline it yields 'crystal violet' $C(OH)(C_6H_4NMe_2)_3$.

Salts.—$B''H_2Cl_2$: small radially-grouped prisms (from alcohol). Decomposed by water, with separation of the base (Fehrmann, *B.* 20, 2844).—$B''H_2PtCl_6$: yellow granules, insol. water, v. sl. sol. alcohol.—Picrate $B''C_6H_2(NO_2)_3OH$. [157°]. Small, purple, radially-grouped, prisms (from alcohol); insol. cold, v. sl. sol. hot, water; m. sol. alcohol.

Di-methyl-di-iodide $B''Me_2I_2$. [105°]. Light yellow plates (from alcohol), sl. sol. cold, v. sol. hot, water and alcohol. Split up at 150° into MeI and the base (Nathansohn a. Müller, *B.* 22, 1876).

Di-methylo-di-hydroxide $B''Me_2(OH)_2$. From the preceding and moist Ag_2O. Small yellow plates (from alcohol), quickly becoming dark and resinous (N. a. M.).

Oxim $HON:C(C_6H_4.NMe_2)_2$: [233°]; colourless crystals (Munchmeyer, *B.* 19, 1852; 20, 1852).

Phenyl-hydrazide $C_{22}H_{26}N_4$ *i.e.* $(NMe_2.C_6H_4)_2C:N_2HPh$. [175°]. Needles (from benzene-alcohol); m. sol. warm alcohol, v. sol. ether. Coloured green by acid oxidising agents (Ziegler, *B.* 20, 1111). Conc. H_2SO_4 gives a red colouration.

Imide $(NMe_2.C_6H_4)_2C:NH$. *Auramine base.* [136°]. Formed by heating tetra-methyl-di-amido-benzophenone with NH_4Cl and $ZnCl_2$ at 150° to 160°. Formed also by treating a solution of tetra-methyl-di-amido-benzophenone in CS_2 with PCl_3 and subsequently adding ammonia (Caro a. Kern) (*cf.* AURAMINE in THORPE'S DICTIONARY OF APPLIED CHEMISTRY). Lemon-yellow plates, insol. water and ether, m. sol. alcohol. Dilute HClAq readily converts it, even in the cold, into tetra-methyl-di-amido-benzophenone.

Reactions.—1. *Sodium-amalgam* reduces it (in alcoholic solution) to leucauramine $(C_6H_4NMe_2)_2CH.NH_2$ [135°]. This substance forms colourless crystals which when treated with HOAc yield an intense blue solution (Græbe, *B.* 20, 3265).—2. H_2S in alcoholic solution at 60° forms tetra-methyl-di-amido-thio-benzophenone [164°].—3. CS_2 also forms $(NMe_2.C_6H_4)_2CS$ together with thiocyanic acid (Fehrmann, *B.* 20, 2847).

Salts.—B'HCl aq. *Auramine.* Yellow six-sided tables (from water at 70°). After expulsion of the water it melts (G.) or decomposes (F.) at 267°. M. sol. cold water, m. sol. alcohol. Boiling water converts it into tetra-methyl-di-amido-benzophenone. Dyes wool and silk greenish-yellow. Cotton prepared with tannin is also dyed yellow by auramine.—$B'_2H_2PtCl_6$: granules, insol. water; sl. sol. alcohol.—B'HI. [268°]. Minute columns.—B'HSCy aq. [200°–210°].—$B'H_2C_2O_4$. [194°]. Orange needles, sl. sol. water, m. sol. warm alcohol.—$B'C_6H_2(NO_2)_3OH$. [230°–236°]. Plates, insol. cold, v. sl. sol. hot, water; m. sol. hot alcohol.

Phenyl-imide $(NMe_2.C_6H_4)_2C:NPh$. Formed by heating the hydrochloride of the imide (auramine) with aniline at 180° (F.). Small greyish-yellow radially grouped needles (from alcohol), decomposing at 80°. Insol. water and ether.—B'HCl: reddish-crystalline mass, sol. water and alcohol. Its aqueous solution gradually decomposes, yielding aniline and tetra-methyl-di-amido-benzophenone.—$B'_2H_2PtCl_6$.—$B'C_6H_2(NO_2)_3OH$.

p-Tolyl-imide $(NMe_2.C_6H_4)_2C:NC_6H_4Me$. Resembles the phenyl-imide.—$B'_2H_2PtCl_6$.

Ethylene-di-amide $C_{19}H_{26}N_4$ *i.e.* $(NMe_2.C_6H_4)_2C\left<\begin{matrix}NH.CH_2\\ |\\ NH.CH_2\end{matrix}\right.$. Formed by heating auramine (hydrochloride) with ethylene-diamine at 100°–110° (Fehrmann, *B.* 20, 2855). Yellowish plates (from alcohol), insol. water, m. sol. warm alcohol. On treatment with HOAc or dilute HClAq it decomposes into ethylene-diamine and $(NMe_2.C_6H_4)_2CO$. In alcoholic solution it is decomposed by H_2S into ethylene-diamine and $(NMe_2.C_6H_4)_2CS$.—$B''H_2Cl_2$: yellow needles.—$B''H_2PtCl_6$: amorphous flakes, insol. water and ether, v. sol. warm alcohol.—$B''2C_6H_2(NO_2)_3OH$: flakes, v. sl. sol. water, v. sol. alcohol.

Tolylene-di-amide $(NMe_2.C_6H_4)_2C\left<\begin{matrix}NH\\ NH\end{matrix}\right>C_6H_3Me$. Formed by heating the hydrochloride of the imide (auramine) with (1, 2, 4)-tolylene-diamine at 160°, and treating the product with ammonia. Small brown scales. In dilute acetic acid solution it dyes cotton, mordanted with tannin, reddish-brown. Dilute HClAq regenerates the original ketone.—$B''H_2PtCl_6$.—$B''2C_6H_2(NO_2)_3OH$.

Tetra-methyl-tri-amido-benzophenone $C_{17}H_{21}N_3O$ *i.e.* $NMe_2.C_6H_4.CO.C_6H_3(NH_2)(NMe_2)$. [82°]. Obtained by reducing nitro-tetra-methyl-di-amido-benzophenone (Nathansohn a. Müller, *B.* 22, 1884). Amorphous yellow powder, v. sol. hot, sl. sol. cold, alcohol and benzene, insol. ether.—$B'C_6H_2(NO_2)_3OH$: minute plates, v. sol.

hot alcohol, insoluble in benzene and ether.—$B'_2H_2PtCl_6$: light-red crystalline pp., v. sol. warm alcohol, sl. sol. benzene, insol. water and ether.

METHYL-α-AMIDO-n-BUTYRIC ACID $C_5H_{11}NO_2$ *i.e.* $CH_3.CH_2.CH(NHMe).CO_2H$. Formed by heating α-bromo-butyric acid with a concentrated solution of methylamine in sealed tubes at 100°. The product is boiled with baryta to expel NH_2Me, the Ba exactly ppd. by H_2SO_4, and the HBr by Ag_2CO_3 (Duvillier, *A. Ch.* [5] 20, 188; *C. R.* 88, 425). Glistening leaflets (from alcohol), subliming above 120° without fusion. V. e. sol. water, m. sol. hot alcohol, insol. ether. Has a sweet taste. Feebly acid in reaction. By the prolonged action (several months) of cyanamide (1 mol.) in concentrated and slightly ammoniacal solution it is converted into butyro-creatinine $CH_3.CH_2.CH{<}^{CO.NH}_{N(CH_3)}{>}C:NH$ which crystallises from alcohol in slender silky needles composed of small rectangular plates (Duvillier, *C. R.* 95, 456; *Bl.* [2] 39, 539).

Salts.—HA'HCl. [150°]. Badly defined crystals; sol. alcohol, insol. ether. Gives off HCl on fusion.—$H_2A'_2H_2PtCl_6$: orange-red crystals; v. sol. water and alcohol, insol. ether.—$H_2A'_2H_2PtCl_6 5aq$. Formed at 0°.—$HA'HAuCl_4aq$: transparent yellow prisms; sol. water, alcohol, and ether.—The nitrate and sulphate crystallise with difficulty in long needles.—$CuA'_2 2aq$: light-blue prisms; sol. alcohol.

Di-methyl-α-amido-butyric acid. *Anhydride* of the *methylo-hydroxide* $C_7H_{15}NO_2$ *i.e.* $\begin{array}{l}CH_3.CH_2.CH—CO\\ \quad\quad\quad\quad | \quad\quad |\\ \quad (CH_3)_3N — O\end{array}$. *Tri-methyl-α-amido-butyro-betaïne.* Prepared by the action of bromo-butyric ether on an excess of tri-methyl-amine in alcoholic solution (Duvillier, *C. R.* 104, 1520). Large transparent crystals, containing aq, which they lose at 120°, becoming opaque; v. sol. water and alcohol, insol. ether. Has a bitter taste.—B'HCl. Uncrystallisable.—$B'_2H_2PtCl_6$: orange prisms; sl. sol. alcohol. The aurochloride forms yellowish-white crystals.

METHYL-AMIDO-CAPROIC ACID *v.* METHYL-AMIDO-HEXOIC ACID.

METHYL-AMIDO-CHLORO- *v.* CHLORO-METHYL-AMIDO-.

METHYL-AMIDO-CYANURIC ACID *v.* CYANIC ACID.

METHYL-AMIDO-ETHANE SULPHONIC ACID $C_3H_9NSO_3$ *i.e.* $CH_3NH.CH_2CH_2.SO_3H$. *Methyl-taurine.* [242°].

Formation.—From methyl-ethylene-ψ-thio-urea and bromine-water (Gabriel, *B.* 22, 1148).

Preparation.—Silver chloro-ethane sulphonate is heated with 3 times its weight of a solution of methylamine, saturated at 0°, for 5 hours at 120°. The product is boiled with baryta to expel excess of methylamine, freed from excess of baryta by H_2SO_4, and evaporated to crystallisation. The crystals are washed with alcohol and recrystallised from water. The yield is 25 p.c. (E. Dittrich, *J. pr.* [2] 18, 68).

Properties.—Transparent triclinic crystals. Sol. water, insol. alcohol and ether. Its aqueous solution is acid to litmus. Crystallises unaltered from strong HCl. Does not form salts with acids and alkalis.

Reactions.—1. N_2O_3 forms isethionic acid, $(HO)CH_2.CH_2.SO_3H$.—2. With *cyanamide* it combines to methyl-taurocyamine or methyl-guanido-ethane sulphonic acid.

Di-methyl-amido-ethane sulphonic acid $NMe_2.CH_2.CH_2.SO_3H$. Formed by heating di-methylamine β-chloro-ethane sulphonate (20 g.) with aqueous (33 p.c.) dimethylamine (5 g.) at 160° for 10 hours (James, *J. pr.* [2] 31, 416; *C. J.* 47, 370). Large tables (from water); v. e. sol. water, insol. ether. Decomposes at 270°–280° without fusion. Does not combine with HCl.

Anhydride of the *methylo-hydroxide* ${<}^{CH_2.NMe_3}_{CH_2.SO_2}{>}O$. Formed by heating β-chloro-ethane sulphonic acid with aqueous tri-methyl-amine. Slender prisms (from water); v. sol. water, insol. alcohol and ether. Neutral in reaction. Tastes sweet. Not decomposed at 300°. Not acted upon by cyanamide. Baryta gives NMe_3 and isethionic acid (James, *C. J.* 49, 489).

DI-METHYL-AMIDO-ETHYL ALCOHOL *v.* DI-METHYL-OXYETHYL-AMINE.

DI-METHYL-AMIDO-ETHYL-BENZENE *v.* DI-METHYL-AMIDO-PHENYL-ETHANE.

METHYL-AMIDO-ETHYL KETONE $CH_3.CO.CH(NH_2).CH_3$. Perhaps formed by reducing methyl nitroso-ethyl ketone, but if so it quickly changes to *s*-tetra-METHYL-PYRAZINE.

METHYL-AMIDO-FORMIC ACID *v.* METHYL-CARBAMIC ACID.

METHYL-α-AMIDO-n-HEXOIC ACID $C_7H_{15}NO_2$ *i.e.* $CH_3.CH_2.CH_2.CH_2.CH(NHMe).CO_2H$. *Methyl-amido-caproic acid.* S. 10·2 at 11°. Formed by heating α-bromo-hexoic acid (1 mol.) with aqueous methylamine (2 or 3 mols.) at 100° for several hours (Duvillier, *C. R.* 90, 822; *A. Ch.* [5] 29, 165). Silky needles (from water) or pearly plates (from alcohol). Sl. sol. cold alcohol, insol. ether. Neutral in reaction. Volatilises above 100°. Does not reduce silver or mercurous nitrate. Gives with ferric chloride an intense red colouration and a yellowish-brown pp. An equivalent quantity of cyanamide in cold concentrated solution containing a few drops of NH_3 forms in a few weeks crystals of 'hexoic creatinine' $C_4H_9.CH{<}\begin{array}{l}NMe.C:NH\\ \quad\quad\quad |\\ CO.\ NH\end{array}$. Sl. sol. cold water, v. sol. alcohol (Duvillier, *C. R.* 96, 1583; *Bl.* [2] 40, 307).—HA'HCl: transparent plates; v. sol. water and alcohol, insol. ether.—$H_2A'_2H_2PtCl_6$: orange crystals; v. e. sol. water, v. sol. alcohol, v. sl. sol. ether.—The aurochloride forms golden needles; the sulphate forms very indistinct crystals.—$CuA'_2 2aq$: blue scales, S. 1.

Di-methyl-amido-hexoic acid. *Methylo-hydroxide* $HO.NMe_3.C_5H_{10}.CO_2H$. Formed by heating leucine (1 mol.) derived from caseïn with aqueous KOH (3 mols.), and MeI (3 mols.). The resulting $INMe_3.C_5H_{10}.CO_2K$, which crystallises from alcohol in needles, being decomposed by moist Ag_2O (Körner a. Menozzi, *G.* 13, 353). Strongly alkaline. Decomposes at 120°–130° into trimethylamine, an acid, $C_6H_{10}O_2$, and oxy-hexoic acid. Forms the platinochloride

$(ClNMe_3.C_5H_{10}.CO_2H)_2PtCl_4aq$, aurochloride $Cl_4AuNMe_3.C_5H_{10}.CO_2H$ [163°], and periodide. The periodide forms lustrous green crystals, decomposed by H_2S, yielding $INMe_3.C_5H_{10}.CO_2H$ [191°], crystallising in small prisms.

DI-METHYL-AMIDO-HYDROQUINONE $C_6H_3(NMe_2)(OH)_2$ [2:4:1]. *Di-methyl derivative* $C_6H_3(NMe_2)(OMe)_2$.

Methylo-iodide B'MeI. [202°]. Formed by heating the di-methyl derivative of amido-hydroquinone with methyl iodide (Bæssler, *B.* 17, 2122). White needles; v. sol. water, sl. sol. absolute alcohol, nearly insol. benzene, chloroform, and ligroine.

Methylo-hydroxide B'MeOH: soluble needles.

Methylo-chloride B'MeCl: white easily soluble needles [172°].—$(B'MeCl)_2PtCl_4$: yellow crystalline pp.

TRI-METHYL-AMIDO-IMIDO-IMIDO-DI-PHENYL SULPHIDE. *Methylo-chloride* $C_{16}H_{18}N_3SCl$ *i.e.* $N{<}^{C_6H_3(NMe_2)}_{C_6H_3}{>}S$, with NMe_2Cl linking N and C_6H_3. *Methylene-blue. Chloride of tetra-methyl-thionine.*

Formation.—1. By the action of H_2S on an acid solution of nitroso-di-methyl-aniline and oxidation of the resulting leuco-methylene-blue. In this reaction di-methyl-*p*-phenylene-diamine is an intermediate product (Caro, *E. P.* 1877, 3751; Koch, *B.* 12, 593; Bernthsen, *A.* 230, 137).—2. By dissolving nitroso-di-methyl-aniline in H_2SO_4 (S.G. 1·4), treating with sulphide of zinc, and oxidising the resulting leuco-methylene-blue (Oehler, *G. P.* 1882, 24,125; Mühlhäuser, *D. P. J.* 262, 371).—3. By oxidation of di-methyl-*p*-phenylene diamine in presence of $Na_2S_2O_3$, and further oxidation of the resulting $C_6H_3(NMe_2)(NH_2)S.SO_3H$ by chromic acid (Bernthsen).—4. By reducing the compound $C_6H_3(NMe_2)(NH_2)S.SO_3H$ to $C_6H_3(NMe_2)(NH_2)SH$ and oxidising a mixture of this mercaptan with di-methyl-aniline with HCl and $K_2Cr_2O_7$; the resulting 'soluble green' $C_{16}H_{19}N_3S$ or $N{<}^{C_6H_3(NMe_2)}_{C_6H_4.NMe_2}{>}S$ (N linked to C_6H_4) slowly changing in aqueous solution to methylene-blue (Bernthsen, *A.* 251, 10).

Properties.—Minute dark-blue laminæ (containing 3aq), v. sol. water and alcohol. Dyes mordanted cotton blue. Its aqueous solution is blue and not affected by HCl or ammonia. NaOH gives a violet colour and, when added in large quantity, a dirty violet pp. Conc. H_2SO_4 gives a yellowish-green solution, becoming blue on dilution. The aqueous solution is decolourised by H_2S or $Na_2S_2O_3$; the colour is restored even by feeble oxidising agents. Sodium hyposulphite $Na_2S_2O_4$ reduces it to the leuco-base. Fuming HClAq at 260° decomposes it, giving off H_2S. Boiling dilute HNO_3 oxidises it, forming H_2SO_4. Boiling aqueous KOH forms 'thionol,' the anhydride of di-oxy-imido-di-phenyl sulphide $N{<}^{C_6H_3(OH)}_{C_6H_3}{>}S$, with O linking N and C_6H_3.

Salt.—$(C_{16}H_{18}N_3SCl)_2ZnCl_2aq$.

Methylo-hydroxide $N{<}^{C_6H_3(NMe_2)}_{C_6H_3}{>}S$, with NMe_2OH linking N and C_6H_3. Formed by treating methylene-blue with moist Ag_2O. Amorphous, dark-blue mass; v. e. sol. water and alcohol, insol. ether.

Methylo-iodide $C_{16}H_{18}N_3SI$: bronzy needles (from hot water). The di-chloro-derivative of this iodide $C_{16}H_{16}Cl_2N_3SI$ is formed by successive treatment of di-chloro-di-methyl-*p*-phenylene-diamine $C_6H_2Cl_2(NMe_2)(NH_2)$ with H_2S, $FeCl_3$, and KI (Möhlau, *B.* 19, 2012).

TRI-METHYL-AMIDO-IMIDO-IMIDO-DI-PHENYL-SULPHONE. *Methylo-iodide* $C_{16}H_{18}N_3SO_2I$ *i.e.* $N{<}^{C_6H_3(NMe_2)}_{C_6H_3}{>}SO_2$, with NMe_2I linking N and C_6H_3. *Methylene-azure.* Formed, together with methylene violet, by boiling methylene blue with Ag_2O and a large quantity of water (Bernthsen, *A.* 230, 175). Slender needles with green lustre, sol. water, forming a violet solution from which it is ppd. by KI. Alkalis destroy the colour of the solution. The corresponding $C_{16}H_{18}N_3SO_2Cl$ crystallises in needles, v. e. sol. water. It dyes silk like methylene blue.

TETRA-METHYL-DI-AMIDO-IMIDO-DI-PHENYL METHANE *v. Imide of Tetra*-METHYL-DI-AMIDO-BENZOPHENONE.

METHYL-DI-AMIDO-IMIDO-DI-PHENYL SULPHIDE $C_{13}H_{13}N_3S$ *i.e.* $NMe{<}^{C_6H_3(NH_2)}_{C_6H_3(NH_2)}{>}S$. *Methyl-di-amido-thio-diphenylamine.* Formed by reduction of di-nitro-methyl-imido-di-phenyl sulphide with tin and HCl (Bernthsen, *A.* 230, 130). Insol. water, sol. ether. The dilute solution of its hydrochloride is coloured blue by $FeCl_3$.—$B''H_2Cl_2$. Needles, v. sol. water, almost insol. HClAq.

Tetra-methyl-di-amido-imido-di-phenyl sulphide $C_{16}H_{19}N_3S$ *i.e.* $NH{<}^{C_6H_3(NMe_2)}_{C_6H_3(NMe_2)}{>}S$. *Leuco-methylene blue.* Formed by treating methylene-blue with sodium hyposulphite $Na_2S_2O_4$ (Bernthsen, *A.* 230, 147). Needles (from alcohol), sl. sol. water, m. sol. cold alcohol. Gives an acetyl derivative, v. sol. alcohol, ether, and benzene. With MeI it forms $NMe{<}^{C_6H_3(NMe_3I)}_{C_6H_3(NMe_3I)}{>}S$ crystallising in plates, v. sl. sol. water and alcohol, insol. ether. Oxidised by air to methylene blue.—$B'H_2ZnCl_4$: prisms.

Di-methyl-amido-imido-phenyl disulphide *Methylo-chloride* $C_8H_9N_2S_2Cl$ *i.e.* $NMe_2Cl{<}^{C_6H_3}_{N-S}{>}S$ (C_6H_3 linked to N). *Methylene red.* A by-product in the manufacture of methylene-blue from di-methyl-*p*-phenylene-diamine and H_2S followed by $FeCl_3$ (Bernthsen, *A.* 230, 165; 251, 22; Koch, *B.* 12, 594). Small green glittering prisms (from alcohol), v. e. sol. water, insol. ether. Its aqueous and alcoholic solutions are purple. Not affected by HCl. Alkalis decompose it.—Zinc salt $(C_8H_9N_2S_2Cl)_2ZnCl_2aq$.

DI-METHYL-AMIDO-JUGLONE *v.* JUGLONE.

METHYL-AMIDO-MESITYLENE *v.* METHYL-MESIDINE.

METHYL-AMIDO-METHYL-BENZENES *v.* METHYL-PHENYL-METHYL-AMINES.

DI-METHYL-AMIDO-METHYL-PHENAZINE $C_6H_3(NMe_2)\langle\begin{smallmatrix}N\\|\\N\end{smallmatrix}\rangle C_6H_3Me$. Formed by elimination of the NH_2 group from 'tolylene-red' by means of nitrous acid and alcohol (Bernthsen a. Schweitzer, *B.* 19, 2605). Red greenish-glistening needles or flat prisms. Has basic properties. Dissolves in dilute acids with a violet colour, in conc. H_2SO_4 with a reddish-brown, which on dilution first becomes green, then blue, and finally violet. Soluble in ether with a yellowish-red colour and yellow fluorescence. Sublimable.

Di-methyl-di-amido-methyl-phenazine $C_{15}H_{16}N_4$ *i.e.* $C_6H_3(NMe_2)\langle\begin{smallmatrix}N\\|\\N\end{smallmatrix}\rangle C_6H_2Me(NH_2)$. *Tolylene-red.* Formed by oxidation of nitroso-or amido-dimethyl-aniline together with tolylene-*m*-diamine. The leuco- base has the formula $C_6H_3(NMe_2)\langle\begin{smallmatrix}NH\\NH\end{smallmatrix}\rangle C_6H_2Me(NH_2)$ (Bernthsen a. Schweitzer, *B.* 19, 2604).

DI-METHYL-AMIDO-METHYL-QUINOLINE TETRAHYDRIDE. *Di-methylo-di-iodide* $C_9H_9MeN.NMe_2Me_2I_2$. [171°]. Formed by heating (*Py.* 1)-amido-quinoline tetrahydride with methyl alcohol and MeI (Ziegler, *B.* 21, 862). Crystals.

METHYL-AMIDO-METHYL-THIAZOLE $C_5H_8N_2S$ *i.e.* $\begin{matrix}S.C(NHMe)\\|\\CH{=\!=}CMe\end{matrix}\rangle N$. *Methyl-thiazyl-amine.* [42°]. Formed by the action of chloro-acetone on methyl-thio-urea (Traumann, *A.* 249, 44). Crystalline but extremely hygroscopic, m. sol. ether. Strongly alkaline in reaction. When heated with HClAq in a sealed tube it yields methylamine. Br completely decomposes it.

Salts.—B'HI: small white needles; melts, when anhydrous, at 136° (T.).—Platinochloride: orange-yellow plates [167°].

Acetyl derivative $C_5H_7AcN_2S$. [110°]. White needles.

Methyl-amido-methyl-thiazole $\begin{matrix}S.C(NH)\\|\\CH{:}CMe\end{matrix}\rangle NMe$. *Imido-di-methyl-thiazole.* [47·5°]. Formed from chloro-acetone by treatment with ammonium sulpho-cyanide (Tcherniak a. Norton, *B.* 16, 345) and heating with MeI the resulting amido-methyl-thiazole (so-called propinine sulphocyanide) (Hantzsch a. Weber, *B.* 20, 3122, 3336). Crystalline, but very hygroscopic. Strongly alkaline. When heated with HClAq in sealed tubes it yields ammonia. Conc. KOHAq has no action.

Salts.—B'HIaq. Tables [164°].—Platinochloride: orange tables [193°].

Acetyl derivative $C_5H_7AcN_2S$. [113°]. White needles (containing 6 aq).

Di-methyl-amido-methyl-thiazole $C_6H_{10}N_2S$ *i.e.* $\begin{matrix}S\,.\,C(NMe)\\|\\CH{=\!=}CMe\end{matrix}\rangle NMe$. *Methyl-imido-dimethyl-thiazole.* [96°]. Formed by adding conc. KOHAq to its hydro-iodide (Hantzsch a. Weber, *B.* 20, 3123). White needles, sol. alcohol, water, and ether. Bromine reacts with formation of $C_3MeBr(NMe_2)SN$ [114°].

Salts.—B'HIaq. [54°]. From MeI and $C_3MeH(NHMe)SN$. Melts at 155° when anhydrous.

Methylo-iodide B'MeI. [85°]. White needles, v. e. sol. water and alcohol.

DI-METHYL-AMIDO-NAPHTHOIC ACID $C_{10}H_6(NMe_2)(CO_2H)$ [1:4]. [165°]. Formed by heating di-methyl-(α)-naphthylamine with $COCl_2$ at 70° for 4 hours (Friedländer, *B.* 21, 3126). Needles (from dilute alcohol), sol. dilute acids and alkalis. When acted upon by diazo- compounds the azo- group displaces the CO_2H.—$(HA')_2H_2PtCl_6$: yellow needles.

DI-METHYL-AMIDO-NAPHTHO-PHENAZINE $C_{10}H_6\langle\begin{smallmatrix}N\\|\\N\end{smallmatrix}\rangle C_6H_3.NMe_2$. *Di-methyl-naphth-eurhodine.* [205°]. Formed from nitroso-di-methyl-aniline hydrochloride, (β)-naphthyl-amine, and AcHO (Witt, *B.* 21, 720). Rhombic tables (from toluene or xylene), red by transmitted, and red or green, according to the faces, by reflected light; sol. alcohol, ether, and benzene, forming yellow solutions with yellow fluorescence. Is volatile with slight decomposition, and sublimes readily in woolly flocks. The violet-red solution in conc. H_2SO_4 becomes successively black, green, grey, and blue-violet on dilution. The salts crystallise readily, have a bronzy lustre, and are dissociated by water. AcHO dissolves it with red-violet colour. Conc. HNO_3 with violet, soon becoming bright yellow and depositing the nitro- compound.

METHYL-AMIDO-NAPHTHOQUINONE $C_{11}H_9NO_2$ *i.e.* $C_{10}H_5O_2(NHMe)$. [232°]. Formed by adding a solution of methylamine acetate to an alcoholic solution of (α)-naphthoquinone, evaporating nearly to dryness, adding water, and crystallising the pp. from alcohol (Plimpton, *C. J.* 37, 639). Glittering red needles, v. sol. alcohol. Aqueous SO_2 at 150° forms an unstable colourless reduction-product.

Di-methyl-amido-naphthoquinone $C_{10}H_5O_2(NMe_2)$. [118°]. From (α)-naphthoquinone and di-methyl-amine in alcoholic solution (Plimpton). Red needles.

DI-METHYL-AMIDO-NAPHTHYLAMINE *v.* NAPHTHYLENE-DI-METHYL-DIAMINE.

TETRA-METHYL-DI-AMIDO-DI-NAPHTHYL-PHENYL-METHANE $Ph.CH(C_{10}H_6NMe_2)_2$. [189°]. Formed by the action of benzoic aldehyde on di-methyl-(α)-naphthylamine in presence of $ZnCl_2$ (Friedländer, *B.* 21, 3128). Colourless crystals, v. sol. HOAc, benzene, CS_2, and dilute mineral acids, sl. sol. alcohol, ether. Does not yield a colour on oxidation.

Hexa-methyl-tri-amido-di-naphthyl-phenyl-methane $HC(C_{10}H_6NMe_2)_2C_6H_4NMe_2$. [179°]. Formed by condensing di-methyl-*p*-amido-benzoic aldehyde with di-methyl-(α)-naphthylamine in presence of $ZnCl_2$ (Friedländer, *B.* 21, 3129). White needles. Does not yield a colour on oxidation.

METHYL-AMIDO-NITRO- compounds *v.* NITRO-METHYL-AMIDO- compounds.

METHYL-AMIDO-OXY- compounds *v.* OXY-METHYL-AMIDO- compounds.

METHYL-AMIDO-PEREZONE *v.* METHYL-AMIDO-PIPITZAHOIC ACID.

METHYL-o-AMIDO-PHENOL. *Methyl derivative* $C_8H_{11}NO$ *i.e.* $C_6H_4(NHMe)(OMe)$ [1:2]. *Methyl anisidine.* (219°). Formed by mixing the methyl derivative of o-amido-phenol with MeI at 0° (Mühlhäuser, *A.* 207, 247). Oil.—$B'_2H_2PtCl_6$: short yellow prisms, m. sol. water.

Methyl-*p*-amido-phenol. *Ethyl derivative* $C_9H_{13}NO$ *i.e.* $C_6H_4(NHMe)(OEt)$ [1:4]. (251°). Formed by heating the ethyl derivative of *p*-oxy-phenyl-amido-acetic acid at 260° (Bischoff a. Nastvogel, *B.* 22, 1789). Sl. sol. water, v. sol. alcohol and ether.—B'HCl: needles.

Di-methyl-o-amido-phenol $C_8H_{11}NO$ *i.e.* $C_6H_4(NMe_2)(OH)$ [1:2]. [45°]. Obtained, together with MeCl, by the dry distillation of the methylo-chloride (Griess, *B.* 13, 248). Small white prisms, v. sl. sol. hot water, v. sol. alcohol, ether, HOAc, and aqueous KOH. $FeCl_3$ gives a reddish-violet colour. Its hydrochloride is gummy.

Methylo-hydroxide $C_6H_4(NMe_3OH)(OH)$ or $C_6H_4<\begin{matrix}O\\|\\NMe_3\end{matrix}$ aq. Prepared by the action of MeI and KOH on a solution of *o*-amido-phenol in methyl alcohol (Griess, *B.* 13, 246). Prisms, which become $C_6H_4<\begin{matrix}O\\|\\NMe_3\end{matrix}$ at 105°. V. sol. water and alcohol, insol. ether. Has an intensely bitter taste. On distillation it is converted into $C_6H_4(NMe_2)(OMe)$. With acids it forms the following salts:—$C_6H_4(NMe_3I)(OH)$ aq: white soluble prisms. Its solution, neutralised by ammonia, deposits sparingly soluble needles or prisms of $C_6H_4(NMe_3I)(OH)C_6H_4<\begin{matrix}O\\|\\NMe_3\end{matrix}$.—$C_6H_4(NMe_3Cl)(OH)$ 2aq: long soluble prisms.—$(C_6H_4(NMe_3Cl).OH)_2PtCl_4$: yellowish-red needles, sl. sol. cold water.—The periodide forms brown insoluble leaflets.—The nitroprusside $(C_9H_{13}NO)_2H_2FeCy_5NO$ forms crystals, sl. sol. cold water.

Methyl-derivative $C_9H_{13}NO$ *i.e.* $C_6H_4(NMe_2)(OMe)$ [1:2]. (211°). S.G. $\frac{23}{}$ 1·016. Formed by an isomeric change by distilling $C_6H_4<\begin{matrix}O\\|\\NMe_3\end{matrix}$ (Griess, *B.* 13, 248). Formed also from MeI and the methyl derivative of *o*-amido-phenol (Mühlhäuser, *A.* 207, 248). Colourless liquid, with burning taste.—$B'_2H_2PtCl_6$: sparingly soluble golden-yellow prisms.

Methylo-iodide of the *methyl derivative* $C_6H_4(NMe_3I)(OMe)$. From the preceding and MeI. Long white needles (G.) or tables (M.), sol. hot water and hot alcohol. With moist Ag_2O it yields a strongly alkaline hydroxide. It also yields a platinochloride $(C_6H_4(NMe_3Cl).OMe)_2PtCl_4$, which crystallises in sparingly soluble yellow plates or tables.

Di-methyl-*m*-amido-phenol. $C_6H_4(OH)NMe_2$ Prepared by fusing di-methyl-amido-benzene *m*-sulphonic acid with KOH. Also by heating resorcin with di-methyl-amine under pressure.

Ethyl ether $C_6H_4(OEt)(NMe_2)$ [1:3]. (247°). Obtained by boiling a solution of *m*-amido-phenetol and methyl iodide and slowly running in the calculated quantity of potash. The base is distilled over with steam (P. Wagner, *J. pr.* [2] 32, 77; Baur a. Stadel, *B.* 16, 32). Converted by HCl and amyl nitrite into the nitroso- compound $C_6H_3(NO)(OEt)(NMe_2)$.

Di-methyl-*p*-amido-phenol. *Methylo-hydroxide.* The anhydride $C_6H_4<\begin{matrix}O\\|\\NMe_3\end{matrix}$ is formed by the action of MeI and conc. KOHAq upon *p*-amido-phenol in the cold (Griess, *B.* 13, 250). Prisms or plates. Changes on distillation into the isomeric $C_6H_4(NMe_2)(OMe)$ [48°].

Methyl derivative $C_6H_4(NMe_2)(OMe)$ [1:4]. [48°]. Formed as above (Griess, *B.* 13, 249). Prisms or plates (from alcohol).

Methylo-iodide $C_6H_4(NMe_3I)(OMe)$. Formed by the action of MeI on either the methyl derivativo or the methylo-hydroxide. Tables or plates. With moist Ag_2O it yields the methylo-hydroxide as a strongly alkaline mass. The platinochloride $(C_6H_4(NMe_3Cl).OMe)_2PtCl_4$ forms small yellow prisms, sl. sol. water.

Di-methyl-di-amido-phenol. *Anhydride* of the *methylo-hydroxide* $C_9H_{14}N_2O$ *i.e.* $C_6H_3(NH_2)<\begin{matrix}O\\|\\NMe_3\end{matrix}$ $\left[4:\frac{1}{2}\right]$. Prepared by reduction of the methylo-hydroxide of nitro-di-methyl-amido-phenol with tin and HCl (Griess, *B.* 13, 648).—$B''H_2Cl_2$ 4aq: very soluble white plates.—$B''H_2PtCl_6$ 2aq: small prisms, sl. sol. water.

TETRA-METHYL-DI-*p*-AMIDO-DIPHENYL $NMe_2.C_6H_4.C_6H_4.NMe_2$. *Tetra-methyl-benzidine.* [195°]. (above 360°).

Formation.—1. By heating di-methyl-aniline (1 pt.) with H_2SO_4 (4 pts.) at 200°. Formed also in small quantity by oxidising di-methyl-aniline by boiling with PbO_2 and dilute H_2SO_4 (Michler a. Pattinson, *B.* 14, 2161; 17, 115).—2. By heating di-methyl-aniline with $AlCl_3$ in presence of air (Giraud, *Bl.* [3] 1, 692).—3. By methylation of benzidine.

Properties.—Colourless needles; sol. hot, sl. sol. cold, alcohol. Not volatile with steam. Gives a green colouration with $FeCl_3$ or CrO_3.—$B''H_2Cl_2$: sparingly soluble needles.—$B''H_2Br_2$: needles.—$B''H_2I_2$: white needles.—$B''H_2PtCl_6$.

Methylo-iodide B″MeI. [263°]. Needles, sl. sol. water and alcohol. Loses MeI when distilled with soda-lime.

Methylo-chloride B″MeCl. [228°]. Crystals, very solublo in water and alcohol.—$B''MeClHPtCl_6$: yellow pp.

Tetra-methyl-*op*-di-amido-diphenyl [2:1] $NMe_2.C_6H_4.C_6H_4.NMe_2$ [1:4]. *Tetra-methyl-diphenyline.* [52°]. (333°–345°). Formed by heating diphenyline hydrochloride with MeOH in sealed tubes at 180° (Reuland, *B.* 22, 3015). Prisms. Gives with platinic chloride an unstable pp. Chloranil produces a blue colouration.—$B''C_6H_2(NO_2)_3OH$. [200°]. Red needles.

Methylo-iodide B″MeI. [184°]. Needles, v. sol. water, alcohol, and ether.

Di-methylo-di-iodide $B''Me_2I_2$. [196°]. Crystalline, v. sol. water and alcohol.

Tetra-methyl-tetra-amido-diphenyl $NMe_2.C_6H_3(NH_2).C_6H_3(NH_2).NMe_2$. *Tetra-methyl-benzidine.* [168°]. Prepared by reduction of di-

nitro-tetra-methyl-diphenyl (Michler a. Pattinson, *B.* 14, 2165; 17, 118). White silvery plates, v. sol. hot alcohol, sl. sol. cold alcohol, insol. water. $FeCl_3$ gives a violet colouration. $K_2Cr_2O_7$ and H_2SO_4 produce a brownish-red colour.—$B''H_2Cl_2$ (dried at 110°): sparingly soluble colourless needles.—$B''H_2I_2$: sparingly soluble needles.—$B''H_2PtCl_6$: yellow pp.

Methyl-α-amido-phenyl-acetic acid $C_9H_{11}NO_2$ *i.e.* $C_6H_5.CH(NHMe).CO_2H$. Formed from the nitrile of mandelic acid $C_6H_5.CH(OH).CN$ by digesting with alcoholic NH_2Me at 70°, and decomposing the resulting nitrile with HCl (Tiemann a. Piest, *B.* 14, 1982). Slender needles (from hot water). Sublimes at 274°. Sl. sol. cold water, insol. alcohol and ether.

Amide $C_6H_5.CH(NHMe).CO.NH_2$. [155°]. Slender needles.—B'HCl. Needles, sol. alcohol, insol. ether.

DI-METHYL-AMIDO-PHENYL-ω-AMIDO-CRESOL. *Methyl derivative* [4:1] $NMe_2.C_6H_4.NH.CH_2.C_6H_4.OMe$ [1:4]. [104°]. Formed by reducing $NMe_2.C_6H_4.N:CH.C_6H_4.OMe$ with sodium (Steinhart, *A.* 241, 343). Light green plates; v. sol. acids, forming red solutions. Its alcoholic solution decomposes rapidly.

DI-METHYL-AMIDO-DI-PHENYL-AMINE $Me_2N.C_6H_4.NHPh$. [130°]. One of the products formed by the action of phenyl-hydrazine on nitroso-dimethylamine in an alcoholic solution (O. Fischer, *B.* 21, 2612). White needles (from petroleum-ether), v. sol. dilute HCl, m. sol. dilute SO_4H_2. Gives a blue colouration with $FeCl_3$. Dissolves with a red colour in nitric acid.

Nitrosamine $C_{14}H_{15}N_3O$. [116°]. Yellow needles (from alcohol).

Tetra-methyl-di-amido-diphenyl-amine $(NMe_2.C_6H_4)_2NH$. [119°]. Obtained by oxidising a mixture of di-methyl-aniline (1 mol.) and di-methyl-*p*-phenylene-diamine (1 mol.) and reducing the resulting 'dimethyl-phenylene green' (Bindscheidler, *B.* 16, 864). Yellowish dimetric tables.

Hexa-methyl-tri-amido-triphenylamine. *Tri-methylo-trichloride* $(NMe_3Cl.C_6H_4)_3N$. Obtained by heating tri-amido-tri-phenyl-amine hydrochloride with MeOH at 190° (Heydrich, *B.* 19, 758). White needles.—$(NMe_3Cl.C_6H_4)_3N\ 3PtCl_4$.

DI-METHYL-AMIDO-PHENYL-BENZYL-AMINE $NMe_2.C_6H_4.NH.CH_2Ph$. [48°]. Obtained by reducing benzylidene-di-methyl-phenylene-diamine [101°] with sodium-amalgam (Kohler, *A.* 241, 361). Yellowish plates, v. sol. dilute mineral acids, alcohol, ether, benzene, and petroleum ether.

Nitrosamine $NMe_2.C_6H_4.N(NO).CH_2Ph$. [128°]. Slender yellow needles, sol. alcohol.

DI-METHYL-AMIDO-DI-PHENYL-CARBINOL $NMe_2.C_6H_4.CH(OH).C_6H_5$. *Di-methyl-amido-di-phenyl-carbinol.* [70°]. Formed by reducing di-methyl-amido-benzophenone with sodium-amalgam, or by the action of benzoic aldehyde on di-methyl-aniline (Albrecht, *B.* 21, 3292). Thin white needles, insol. water, v. e. sol. ordinary solvents, sl. sol. petroleum ether.

Di-methyl-di-amido-di-phenyl-carbinol $NMe_2.C_6H_4.CH(OH).C_6H_4.NH_2$. [165°]. Formed by carefully reducing *p*-nitro-di-methyl-amido-di-phenyl-carbinol with zinc-dust and HCl (Albrecht, *B.* 21, 3295). Dissolves in HOAc with blue colouration. Crystallises from benzene in needles containing benzene and melting at 142°. Gives off water (1 mol.) when heated above its melting-point. Boiling with zinc-dust and HCl reduces it to di-methyl-diamido-di-phenyl-methane [93°].

Tetra-methyl-di-amido-di-phenyl-carbinol $C_{17}H_{22}N_2O$ *i.e.* $(NMe_2.C_6H_4)_2CH(OH)$. [96°]. Obtained by reducing tetra-methyl-di-amido-benzophenone in hot alcoholic solution with sodium-amalgam (Michler a. Dupertuis, *B.* 9, 1899; Nathansohn a. Müller, *B.* 22, 1879). Colourless triclinic prisms, v. sol. alcohol, HOAc, benzene, and ether. Its solution in HOAc is blue, the benzene solution is colourless.

Salts.—B''HCl. Formed by passing HCl into a solution of the base in ether. Small colourless slender radially grouped needles. In air it turns blue and deliquesces. It is dissociated by water.—$B''H_2PtCl_6$: minute yellow needles, v. sol. hot alcohol.—$B''C_6H_2(NO_2)_3OH$: dark-green crystalline mass, v. sol. hot alcohol, sl. sol. benzene, insol. ether.

Di-methylo-di-iodide $B''Me_2I_2$. [195°]. Small plates (from alcohol), sl. sol. cold, v. sol. hot, alcohol and water, insol. benzene and ether.

Tetra-methyl-di-amido-tri-phenyl-carbinol $C_{23}H_{26}N_2O$ *i.e.* $C_6H_5.C(OH)(C_6H_4NMe_2)_2$. [132°]. *Malachite green. Benzaldehyde green.*

Formation.—1. By the action of dimethyl-aniline on benzotrichloride in presence of a metallic chloride (Doebner, *B.* 11, 1238; 13, 2222).—2. By the oxidation of a slightly acid solution of tetra-methyl-di-amido-tri-phenyl-methane with MnO_2 or PbO_2 (E. a. O. Fischer, *B.* 12, 796), or with tetra-chloro-quinone (O. Fischer, *A.* 206, 130).—3. By heating di-methyl-aniline (4 pts.) with BzCl (2 pts.) and $ZnCl_2$ (3 pts.) (Fischer).

Preparation.—1. From di-methyl-aniline (2 mols.), $ZnCl_2$ (half its weight), sand, and benzo-trichloride at 100°. The product is distilled with steam and the dye ppd. from the aqueous residue by NaCl. The pp. is the zinc double chloride, which may be converted by KOH into the base. This is converted into the oxalate which may be purified by crystallisation from water and then decomposed by ammonia (Doebner, *A.* 217, 250)—2. By heating benzoic aldehyde (40 g.) with dimethylaniline (100 g.) and 93 p.c. alcohol (40 g.) over a water-bath. $POCl_3$ (65 g.) is then added gradually, and when cool the mass is extracted with warm water and the base ppd. with NaOH. The yield is nearly theoretical (Nencki, *M.* 9, 1148).—3. By heating benzoic aldehyde with $ZnCl_2$ and di-methyl-aniline, and oxidising the resulting leuco- base with PbO_2 (Mühlhäuser, *D. P. J.* 263, 249).

Properties.—Nearly colourless cubes. Insol. water. V. sol. alcohol forming a green solution. When freshly ppd. it is v. sol. ether, but when crystalline it is sl. sol. ether; m. sol. CS_2, acetone, benzene or light petroleum.

Reactions.—1. HClAq at 250° splits it into dimethylaniline and di-methyl-*p*-amido-benzophenone.—2. On *reduction* it yields leuco-malachite green (tetra-methyl-di-amido-tri-phenyl-methane) [101°].—3. Fuming HNO_3 in HOAc forms an amorphous hexa-nitro-derivative.

Salts.—The salts of organic acids and

neutral salts of mineral acids are green and dye emerald-green. They are v. sol. water, the oxalate being m. sol. water and the picrate sl. sol. water. Concentrated mineral acids turn the solutions orange, forming acid salts. Diluting with water restores the green colour. In the cold, dilute acids dissolve the base, forming a nearly colourless solution, which turns deep green when heated, a molecule of water being probably split off. Thus the hydrochloride becomes $C_6H_5.C<^{C_6H_4NMe_2}_{C_6H_4NMe_2Cl}$.—

$(C_{23}H_{24}N_2HCl)_3(ZnCl_2)_22aq$. [c. 130°]. *Malachite green.* Thick, dark-green prisms, sol. water (Fischer, *B.* 14, 2520).—$C_{23}H_{24}N_2ZnCl_2aq$.—$C_{23}H_{24}N_2H_2SO_4$.—$C_{23}H_{24}N_2H_2SO_4aq$: lustrous green prisms.—$(C_{23}H_{24}N_2)_23H_2C_2O_4$. *Malachite green.* Large green tables, sol. water and alcohol. — Picrates $C_{23}H_{24}N_2C_6H_2(NO_2)_3OH$. Golden needles (from benzene), insol. water.—$C_{23}H_{24}N_22C_6H_2(NO_2)_3OH$: golden needles.

Di-methylo-di-iodide $C_{23}H_{24}N_2Me_2I_2aq$. [172°]. Formed by heating the base with MeI and MeOH at 100° (Doebner). Green plates, sl. sol. alcohol, ether, benzene, CS_2, and cold water, v. sol. hot water. The same compound is obtained by heating di-*p*-amido-tri-phenyl-carbinol with MeI and alcohol at 120° (Doebner, *B.* 15, 236).

Ethyl derivative $C_6H_5.C(OEt)(C_6H_4NMe_2)_2$. [162°]. From the base by heating with alcohol at 110° (O. Fischer, *B.* 12, 1686).

Sulphonic acid $C_{23}H_{25}(SO_3H)N_2O$. Green needles with reddish-brown lustre, v. e. sol. hot water, forming a green solution. — NaA′. — MgA'_2 4aq.—CaA'_2 3aq.

Derivatives v. Bromo-, Chloro-, Nitro-, and Oxy-tetra-methyl-di-amido-tri-phenyl-carbinol.

Tetra-methyl-*ppo*-tri-amido-tri-phenyl-carbinol $C_{23}H_{27}N_3O$ *i.e.* $NH_2.C_6H_4.C(OH)(C_6H_4NMe_2)_2$. [191°]. Formed by oxidation of the acetyl derivative of the leuco-base (tetra-methyl-di-*p*-amido-*o*-amido-tri-phenyl-methane) with lead peroxide and dilute H_2SO_4 (Fischer a. Schmidt, *B.* 17, 1892). Glistening prisms (from ether). The salts are soluble in water with a bluish-green colour.

Tetra-methyl-tri-*p*-amido-tri-phenyl-carbinol $NH_2.C_6H_4.CH(OH)(C_6H_4NMe_2)_2$. *Tetra-methyl-pararosaniline.* Obtained by oxidising the acetyl derivative of tetra-methyl-tri-*p*-amido-tri-phenyl-methane with PbO_2, and boiling the resulting acetyl derivative with HCl (O. Fischer a. G. Körner, *B.* 16, 2904). Small crystals (from ether).

Penta-methyl-tri-amido-tri-phenyl-carbinol $C_{24}H_{29}N_3O$ *i.e.* $(NMe_2.C_6H_4)_2C(OH).C_6H_4NHMe$. *Methyl-violet.* [130°]. Prepared by oxidising dimethylaniline with $SnCl_4$, with ICl, with $HgCl_2$ and $KClO_3$, with $KClO_3$ and $CuSO_4$, or with NaCl and $Cu(NO_3)_2$ (Lauth, *Rép. Chim. app.* 1861, 345; Poirrier a. Chappat, *Bl.* [2] 6, 502; Hofmann, *B.* 6, 357). Formed also by heating dimethylaniline with $C_6H_5SO_2Cl$ at 100° (Hassencamp, *B.* 12, 1275), and, together with formic aldehyde, by shaking hexa-methyl-tri-amido-tri-phenyl-carbinol with MnO_2 and dilute H_2SO_4 (E. a. O. Fischer, *B.* 11, 2097). Commercial methyl-violet may be freed from admixed hexa-methyl-tri-amido-tri-phenyl-carbinol by boiling with ligroïn (Wichelhaus, *B.* 16, 2006; 19, 108). Methyl-violet occurs in Hofmann's violet.

Properties.—Brown powder, melting under water. Insol. water, ether, and ligroïn. Its alcoholic solution is violet. Its solution in HCl is reddish-violet, and is ppd. by NaOH, but not by ammonia. Reduced by ammonium sulphide to its leuco- base. Tin and HCl reduce it, forming a substance melting at 155°. Boiling HClAq splits it up into di-methyl-aniline and tri-methyl-di-amido-benzophenone.

Salts.—Chloride $C_{24}H_{28}N_3Cl$ *i.e.* $(NMe_2.C_6H_4)_2C.C_6H_4.NMeHCl$. Amorphous mass, with green metallic lustre. Its aqueous solution is violet, but on adding HCl it becomes first green, then deep yellowish-brown. It dissolves in alcohol. Conc. H_2SO_4 forms a yellow solution, which on dilution changes through greenish-blue to violet. It dyes silk, wool, and mordanted cotton violet.—$C_{24}H_{28}N_3I$: minute needles.

Picrate $C_{24}H_{27}N_3C_6H_2(NO_2)_3(OH)$. Bronzed needles (from alcohol).

Acetyl derivative. Acetate $(NMe_2.C_6H_4)_2C.C_6H_4.NMeAc.OAc$. [225°]. From methyl-violet, Ac_2O, and NaOAc (O. Fischer a. G. Körner, *B.* 16, 2905).

Hexa-methyl-tri-amido-tri-phenyl-carbinol $C_{25}H_{31}N_3O$ *i.e.* $(NMe_2.C_6H_4)_3COH$. *Crystal violet. Hexa-methyl-para-rosaniline.* [195°].

Formation.—1. Together with its methylo-iodide, by heating methyl-violet with MeI and MeOH at 120° (Hofmann, *B.* 6, 363).—2. By the action of dimethylaniline on tetra-methyl-di-amido-benzophenone in presence of dehydrating agents (Kern a. Caro). In this reaction tetra-methyl-di-amido-thio-benzophenone may also be used.—3. By the action of $COCl_2$, of $ClCO_2Et$, or of $ClCO_2CCl_3$, in presence of $ZnCl_2$ on dimethylaniline.—4. By condensation of tetra-methyl-di-amido-di-phenyl carbinol with dimethylaniline and oxidation of the resulting leuco-base.—5. By gradually adding tetra-chloro-quinone (1 pt.) to dimethylaniline (2 pts.), and heating the product to 65° (Meister, Lucius, a. Brüning, *B.* 13, 212, 2100; Wichelhaus, *B.* 16, 2005). Perhaps the substance formed in this case is wholly or partially the penta-methyl compound.—6. By the action of $COCl_2$ or of $ClCO_2Et$ on dimethylaniline in presence of $AlCl_3$ (Hofmann, *B.* 18, 767; Wichelhaus, *B.* 19, 109).

Properties.—Dark reddish-violet monoclinic tables. Needles containing benzene (from benzene). Insol. water, sol. ether, acetone, and ligroïn, sl. sol. alcohol, v. e. sol. chloroform and benzene. Boiling HClAq splits it up into dimethylaniline and tetra-methyl-di-amido-benzophenone. Aqueous ammonium sulphide reduces it to hexa-methyl-tri-amido-tri-phenyl-methane.

Salts.—Chloride $C_{25}H_{30}N_3Cl$ *i.e.* $(NMe_2.C_6H_4)_2C<^{C_6H_4}_{NMe_2Cl}>$. Hexagonal crystals, with greenish-brown lustre (Wada, *B.* 18, 768. Sol. alcohol. Forms a violet solution in water, which on adding HCl becomes first blue, then green, and finally yellow. NaOH gives a violet pp. Conc. H_2SO_4 forms a yellow solution,

changed on dilution through green and blue to violet. Dyes silk, wool, and mordanted cotton bluish-violet.—$C_{25}H_{30}N_3Cl$ 8aq: crystals, with bronze lustre.—$(C_{25}H_{30}N_3Cl)_23PtCl_4$: brick-red crystalline pp., decomposed by water. —$C_{25}H_{31}N_3OH_2I_2$: green crystals. At 100° it gives off MeI, becoming the iodide of penta-methyl-tri-amido-tri-phenyl-carbinol.—*Picrate* $C_{25}H_{29}N_32C_6H_2(NO_2)_3OH$: yellowish-green prisms, with coppery lustre.

Methylo-iodide $C_{25}H_{31}N_3I_2MeI$. From pararosaniline, MeI, and MeOH at 115° (Hofmann, *B.* 6, 365).

TETRA-METHYL-DIAMIDO-DIPHENYL-CUMYL-METHANE $C_{26}H_{32}N_2$ *i.e.* $(NMe_2.C_6H_4)_2CH.C_6H_4C_3H_7$. Prepared by heating cuminic aldehyde with dimethylaniline and $ZnCl_2$ to 120°; the yield is about 80 p.c. On oxidation it gives a dye-stuff closely resembling malachite green.

Salts.—$B''H_2Cl_2$: white crystalline powder. —$B''(C_6H_2(NO_2)_3OH)_2$: green crystals, [156°], explodes at 220°.—$B''H_2Cl_2PtCl_4$: yellow crystals.

Methylo-iodide $B''Me_2I_2$: white needles. [220°]. Sl. sol. cold, v. sol. hot, water (Zeigler, *B.* 13, 786).

DI-METHYL-AMIDO-PHENYLENE-DI-PHENYL-DIKETONE $NMe_2.C_6H_3(CO.C_6H_5)_2$. [55°]. From dimethylaniline and BzCl at 180°. Crystals, v. sol. alcohol and ether.

Hexa-methyl-tri-amido-phenylene-di-phenyl-diketone $C_{26}H_{29}N_3O_2$ *i.e.* $NMe_2.C_6H_3(CO.C_6H_4.NMe_2)_2$. [122°]. From boiling di-methyl-aniline and $COCl_2$ (Michler, *B.* 9, 716; Michler a. Dupertuis, *B.* 9, 1899). Monoclinic crystals; $a{:}b{:}c = \cdot587{:}1{:}\cdot714$; $\beta = 125°\ 18'$.

METHYL-AMIDO-PHENYL-ETHANE. *Nitroso-derivative* [4:1]$Et.C_6H_4.NMe.NO$. [162°]. Formed from di-methyl-amido-phenyl-ethane, HCl, and $NaNO_2$ (Heumann a. Wiernik, *B.* 20, 2423). Needles, insol. water, sl. sol. ether and cold alcohol. Zinc and HOAc reduce it to ethylphenyl-methyl-hydrazine, the acetyl derivative of which melts at 68°.

Di-methyl-amido-phenyl-ethane [4:1]$Et.C_6H_4.NMe_2$. [89°]. Formed, together with hexa-methyl-tri-amido-tri-phenyl-methane, by heating glycol (1 mol.) with dimethylaniline (2 mols.) and $ZnCl_2$ at 100°–120° (H. a. W.). Needles or prisms (from alcohol), v. sol. ether, warm alcohol, and benzene, insol. water. Its salts are deliquescent, and its platinochloride is unstable. Oxidising agents colour it blue.

Methylo-iodide $Et.C_6H_4.NMe_3I$. From *p*-amido-phenyl-ethane and MeI (Hofmann, *B.* 7, 527).

Tetra-methyl-di-amido-di-phenyl-ethane $C_{18}H_{24}N_2$ *i.e.* $NMe_2.C_6H_4.CH_2.CH_2.C_6H_4.NMe_2$. [50°]. (over 300°). Prepared by heating ethylene bromide with dimethylaniline at 100° (Schoop, *B.* 13, 2196). Slender needles; sol. ether, ligroïn, hot wood spirit, and alcohol, insol. water. With $FeCl_3$ it gives a green colouration, and finally quinone. But it does not yield a dye on oxidation.—$B''H_2I_2$. Sol. water and alcohol.—*Oxalate* $B''2H_2C_2O_4$.—*Picrate* $B''C_6H_2(NO_2)_3OH$: yellow pp., sol. hot alcohol.

Methylo-iodide $C_{18}H_{24}N_2MeI$. From di-amido-di-phenyl-ethane, MeI, and a little KOH at 150°–180° (Heumann a. Wiernik, *B.* 20, 909).

Tetra-methyl-di-amido-tri-phenyl-ethane $C_6H_5.CMe(C_6H_4.NMe_2)_2$. This is the chief product of the action of acetophenone on dimethylaniline in presence of $ZnCl_2$ (Doebner a. Petschoff, *A.* 242, 339). Yellow oil, v. sol. ether, benzene, petroleum-ether, and hot alcohol. It boils above 360° with partial decomposition. It is not volatile with steam.

Hexa-methyl-tri-amido-tri-phenyl-ethane $NMe_2.C_6H_4.CH_2.CH(C_6H_4.NMe_2)_2$. [125°]. Formed by heating $CH_2Cl.CHCl_2$ with dimethylaniline and $ZnCl_2$ at 110°–120° (Heumann a. Wiernik, *B.* 20, 2424). White needles, insol. water, v. sl. sol. cold, sl. sol. hot, alcohol, v. sol. ether. With PbO_2 and HOAc it gives a greenish-blue colour.

Octo-methyl-tetra-amido-tetra-phenyl-ethane $C_{34}H_{42}N_4$ *i.e.* $(NMe_2.C_6H_4)_2CH.CH(C_6H_4NMe_2)_2$. [90°]. (300°). Formed by heating acetylene tetra-bromide with dimethylaniline at 100° (Schoop, *B.* 13, 2199). Prisms, sol. alcohol, ether, and benzene, insol. water. With $FeCl_3$ or CrO_3 it produces quinone.—$B^{iv}2H_4PtCl_6$: yellow amorphous pp.—*Picrate* $B''C_6H_2(NO_2)_3OH$: yellow plates, sol. hot water.

Deca-methyl-penta-amido-penta-phenyl-ethane $C_2H(C_6H_4.NMe_2)_5$. [184°]. Formed by heating a mixture of dimethylaniline (50 g.), chloral hydrate (20 g.), and $ZnCl_2$ (10 g.) at 100°; the yield being 10 g. (O. Fischer, *B.* 11, 951; *A.* 206, 120; Boessneck, *B.* 18, 1516). Colourless needles (containing aq) (from alcohol), v. sol. chloroform. Sol. benzene, v. sl. sol. alcohol and ether. On oxidation it gives a greenish-blue dyestuff.

DI-METHYL-α-AMIDO-ωα-DI-PHENYL-ETHYL ALCOHOL $NMe_2.CHPh.CHPh.OH$ [110°]. From $NH_2.CHPh.CHPh.OH$, MeI, and EtOH (Goldschmidt a. Polonowska, *B.* 20, 494). White needles.—$B'_2H_2PtCl_6\frac{1}{2}aq$.

DI-METHYL-AMIDO-PHENYL ETHYL DI-THIO-CARBONATE $EtO.CS.SC_6H_4NMe_2$. [54°]. Formed from di-methyl-*p*-phenylene-diamine by diazotising and heating the product with aqueous potassium xanthate at 70° (Leuckhart, *J. pr.* [2] 41, 206). Light-yellow crystals, insol. water, sol. ordinary menstrua. With alcoholic potash it gives $S(C_6H_4NMe_2)_2$.

TETRA-METHYL-DI-AMIDO-DI-PHENYL-FURFURYL-METHANE $C_4H_3O.CH(C_6H_5NMe_2)_2$. [83°]. Prepared by the action of furfuraldehyde on dimethylaniline (O. Fischer, *B.* 11, 950).

DI-METHYL-AMIDO-PHENYL-GLYOXYLIC ACID $C_{10}H_{11}NO_3$ *i.e.* $NMe_2.C_6H_4.CO.CO_2H$. [187°]. Obtained by saponifying its ethyl ether which is produced by adding $Cl.CO.CO_2Et$ to dimethylaniline at 100° (Michael a. Hanhardt, *B.* 10, 2081). Small plates or needles. Sol. water and alcohol.—NaA′ (dried at 150°). Small needles. —BaA'_2 (dried at 150°). Plates.

Ethyl ether EtA′. [95°]. Yellow plates (from alcohol). Cannot be distilled.

TETRA-METHYL-DI-AMIDO-DI-PHENYL-HEPTANE $(NMe_2.C_6H_4)_2CH.C_6H_{13}$. [59·5°]. (275° at 15 mm.). Formed from dimethylaniline, heptoic aldehyde (œnanthol) and $ZnCl_2$ (Krafft, *B.* 19, 2987). Crystalline solid, not readily oxidised.—$B''H_2PtCl_6$: yellow crystalline pp., v. sl. sol. water and ether-alcohol.

DI - METHYL - AMIDO - PHENYL - IMIDO-QUINOLINE TETRAHYDRIDE THIOSULPHONIC ACID

$C_3H_6\langle\begin{smallmatrix}N\\|\\C_6H_3\end{smallmatrix}\rangle N.C_6H_3(NMe_2).S.SO_3H$. Formed by oxidising a mixture of quinoline tetrahydride (1 mol.) with di-methyl-*p*-phenylene-diamine thio-sulphonic acid (1 mol.) by $K_2Cr_2O_7$ (Lellmann a. Boye, *B.* 23, 1374). Small lustrous green needles, sl. sol. water. Changes after some time to a brown powder. Zinc-dust and HCl reduce it, and the product yields a blue dye on oxidation.

DI-METHYL-AMIDO-PHENYL HEXYL KETONE $C_{15}H_{23}NO$ *i.e.* $NMe_2.C_6H_4.CO.C_6H_{13}$. [49°]. (190° at 20 mm.). Formed, together with the leuco- base $C_{23}H_{32}N_2$, by adding heptoyl chloride to a mixture of $ZnCl_2$ and dimethylaniline (Krafft, *B.* 19, 2987; Auger, *Bl.* [2] 47, 44). Colourless needles. Gives with conc. HNO_3 a nitro- compound $C_6H_{13}.CO.C_6H_3(NO_2)(NMe_2)$ [65°].

Oxim $NMe_2.C_6H_4.C(NOH).C_6H_{13}$. [99°]. Colourless leaflets.

DI-METHYL-DI-AMIDO-DI-PHENYL-KETONE *v.* DI-METHYL-DI-AMIDO-BENZOPHENONE.

DI-METHYL-AMIDO-PHENYL MERCAPTAN $NMe_2.C_6H_4.SH$. [28°]. (260°). Obtained by reducing tetra-methyl-di-amido-di-phenyl sulphide with tin and HCl (Merz a. Weith, *B.* 19, 1575; Leuckart, *J. pr.* [2] 41, 207). Oil. Dissolves in NaOHAq. Re-oxidised by air to $(NMe_2.C_6H_4)_2S_2$ [118°].—$Pb(SC_8H_{10}N)_2$: plates.

Di-methyl-di-amido-phenyl mercaptan $C_8H_{12}N_2S$ *i.e.* $C_6H_3(NMe_2)(NH_2)(SH)$ [4:1:2]. Formed by reducing methylene red (Jacobsen, *B.* 21, 3104; Bernthsen, *A.* 251, 1). Gives a diazo - sulphide $C_6H_3(NMe_2)\langle\begin{smallmatrix}N\\S\end{smallmatrix}\rangle N$ [78°]. $FeCl_3$ gives a blue colouration. With AcCl in benzene it gives the hydrochloride of ethenyl-amido - dimethylamido - phenyl mercaptan $NMe_2.C_6H_3\langle\begin{smallmatrix}N\\S\end{smallmatrix}\rangle CMe$.—$Zn(C_8H_{11}N_2S)_2$.

DI-METHYL - AMIDO - DI - PHENYL - METHANE $NMe_2.C_6H_4.CH_2.C_6H_5$. This is perhaps the base, boiling at 335°, produced by heating di-methyl-aniline benzylo-chloride in a sealed tube at 230° (Michler, *B.* 10, 2079).

Di-methyl-di-amido-di-phenyl-methane $NMe_2.C_6H_4.CH_2.C_6H_4.NH_2$. [93°]. Formed by boiling *p*-nitro-di-methyl-amido-di-phenyl-carbinol with zinc-dust and HCl (Albrecht, *B.* 21, 3296). Colourless needles, coloured bluish-violet by PbO_2 or by tetra-chloro-quinone.

Tetra-methyl-di-*p*-amido-di-phenyl-methane $C_{17}H_{22}N_2$ *i.e.* $CH_2(C_6H_4NMe_2)_2$. [91°].

Formation.—1. By heating methylene iodide, $CHCl_3$ or CCl_4 with dimethylaniline (Hanhart, *B.* 12, 680; Doebner, *B.* 12, 810; *cf.* Hanniman, *B.* 10, 1235).—2. By heating methylal $CH_2(OMe)_2$ (1 mol.) with dimethylaniline (2 mols.) in presence of $ZnCl_2$ to 120° (O. Fischer, *B.* 12, 1689; *A.* 206, 117); or by acting on a mixture of methylal and dimethylaniline with conc. HClAq (Tröger, *J. pr.* [2] 36, 237).—3. One of the products of the action of acetophenone or of di-ethyl-ketone on dimethylaniline in presence of $ZnCl_2$ (Doebner a. Petschoff, *A.* 242, 338).—4. By heating dimethylaniline with $CCl_3.SO_2Cl$ at 100° (Michler a. Moro, *B.* 12, 1170).—5. One of the products of the action of (α)-naphthylamine sulphonic chloride on dimethylaniline (Michler a. Salathé, *B.* 12, 1789).—6. From C_2Cl_6, dimethylaniline and $ZnCl_2$ (Heumann a. Wiernik, *B.* 20, 2426).—7. One of the products of the action of zinc and HCl on a mixture of dimethylaniline and CS_2 (Wiernik, *B.* 21, 3204; *cf.* Tröger, *J. pr.* [2] 36, 241).—8. By distilling tetra-methyl-di-amido-benzophenone (1 pt.) with zinc-dust (10 pts.) (Nathansohn a. Müller, *B.* 22, 1882).—9. A product of the action of Ac_2O on dimethylaniline (Reverdin a. De la Harpe, *B.* 22, 1006).—10. The chief product of the action of methyl hexyl ketone on dimethylaniline (Doebner a. Petschoff, *A.* 242, 342).—11. By distilling tetra-methyl-di-amido-thio-benzophenone with zinc-dust (Baither, *B.* 20, 1737).

Properties.—Four-sided tables or glistening leaflets (from alcohol). Insol. water, sl. sol. cold, m. sol. hot, alcohol, v. sol. benzene, ether, and CS_2. Not volatile with steam. On oxidation with HOAc and MnO_2 it gives a fugitive blue colour. When boiled with MnO_2 and H_2SO_4 it yields quinone. Its alcoholic solution is turned blue by boiling with tetra-chloro-quinone. It may be oxidised to tetra-methyl-di-amido-benzophenone (N. a. M.). Conc. HNO_3 in HOAc forms a tetra-nitro- derivative which decomposes at 218°. With tri-nitro-benzene it forms a compound $C_{17}H_{22}N_2C_6H_3(NO_2)_3$ [114°], and with *m*-di-nitro-benzene a compound $(C_{17}H_{22}N_2)_2C_6H_4(NO_2)_2$ [74°] (Van Romburgh, *R. T. C.* 7, 226).

S a l t s.—$B''H_2I_2$: sparingly soluble tables. $B''H_2PtCl_6$: yellow precipitate.—P i c r a t e. $B''_2C_6H_2(NO_2)_3OH$. [178°].

Methylo-iodide $B''Me_2I_2$. [214°]. Yellow plates, v. sol. hot water and alcohol, insol. ether (D. a. P.).

Tetra - methyl - *exo* - *pp* - tri - amido - di-phenyl - methane $(NMe_2.C_6H_4)_2CH.NH_2$. [135°]. Obtained by reducing the imide of tetra-methyl-di-amido-benzophenone (auramine) with sodium-amalgam (Græbe, *B.* 20, 3265). Colourless crystals; v. sl. sol. water, m. sol. alcohol. Gives an intense blue colouration with HOAc.

Methyl-*exo*-amido-tri-phenyl-methane $C_{20}H_{19}N$ *i.e.* $(C_6H_5)_3C.NHMe$. [73°]. Obtained by passing methylamine into a hot solution of Ph_3CBr in benzene (Hemilian a. Silberstein, *B.* 17, 745). Prisms (from ligroïn). Insol. water, v. sol. alcohol.—$B'_2H_2PtCl_6$ 6aq.—B'_2I_7. Ppd. as lustrous blue-black needles by adding iodine to its solution in CS_2.

Di-methyl-*exo*-amido-tri-phenyl-methane $C_{21}H_{21}N$ *i.e.* $(C_6H_5)_3CNMe_2$. [97°]. From *exo*-bromo-tri-phenyl-methane and $NHMe_2$ in benzene (H. a. S.). Insol. water, v. sol. alcohol.—$B'_2H_2PtCl_6$.

Di-methyl-amido-tri-phenyl-methane $C_{21}H_{21}N$ *i.e.* $(C_6H_5)_2CH.C_6H_4NMe_2$. [132°].

Formation.—1. By heating di-phenyl-carbinol with di-methyl-aniline and P_2O_5 at 150° (O. Fischer, *B.* 11, 951: 12, 1690; *A.* 206, 114). 2. By heating benzophenone chloride Ph_2CCl_2 with dimethylaniline and $ZnCl_2$ (F.; *cf.* Pauly, *A.* 187, 209).

Preparation. — Benzophenone (10 g.), dimethylaniline (13 g.), and zinc chloride (10 g.)

are heated in sealed tubes for ten hours to 190°. After driving over excess of dimethylaniline and benzophenone the residuo is extracted with ether, and after distilling this off the base is re-crystallised from alcohol (Doebner a. Petschow, *A.* 242, 342).

Properties.—Colourless needles; sl. sol. alcohol, v. sol. ether and benzene. Doos not give a colouring matter on oxidation. Is a weak base, and does not combine with HOAc.

Salts.—B'HCl.—$B'_2H_2PtCl_6$: needles; sl. sol. hot water.

Methylo-iodide $C_{21}H_{21}NMeI$. [186°]. Large white plates.

Tetra-methyl-di-amido-tri-phenyl-methane $C_{23}H_{26}N_2$ *i.e.* $(NMe_2.C_6H_4)_2CH.C_6H_5$. *Leuco-base of malachite green.* [102°] and [94°].

Formation. — 1. By heating a mixture of benzoic aldehyde (10 pts.) and dimethylaniline (23 pts.) with $ZnCl_2$. The yield is 90 p.c. (O. Fischer, *B.* 10, 799, 1624; 11, 950, 2274; 12, 1685; *A.* 206, 122). — 2. From benzylidene chloride, dimethylaniline, and $ZnCl_2$.—3. By heating di-amido-tri-phenyl-methane with MeI and MeOH at 130° (F.).—4. By heating its carboxylic acid (di-methyl-aniline phthalin) $(NMe_2.C_6H_4)_2CH.C_6H_4.CO_2H$ with barium hydroxide.—5. From tetra-methyl-di-amido-tri-phenyl-carbinol (malachite green) by reduction with zinc-dust and HCl (Doebner, *B.* 11, 1239; *A.* 217, 256).—6. A by-product in the action of phthalyl chloride and in that of benzoyl chloride on dimethylaniline. — 7. By heating phenyl-glyoxylic acid with dimethylaniline and $ZnCl_2$ (Peter, *B.* 18, 539).—8. A by-product in the action of $ZnCl_2$ on a mixture of dimethylaniline and acetophenone (Doebner a. Petschoff, *A.* 242, 333).

Preparation.—A mixture of benzoïc aldehyde (40 g.), dimethylaniline (100 g.), and 93 p.c. alcohol (40 g.) is heated on a water-bath, and $POCl_3$ (65 g.) added slowly. The product is extracted with water, the filtrate ppd. by soda and the pp. recrystallised from alcohol (Nencki, *M.* 9, 1148).

Properties.—Crystallises from benzene in (apparently triclinic) needles, melting at 102°, and from alcohol in triclinic leaflets, melting at 94° (E. a. O. Fischer, *B.* 12, 796). Insol. water, v. sol. ether and benzene, sl. sol. petroleum. In small quantities it can be distilled. Its salts are oxidised by MnO_2 or PbO_2 to malachite green. Nitric acid forms a hexa-nitro-derivative [200°]. When distilled with zinc-dust it is reduced to aniline, dimethylanilinc, and *p*-amido-di-phenyl-methane (Manns, *C. C.* 1888, 1363).

Salts.—$B''H_2Cl_2$: colourless hygroscopic needles; v. sol. water. Gives off HCl at 100°, becoming B''HCl.—$B''H_2PtCl_6$: white pp., soon becoming yellowish-green.—The aurochloride is a golden-yellow flocculent pp.—Picrate $B''2C_6H_2(NO_2)_3OH$. [220°]. Aggregations of needles; m. sol. water.

Di-methylo-di-iodide $B''Me_2I_2$. [218°–222°] (F.); [231°] (Doebner, *B.* 13, 2228). Plates, tables, or leaflets; v. sol. water. Decomposed on fusion into MeI and the base.

Tetra-methyl-*pp*o-tri-amido-tri-phenyl-methane ([4:1]$NMe_2.C_6H_4)_2CH.C_6H_4NH_2$ [1:2]. [135°]. *o-Amido-leuco-malachite green.* Formed by reducing, by means of zinc-dust and HCl, the product of the condensation of *o*-nitro-benzoic aldehyde with dimethylanilino (Fischer a. Schmidt, *B.* 15, 683; 17, 1891). Colourless crystals (containing C_6H_6). Gives a reddish-brown dye-stuff on oxidation.

Acetyl derivative $C_{19}H_{13}(NMe_2)_2(NHAc)$. [186°]. Glistening crystals. Gives on oxidation $(NMe_2.C_6H_4)_2.C(OH).C_6H_4.NHAc$.

Tetra-methyl-tri-amido-tri-phenyl-methane $C_{23}H_{27}N_3$ *i.e.* $(NMe_2.C_6H_4)_2CH.C_6H_4.NH_2$. [65°]. Prepared by dissolving tetra-methyl-di-*pp*-amido-di-phenyl-carbinol (20 pts.) in HClAq (12 pts. of S.G. 1·18) and water (100 pts.), heating to 100°, and adding aniline hydrochloride (10 pts.) (Nathansohn a. Müller, *B.* 22, 1886). Small needles (from warm alcohol); v. sol. alcohol, ether, and benzene; insol. water. According to analogy it should be identical with the preceding body. With MeI it gives $CH(C_6H_4.NMe_3I)_3$ [172°].

Salts.—$B''H_2Cl_2$: yellowish-green crystalline pp., got by adding HCl to an ethereal solution of the base. V. sol. hot alcohol, sl. sol. ether, insol. benzene.—$B''H_2PtCl_6$: light-yellow flocculent pp.; v. sl. sol. water and alcohol.—Picrate $B''C_6H_2(NO_2)_3OH$: light-green flocculent pp.; v. sol. hot alcohol, insol. benzene and ether.

Benzoyl derivative $(NMe_2.C_6H_4)_2CH.C_6H_4.NHBz$. [128°]. Small, slender blue plates (from warm alcohol); v. sol. hot alcohol and benzene, sl. sol. ether, insol. water.

Tetra-methyl-*ppm*-tri-amido-tri-phenyl-methane ([4:1] $NMe_2.C_6H_4)_2CH.C_6H_4.NH_2$ [1:3]. [130°]. Prepared by reducing *m*-nitro-tetra-methyl-di-amido-tri-phenyl-carbinol (E. a. O. Fischer, *B.* 12, 803). Colourless prisms or needles. Gives a green dye on oxidation.

Tetra-methyl-tri-*p*-amido-tri-phenyl-methane $C_{23}H_{27}N_3$ *i.e.* ([4:1]$NMe_2.C_6H_4)_2CH.C_6H_4.NH_2$[1:4]. [152°]. Prepared by reducing the hydrochloride of *p*-nitro-tetra-methyl-di-*p*-amido-tri-phenyl-methane with zinc-dust (Fischer, *B.* 14, 2527). Colourless plates, sl. sol. alcohol. Gives on oxidation tetra-methyl-pararosaniline, a reddish-violet dye.

Acetyl derivative [108°]. Needles. Yields on oxidation the corresponding carbinol, a splendid green dye (Fischer a. German, *B.* 16, 708).

Penta-methyl-tri-*p*-amido-tri-phenyl-methane $C_{24}H_{29}N_3$ *i.e.* $(NMe_2.C_6H_4)_2CH.C_6H_4.NMeH$. [116°]. Obtained by heating penta-methyl-para-rosaniline with alcoholic ammonium sulphide at 100° (Hofmann, *B.* 6, 360; E. a. O. Fischer, *B.* 12, 799; Fischer a. Körner, *B.* 16, 2906). Large colourless needles (from alcohol). Sl. sol. hot water, v. sol. alcohol and ether.—$B'''_23H_2PtCl_6$.

Acetyl derivative [143°].

Hexa-methyl-tri-amido-tri-phenyl-methane $C_{25}H_{31}N_3$ *i.e.* $HC(C_6H_4.NMe_2)_3$. *Hexa-methyl-paraleucaniline.* [173°].

Formation.—1. By treating chloral with dimethylaniline and $ZnCl_2$ (E. a. O. Fischer, *B.* 11, 2097). Tho base so prepared melted, however, at 250°.—2. From orthoformic ether (1 pt.) and di-methylaniline (3½ pts.) at 100° (Fischer a. Knorr, *B.* 17, 98).—3. By condensation of *p*-di-methyl-amido-benzaldehyde with di-methyl-aniline in presence of dry HCl gas or $ZnCl_2$ (Boess-

neck, *B.* 19, 366).—4. From glycol, dimethylaniline, and $ZnCl_2$ at 100°–120° (Heumann a. Wiernik, *B.* 20, 2421). Needles or prisms. When oxidised with MnO_2 and H_2SO_4 it gives formic aldehyde and methyl violet (Fischer).

Tri-methylo-tri-iodide $C_{28}H_{40}N_3I_3$ *i.e.* $CH(C_6H_4.NMe_3I)_3$. [185°]. From tetra- and hexa-methyl-tri-*p*-amido-tri-phenyl-methane, MeI, and MeOH at 100° (Hofmann a. Girard, *B.* 2, 448; Fischer, *B.* 12, 2344). Yellow needles (containing aq), decomposes and becomes dark blue on fusion. Gives $(C_{28}H_{40}N_3Cl_3)_2 3PtCl_4 2aq$.

Hexa-methyl-*opp* (?)-tri-amido-tri-phenyl-methane. *Tri-methylo-tri-iodide* $CH(C_6H_4NMe_3I)_3$. [172°]. Obtained by heating the corresponding tetra-methyl-tri-amido-tri-phenyl-methane with MeI (Nathansohn a. Müller, *B.* 22, 1887). Small brown needles (from warm alcohol); v. sol. alcohol and hot water, almost insol. ether and benzene.

Hexa-methyl-*mpp*-tri-amido-tri-phenyl-methane. *Tri-methylo-tri-iodide* $[3:1]NMe_3I.C_6H_4.CH(C_6H_4.NMe_3I[1:4])_2$. Formed by heating the base $C_{23}H_{27}N_3$ or the corresponding $CH(C_6H_4.NH_2)_3$ with MeI and MeOH at 120° (Fischer, *B.* 12, 802; 13, 673). Crystallises with difficulty, and is v. e. sol. water. Gives rise to $3PtCl_4 2CH(C_6H_4NMe_3Cl)_3$.

References.—Chloro-, Chloro-nitro-, and Nitro-, Methyl-amido-phenyl-methanes.

TETRA-METHYL-DI-AMIDO-TRI-PHENYL-METHANE CARBOXYLIC ACID $C_{24}H_{26}N_2O_2$ *i.e.* $(NMe_2.C_6H_4)_2CH.C_6H_4.CO_2H$. *Di-methyl-aniline phthalin.* [200°]. Obtained by treating di-methyl-amido-phthalide with zinc-dust and HCl (Fischer, *A.* 206, 101). Formed also by treating *p*-aldehydo-benzoic acid with dimethylaniline and $ZnCl_2$ (Löw, *A.* 231, 367). Plates (from alcohol), v. sol. ether, sl. sol. ligroïn, m. sol. alcohol. Conc. H_2SO_4 forms a bluish-violet solution. Its zinc salt melts at 147° (L.).—Platinochloride $C_{24}H_{26}N_2O_2H_2PtCl_6$.—Picrate: $C_{24}H_{26}N_2O_2C_6H_2(NO_2)_3OH$.

TETRA-METHYL-DI-AMIDO-TRI-PHENYL-METHANE CARBOXYLIC ALDEHYDE $C_{24}H_{26}N_2O$ *i.e.* $(NMe_2.C_6H_4)_2CH.C_6H_4.CHO$. From terephthalic aldehyde, dimethylaniline, alcohol, and $ZnCl_2$ (Löw, *A.* 231, 381). Needles (from chloroform). Sl. sol. alcohol, m. sol. benzene, v. sol. chloroform. Its phenylhydrazide melts at 225°.—$B''H_2PtCl_6$.

DI-METHYL-AMIDO-PHENYL (α)-NAPHTHYL SULPHONE $C_{18}H_{17}NSO_2$ *i.e.* $NMe_2.C_6H_4.SO_2.C_{10}H_7$. Formed, together with tetra-methyl-di-amido-di-phenyl-methane, by heating dimethylaniline (2 mols.) with the chloride of naphthalene (α)-sulphonic acid (Michler a. Salathé, *B.* 12, 1789). Crystals, v. sol. alcohol and ether. Conc. HClAq at 180° splits it up into naphthalene, H_2SO_4, aniline, and MeCl. Zinc and H_2SO_4 give dimethylaniline and naphthyl mercaptan. Fuming HNO_3 gives tetra-nitro-methyl-aniline and nitro-naphthalene sulphonic acid.

Di-methyl-amido-phenyl (β)-naphthyl sulphone. Resembles the preceding body in its mode of preparation, properties, and decompositions (M. a. S.).

DI-METHYL-*p*-AMIDO-PHENYL-OXAMIC ACID $C_{10}H_{12}N_2O_3$ *i.e.* $NMe_2.C_6H_4.NH.CO.CO_2H$. [192°]. The ethyl ether is formed by boiling di-methyl-*p*-phenylene-diamine with oxalic ether, and separated by solution in alcohol from the accompanying tetra-methyl-di-amido-di-phenyl-oxamide (Sendtner, *B.* 12, 530). The ether is then saponified by alcoholic KOH. Needles (from water) or plates (from alcohol).

Ethyl ether EtA'. [117°]. Yellow plates or needles, v. sol. warm alcohol.

DI-METHYL-AMIDO-PHENYL-OXAMIDE $C_{10}H_{13}N_3O_2$ *i.e.* $NMe_2.C_6H_4.NH.CO.CO.NH_2$. [259°]. Formed by treating di-methyl-amido-phenyl-oxamic ether with alcoholic NH_3 (Sendtner, *B.* 12, 532). Nodules (from alcohol).—$B'_2H_2SO_4$: crystals.

Tetra-methyl-di-amido-di-phenyl-oxamide $NMe_2.C_6H_4.NH.CO.CO.NH.C_6H_4.NMe_2$. Formed as described under di-methyl-amido-phenyl-oxamic acid (Sendtner). Small yellow needles, insol. water, sl. sol. boiling alcohol. Does not melt at 270°. Diacid base, forming salts soluble in water.

TETRA-METHYL-DI-AMIDO-DI-PHENYL OXIDE $C_{16}H_{20}N_2O$ *i.e.* $(NMe_2.C_6H_4)_2O$. [119°]. Formed by boiling the corresponding sulphide ('thiodimethylaniline') with an ammoniacal alcoholic solution of $AgNO_3$ (Holzmann, *B.* 21, 2056). Stellate groups of colourless needles, insol. water, sl. sol. cold alcohol, ether, and benzene. Readily soluble in acids. Conc. HClAq at 200° gives MeCl and aniline.—$B''H_2PtCl_6$: minute bright yellow plates, sl. sol. hot alcohol.—Picrate. $B''2C_6H_2(NO_2)_3OH$. [150°]. Small yellow needles, sl. sol. cold alcohol and benzene.

Tetra-methyl-di-amido-di-phenyl-di-oxide $(NMe_2.C_6H_4)_2O_2$. *Di-oxy-di-methyl-aniline.* [91°]. Obtained by adding (4 mols. of) silver nitrate to an alcoholic solution of tetra-methyl-di-amido-di-phenyl-di-sulphide $(NMe_2.C_6H_4)_2S_2$ (1 mol.) treated with conc. NH_3. It is also formed by the action of Fe_2Cl_6 upon the conc. HCl solution of the same base. Thin silky needles, or plates. V. e. sol. alcohol, ether, and benzene, sol. hot water. It dissolves in acids, but its salts are not crystalline (Merz a. Weith, *B.* 19, 1573).

TETRA-METHYL-DI-AMIDO-DI-PHENYL-OXINDOLE $C_{24}H_{25}N_3O$ *i.e.*

C_6H_4—$C(C_6H_4.NMe_2)_2$
| |
NH — CO

. *Di-methyl-aniline-isatin.* [234°]. Formed by heating isatin with dimethylaniline and $ZnCl_2$ (Baeyer a. Lazarus, *B.* 18, 2642). Glistening colourless prisms. Sl. sol. ether, alcohol, and ligroïn, insol. water. Dissolves in acids. On oxidation it gives a splendid bluish-green dye-stuff.

DI-METHYL-AMIDO-TRI-PHENYL-PHOSPHINE $C_{20}H_{20}NP$ *i.e.* $NMe_2.C_6H_4.P(C_6H_5)_2$. [152°]. Formed by the action of sodium on a mixture of chloro-benzene and $NMe_2.C_6H_4PCl_2$ (Schenk a. Michaelis, *B.* 21, 1502). Colourless crystals, v. e. sol. benzene, sl. sol. alcohol and ether. Weak base, being almost entirely ppd. by water from its solution in HClAq.

Hexa-methyl-tri-amido-tri-phenyl-phosphine $(NMe_2.C_6H_4)_3P$. [273°]. Formed by heating dimethylaniline with PCl_5 in a sealed tube (Hanimann, *B.* 9, 845). Formed also as a by-product, in the action of PCl_3 on dimethylaniline in presence of $AlCl_3$ (S. a. M.). Colourless needles,

which turn blue on exposure to air. V. e. sol. chloroform, v. sol. dilute HClAq, m. sol. hot alcohol.

DI - METHYL - AMIDO - PHENYL PHOS - PHINOUS ACID *v.* DI-METHYL-AMIDO-BENZENE PHOSPHINIC ACID.

TETRA - METHYL-DI-AMIDO-DI - PHENYL-PHTHALIDE $C_{24}H_{24}N_2O_2$ *i.e.* $(NMe_2.C_6H_4)_2C\left\langle\begin{matrix}C_6H_4\\ O\end{matrix}\right\rangle CO$. *Dimethylaniline-phthaleïn.* [191°]. Prepared by heating dimethylaniline with $ZnCl_2$ and phthalyl chloride or phthalic anhydride (O. Fischer, *B.* 9, 1753 ; 10, 952 ; 12, 1691 ; *A.* 206, 92). Colourless pointed crystals, insol. water, v. sol. benzene, v. sl. sol. ligroïn. Reduced by zinc-dust and HOAc to tetra-methyl-di-amido-tri-phenyl-methane carboxylic acid (dimethylaniline-phthalin). Potash-fusion gives dimethylaniline, HOBz, and phthalic acid. HNO_3 gives a hexa-nitro- derivative which decomposes at 230°.

Salts.—B''HCl : small needles, m. sol. water. —$B''H_2Cl_2$: hygroscopic crystalline mass, got by passing HCl into the ethereal solution. Gives off HCl (1 mol.) at 100°.—$B''_2H_2PtCl_6$: crystalline pp.—$B''H_2PtCl_6$ aq : prisms. — Picrate $B''2C_6H_2(NO_2)_3OH$.

Methylo-iodide $B''Me_2I_2$. [c. 185°].

Phthal-green $C_{24}H_{24}N_2O_2$. This substance, isomeric with the preceding, is also formed in the action of phthalyl chloride on di-methyl-aniline in presence of $ZnCl_2$ (Fischer). Its hydrochloride, B''HCl, forms greenish-yellow needles, m. sol. water. Its zinc double salt crystallises in brass-yellow needles which form a green solution in water. Zinc and HCl reduce it to a leuco- base $C_{24}H_{24}N_2O$ which crystallises in small prisms [236°], and is easily re-oxidised to phthal-green.

TETRA - METHYL - DI-AMIDO-PHENYL-DI-PHENYLENE-OXIDE-CARBINYL CHLORIDE $C_6H_5.C\left\langle\begin{matrix}C_6H_3NMe_2\\ C_6H_3NMe_2Cl\end{matrix}\right\rangle O$. *Tetra-methyl-rosamine.* Formed from benzotrichloride and di-methyl-*m*-amidophenol at 50°–60° (Heumann a. Rey, *B.* 22, 3002). Dark-red flocculent pp., strongly fluorescent in acid or neutral solution. H_2SO_4 dissolves it giving an orange-yellow colour, becoming dark-red on addition of water. Silk and wool are dyed in feebly acid bath rose to bluish-red.

Salts.—B'HCl : dark-red needles with steel-blue reflex, v. sol. water and EtOH forming solutions with a splendid blue-red colour, and yellow fluorescence.—$(C_{23}H_{23}N_2OCl)_2PtCl_4$: dark-red pp.

DI - METHYL - AMIDO - PHENYL- PROPANE $C_{11}H_{17}N$ *i.e.* $NMe_2.C_6H_4.CH_2.CH_2.CH_3$. *Di-methyl-amido-propyl-benzene.* (230°). From *p*-bromo-di-methyl-aniline, propyl bromide, and sodium (Claus a. Howitz, *B.* 17, 1327). Oil.

Methylo-iodide $NMe_3I.C_6H_4.Pr$. [168°].

Tetra-methyl-di-amido-di-phenyl-propane $(NMe_2.C_6H_4)_2CMe_2$. [83°]. From acetone (1 mol.), dimethylaniline (2 mols.), and $ZnCl_2$ (Doebner, *B.* 12, 813). Long needles.

DI-METHYL - AMIDO - PHENYL - QUINON-IMIDE $C_{14}H_{14}N_2O$ *i.e.* $C_6H_4\left\langle\begin{matrix}O\\ |\\ N.C_6H_4NMe_2\end{matrix}\right.$. *Phenol-blue.* Formed by adding quinone chlorimide to a solution of di-methyl-aniline in concentrated aqueous oxalic acid (Fogh, *B.* 21, 889). Formed also by the action of NaOH on di-methyl-phenylene green (Möhlau, *B.* 18, 2914). Black crystals (containing $\frac{1}{2}$ aq.) Yields, when treated with hot dilute HClAq, quinone and di-methyl-phenylene-*p*-diamine. May be reduced to a leuco- base.

Sulphonic acid $SO_3H.C_6H_3\left\langle\begin{matrix}O\\ |\\ N.C_6H_4NMe_2\end{matrix}\right.$. Formed by passing chlorine into amido-phenol sulphonic acid suspended in water, and then adding di-methyl-aniline (F.). Slender needles, v. sl. sol. hot alcohol, insol. cold water and ether. Its alkaline solutions are blue. Conc. H_2SO_4 forms a cherry-red solution.

TETRA - METHYL-DI-AMIDO-DI-PHENYL-SULPHIDE $(NMe_2.C_6H_4)_2S$. *Thiodimethylaniline.* [126°]. Formed by heating dimethyl-aniline with persulphocyanic acid or SCl_2 (Tursini, *B.* 17, 584 ; Holzmann, *B.* 20, 1640 ; 21, 2056 ; Michaelis a. Godchaux, *B.* 23, 554). Light-yellow needles, sl. sol. alcohol and benzene.

Reactions.—1. Silver nitrate converts it into $(NMe_2.C_6H_4)_2O$.—2. On heating with reduced copper (10 pts.) at 300° it yields NPhMe.

Salts.—$B''H_2Cl_2$. [176°]. White mass becoming coloured in the air, extremely sol. water. — $B''H_2PtCl_6$ 2aq. — $B''H_4FeCy_6$ 6aq : white powder, m. sol. water.—$B''C_6H_2(NO_2)_3OH$. [142°]. Yellow needles (from hot alcohol).—$B''2C_6H_2(NO_2)_3OH$. Amorphous. [146°]. — B'HNCS : [168°] ; pearly plates.

Tetra-methyl-di-amido-di-phenyl-di-sulphide $(NMe_2C_6H_4)_2S_2$. *Di-sulphido-* or *di-thio-di-methyl-aniline.* [118°]. Formed by adding S_2Cl_2, diluted with petroleum-ether, to a dilute solution of dimethylaniline in the same solvent (Merz a. Weith, *B.* 19, 1570). Formed also by heating di-methyl-*p*-amido-phenyl ethyl di-thio-carbonate with an alcoholic solution of aniline at 200° (Leuckart, *J. pr.* [2] 41, 208). Small yellow needles, e. sol. CS_2, more sparingly in hot benzene, alcohol, and petroleum-ether, nearly insol. water. Copper-powder removes the sulphur at c. 230° forming dimethylaniline and other products. By the action of Fe_2Cl_6, or of alcoholic NH_3 and silver nitrate, it is converted into tetra-methyl-di-amido-di-phenyl-di-oxide $(NMe_2.C_6H_4)_2O_2$. By tin and HCl, or by sodium-amalgam, it is reduced to di-methyl-amido-phenyl-mercaptan, which is readily re-oxidised to the di-sulphide. Its salts are gummy and amorphous, they are decomposed by water.

Tetra - methyl - tetra - amido - di - phenyl-disulphide $(NMe_2C_6H_3(NH_2))_2S_2$. Formed by atmospheric oxidation from di-methyl-di-amido-phenyl mercaptan $NMe_2.C_6H_3(NH_2)SH$ (Bernthsen, *A.* 251, 1). Thick oil, sol. ether, alcohol, and benzene. Dissolves in acids, but reppd. by alkalis. In benzene solution it combines with sulphur forming a persulphide [97°], apparently $C_{32}H_{40}N_8S_5$.

DI-METHYL-AMIDO-DI-PHENYL SULPHONE $C_6H_5.SO_2.C_6H_4.NMe_2$. [78°] (R.) ; [82°] (M. a. M.). Formed by heating dimethylaniline with benzene sulphonic chloride (Michler, *B.* 10, 1742 ; Van Romburgh, *R. T. C.* 2, 305 ; Michler a. Meyer, *B.* 12, 1791 ; Hassencamp, *B.* 12,

1275). Needles (from alcohol), insol. water, v. e. sol. alcohol, ether, and benzene. HClAq at 180° splits it up into MeCl, aniline, and benzene. Zinc and H_2SO_4 reduce it to phenyl mercaptan and dimethylaniline. HNO_3 gives yellow crystals of tetra-nitro-methyl-aniline [127°].

METHYL-AMIDO-PHENYL-THIAZOLE
$C_{10}H_{10}N_2S$ *i.e.* $\left.\begin{matrix} S-C(NHMe) \\ | \\ CH{:}CPh\text{———} \end{matrix}\right\rangle N$. [138°]. From ω-bromo-acetophenone and methyl-thio-urea (Traumann, *A.* 249, 46). Yellow plates (from ether), insol. water, m. sol. alcohol. With HClAq at 220° it yields methylamine.

TETRA-METHYL-DI-AMIDO-DI-PHENYL-THIENYL-METHANE $C_{21}H_{24}N_2S$ *i.e.* $(NMe_2.C_6H_4)_2CH.C_4H_3S$. *Thiophene leuco-malachite green.* [93°]. Formed by heating thiophenic aldehyde with dimethylaniline, $ZnCl_2$, and a little alcohol (Peter, *B.* 18, 538; Levi, *B.* 20, 514). Formed also by heating dimethyl-aniline with thienyl-glyoxylic acid $C_4H_3S.CO.CO_2H$ and $ZnCl_2$ (P.). Needles, insol. water, v. sol. alcohol and ether. The alcoholic solution turns green in the air. MnO_2 and dilute H_2SO_4 oxidise it to the carbinol $(NMe_2.C_6H_4)_2C(OH).C_4H_3S$, which is a dark-brown oil, sol. alcohol and ether, and forming salts which dye a splendid yellowish-green (*Thiophene green*).—Platinochloride $C_{21}H_{24}N_2SH_2PtCl_6$. — Picrate $C_{21}H_{24}N_2S2C_6H_2(NO_2)_3(OH)$. [c. 208°]. Yellowish-green needles, sl. sol. cold water, v. sol. alcohol.

Di-methylo-di-iodide $C_4H_3S.CH(C_6H_4.NMe_3I)_2$. [212°]. White plates.

TETRA-METHYL-DI-AMIDO-DI-PHENYL-THIOKETONE *v.* TETRA-METHYL-DI-AMIDO-THIO-BENZOPHENONE.

DI-METHYL-DI-AMIDO-PHENYL THIO-SULPHURIC ACID $NMe_2.C_6H_3(NH_2)S.SO_3H$. [193°–204°]. Obtained by adding an alkali to a $\frac{1}{10}$ p.c. solution of methylene red until the colour is destroyed, then acidulating with HOAc and exposing to the air. Formed also by the action of a strong solution of SO_2 on di-methyl-di-amido-phenyl mercaptan (Bernthsen, *A.* 251, 1). Crystals, sl. sol. water and alcohol. Its dilute aqueous solution gives a purple colour with traces of iodine or of $FeCl_3$. The hydrochloride crystallises in prisms.

Reactions.—1. A mixture of di-methyl-di-amido-phenyl thio-sulphuric acid with *dimethylaniline* when oxidised by $K_2Cr_2O_7$ and HOAc forms the indamine $C_6H_4\left\langle\begin{matrix} N.C_6H_3(NMe_2) \\ | \\ NMe_2\,.\,O\,.\,SO_2 \end{matrix}\right\rangle S$, an emerald-green powder (containing $\frac{1}{2}$aq), and yields $NMe_2.C_6H_4.NH.C_6H_3(NMe_2).S.SO_3H$ on reduction, a body which is v. sol. hot alcohol and acids.—2. A mixture of the thio-sulphuric acid with *aniline hydrochloride* gives on oxidation $C_{14}H_{15}N_3S_2O_3$ *i.e.* $C_6H_4\left\langle\begin{matrix} N.C_6H_3(NMe_2) \\ | \\ NH_2\,.\,O\,.\,SO_2 \end{matrix}\right\rangle S$ (?) an insoluble green compound decomposed by water. Prolonged boiling with dilute $FeCl_3$ gives $C_6H_4\left\langle\begin{matrix} N(NMe_2) \\ | \\ NH\text{———} \end{matrix}\right\rangle S$, a blue powder with bronze lustre.—3. A mixture of di-methyl-di-amido-phenyl thiosulphuric acid with *o*-toluidine yields on oxidation the homologous $C_{15}H_{17}N_3S_2O_3$ as a bluish-grey powder.

Tetra-methyl-di-amido-phenyl thiosulphuric acid $C_6H_3(NMe_2)_2S.SO_3H$. [175°–182°]. Obtained by dissolving tetra-methyl *p*-phenylene diamine (2·7 g.) in HCl (1·56 c.c. of 33 p.c.) and adding aluminium sulphate (10 g.), and sodium thiosulphate (6·6 g.) dissolved in water (36 c.c.). A cold solution of $K_2Cr_2O_7$ (25 c.c. of a 6·67 p.c. solution) is then added, and the resulting liquid left to stand. The precipitate which then separates is recrystallised from alcohol (Bernthsen, *A.* 251, 60). Plates, sol. hot water and acids. Zinc and HCl reduce it to the mercaptan $C_6H_3(NMe_2)_2SH$.

TETRA-METHYL-DI-*p*-AMIDO-DI-PHENYL THIO-UREA $C_{16}H_{22}N_4S$ *i.e.* $(NMe_2.C_6H_4.NH)_2S$. [186°]. Formed by boiling di-methyl-*p*-phenylene-diamine with alcoholic CS_2 (Baur, *B.* 12, 533). White needles, insol. water and cold alcohol.—$B''H_2Cl_2$: crystalline powder.

Acetyl derivative [71°]. White plates.

TETRA-METHYL-DI-AMIDO-DI-ω-PHENYL-TOLUIC ALDEHYDE $C_{24}H_{26}N_2O$ *i.e.* $(NMe_2.C_6H_4)_2CH.C_6H_4CHO$. *Aldehyde of the leuco-base of malachite green.* [143°]. Obtained by boiling an alcoholic solution of terephthalic aldehyde $C_6H_4(CHO)_2$ with di-methyl-aniline and $ZnCl_2$ (W. Löw, *A.* 231, 381). Prismatic needles (from chloroform). Forms a crystalline compound with $NaHSO_3$. Its phenyl hydrazide melts at 225°.—$B''H_2PtCl_6$.

TRI-METHYL-TRI-AMIDO-DI-PHENYL-TOLYL-CARBINOL $C_{23}H_{27}N_3O$. Formed by heating rosaniline chloride (1 pt.) with MeI (2 pts.), MeOH (8 pts.), and KOH (1 pt.) (Hofmann). Formed also by allowing an alcoholic solution containing rosaniline and 'iodine green' to stand in the cold (Girard a. Willm, *Bl.* [2] 25, 200). The salt $NHMe.C_6H_3Me.C\left\langle\begin{matrix} C_6H_4NHMe \\ C_6H_4NHMeCl \end{matrix}\right.$ is one of the substances known as Hofmann's violet (Hofmann, *C. R.* 54, 428; 56, 945, 1033; 57, 1131). Its absorption-spectrum has been studied by Hartley (*C. J.* 51, 172).

Penta-methyl-tri-amido-di-phenyl-tolyl-carbinol
$NMe_2.C_6H_3Me.C(OH)(C_6H_4NMe_2)(C_6H_4NMeH)$.
The chloride $NMe_2.C_6H_3Me.C\left\langle\begin{matrix} C_6H_4NMe_2 \\ C_6H_4.NHMeCl \end{matrix}\right.$ is probably the chief constituent of Hofmann's violet obtained by heating rosaniline with MeCl. It has a green lustre and forms a violet solution in water. The solution is decolourised by zinc-dust. HCl turns the solution first green, then yellow. NaOH gives a brownish-red pp. Conc. H_2SO_4 gives a brownish-yellow solution changed, on dilution, through green to blue. It dyes wool, silk, and mordanted cotton violet.

Hexa-methyl-tri-amido-di-phenyl-tolyl-carbinol $NMe_2C_6H_3Me.C(OH)(C_6H_4NMe_2)_2$. The zinc double salt of the methylo-chloride of this body $C_{27}H_{35}N_3Cl_4Zn$ or
$NMe_2.C_6H_3Me.C\left\langle\begin{matrix} C_6H_4NMe_3Cl \\ C_6H_4.NMe_2ZnCl_3 \end{matrix}\right.$ appears to constitute the dye known as 'iodine green,' which is obtained by heating rosaniline with MeCl, or by the action of MeCl on Hofmann's violet. The

corresponding iodide $C_{27}H_{35}N_3I_2$ aq is obtained by heating MeI (2 pts.) with MeOH (2 pts.) and rosaniline (1 pt.) at 100° (Hofmann a. Girard, *B.* 2, 440). The zinc double chloride forms a bluish-green aqueous solution, turned reddish-yellow by hydrochloric acid, and rendered colourless by caustic soda. It dyes silk green. When heated strongly in the dry state it becomes violet. Its absorption-spectrum has been studied by Hartley (*C. J.* 51, 175). Iodine green may be reduced to penta-methyl-tri-amido-di-phenyl-tolyl-methane $NMe_2.C_6H_3Me.CH(C_6H_4.NMe_2)(C_6H_4NHMe)$ [173°] (O. Fischer a. G. Körner, *B.* 16, 2910). Besides the bodies here described other methylated rosanilines are doubtless formed in the methylation of rosaniline.

DI-METHYL-AMIDO-PHENYL-*p*-TOLYL SULPHONE $C_{15}H_{17}NSO_2$ *i.e.* [4:1]$C_6H_4Me.SO_2.C_6H_4NMe_2$. [95°]. From $C_6H_4Me.SO_2Cl$ and dimethylaniline (Michler a. Meyer, *B.* 12, 1793). Split up by HCl at 180° into MeCl, aniline, H_2SO_4, and toluene. Zinc and H_2SO_4 reduce it to *p*-tolyl mercaptan and dimethylaniline.

DI-METHYL-*p*-AMIDO-PHENYL-UREA $C_9H_{13}N_3O$ *i.e.* $NH_2.CO.NH.C_6H_4NMe_2$. [179°]. From potassium cyanate and di-methyl-*p*-phenylene-diamine (Binder, *B.* 12, 536). Long needles, sol. hot water.—$B'_2H_2PtCl_6$: yellow leaflets.

Tetra-methyl-di-*p*-amido-di-phenyl-urea $C_{17}H_{22}N_4O$ *i.e.* $CO(NH.C_6H_4NMe_2)_2$. [262°] (B.); [246°] (M. a. Z.). Obtained by heating urea with di-methyl-*p*-phenylene-diamine (Binder, *B.* 12, 535). The same body is apparently obtained by the action of $COCl_2$ on di-methyl-*p*-phenylene-diamine (Michler a. Zimmermann, *B.* 14, 2179). — $B''H_2Cl_2$: soluble crystalline powder. — $B''H_2SO_4$: sl. sol. water.—$B''H_2PtCl_6$.

METHYL-AMIDO-PROPANE SULPHONIC ACID $NHMe.CH_2.CHMe.SO_3H$. [220°-223°]. From methyl-propylene-ψ-thio-urea and bromine-water (Gabriel, *B.* 22, 2989). Colourless columns, v. e. sol. water.

METHYL-α-AMIDO-PROPIONIC ACID $C_4H_9NO_2$ *i.e.* $CH_3.CH(NHMe).CO_2H$. [260°]. From α-chloro-propionic ether and aqueous methylamine at 130° (Lindenburg, *J. pr.* [2] 12, 244). Prisms. Decomposed on fusion. Tastes sweet. Its *copper salt* crystallises in dark-blue prisms.—HA'HCl. [110°]. Deliquescent prisms. $H_2A'_2H_2PtCl_6$: triclinic prisms. — $HA'HNO_3$. [126°]. Monoclinic prisms.

Di-methyl-α-amido-propionic acid. *Methylo-chloride* $CH_3.CH(NMe_3Cl).CO_2H$. Formed by treating α-chloro-propionic ether with trimethylamine, saponifying the resulting ether with baryta, and adding HCl (Brühl, *B.* 9, 34). Very hygroscopic, forming $(C_6H_{14}NO_2Cl)_2PtCl_4$ crystallising in roseate prisms, and $C_6H_{14}NO_2AuCl_4$ crystallising in golden needles. The corresponding *Anhydride* of the *Methylo-hydroxide* $CH_3.CH{<}^{CO}_{NMe_3}{>}O$ or 'betaïne' is formed on adding baryta to the methylo-chloride and subsequently neutralising with H_2SO_4. It forms extremely deliquescent crystals, and is neutral in reaction. The iodide $(C_6H_{13}NO_2)_2HI$ forms long colourless prisms, v. sol. alcohol and hot water.

DI-METHYL-AMIDO-PROPYL ALCOHOL *v.* DI-METHYL-OXY-PROPYL-AMINE.

Tetra-methyl-*s*-di-amido-isopropyl alcohol $C_7H_{18}N_2O$ *i.e.* $(NMe_2.CH_2)_2CH.OH$. (170°-185°). Formed from di-chloro-isopropyl alcohol (*s*-di-chlorhydrin) and NMe_2H at 60° (Berend, *B.* 17, 510). Liquid, v. e. sol. water.—$B''H_2PtCl_6$: yellow plates.

Benzoyl derivative $(NMe_2.CH_2)_2CH.OBz$. Forms a platino-chloride $B''H_2PtCl_6$ crystallising in tables.

DI-METHYL-AMIDO-PROPYLENE GLYCOL $C_5H_{13}NO_2$ *i.e.* $NMe_2.CH_2.CH(OH).CH_2OH$. (217°). From dimethylamine and chloro-propylene glycol (chlorhydrin) (Roth, *B.* 15, 1153). Thick syrup; v. e. sol. water, alcohol, and ether.—$B'_2H_2PtCl_6$.

Methylo-chloride $NMe_3Cl.CH_2.CH(OH).CH_2(OH)$. From the chlorhydrin and NMe_3 at 100° (V. Meyer, *B.* 2, 186; Hanriot, *A. Ch.* [5] 17, 99). Needles, v. e. sol. water.—$(C_6H_{16}NO_2Cl)_2PtCl_4$: crystalline tables.—$C_6H_{16}NO_2AuCl_4$. [190°]. Orange crystals, m. sol. alcohol.

Di-benzoyl derivative $NMe_2.CH_2.CH(OBz).CH_2(OBz)$: oil.—*Picrate* $B'C_6H_2(NO_2)_3OH$. [100°]. Laminæ (Roth, *B.* 15, 1153).

DI-METHYL-(B. 2)-AMIDO-QUINOLINE

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                     NMe2.C : CH.C.CH:CH
C9H6(NMe2)N  i.e.         |        ||   ||   . [56°].
                     CH:CH.C . N : CH
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(C.); [58°] (O.). (c. 335°). Prepared by boiling a mixture of *u*-di-methyl-*p*-phenylene-diamine (25 pts.), glycerine (60 pts.), nitro-benzene (15 pts.), and H_2SO_4 (50 pts.) (La Coste, *B.* 16, 672). Colourless crystals. V. sol. alcohol, ether, and benzene.

Picrate $B'(C_6H_2(NO_2)_3OH)$: very fine orange needles [215°].

Methylo-iodide B'MeI: long red needles. —$(BMeCl)_2PtCl_4$.

Methylo-chloride B'MeCl aq. [244°]. Long scarlet hygroscopic needles (Ostermayer, *B.* 18, 596).

Methylo-chloride of the *tetrahydride* $NMe_2.C_9H_{10}NMeCl$ aq: [220°], fine colourless needles. With ICl it forms $NMe_2.C_9H_{10}NMeClICl$: [127°], separating in small yellow crystals (Ostermayer, *B.* 18, 596).

TETRA-METHYL-DI-AMIDO-QUINONE $C_6H_2(NMe_2)_2O_2$. [174°]. Red tables. Formed by dissolving ordinary quinone in aqueous di-methyl-amine (Mylius, *B.* 18, 467).

DI-METHYL-AMIDO-SULPHO-BENZOIC ACID $C_6H_3(NMe_2)(SO_3H).CO_2H$ [4:2:1]. Obtained by heating the silver salt of amido-sulpho-benzoic acid with MeI and MeOH at 100° (Hedrick, *Am.* 9, 413). Easily soluble crystals. —CaA''.—$BaEt_2A''_2$.

TETRA-METHYL-DI-AMIDO-THIOBENZO-PHENONE $C_{17}H_{20}N_2S$ *i.e.* $CS(C_6H_4NMe_2)_2$. [194°] (B.); [202°] (G.). S. (alcohol) ·072 at 18°. S. (ether) ·27 at 18°. S. (chloroform) 4·58 at 18°. Formed by passing H_2S into an alcoholic solution of the hydrochloride of tetra-methyl-di-amido-benzophenone imide (auramine) at 60° (Fehrmann, *B.* 20, 2857; Baither, *B.* 20, 1731, 3289). Formed also by the action of CS_2 on auramine (Graebe, *B.* 20, 3266). Obtained also from $CSCl_2$ and dimethylaniline. Ruby-red crystals, with blue lustre. Insol. water and light petroleum, sl. sol. other solvents. Its

solutions in benzene and CS_2 are dark red with green fluorescence.

Reactions.—1. Hot dilute hydrochloric acid gives H_2S and tetra-methyl-di-amido-benzophenone. — 2. *Water* at 120° under pressure also forms $CO(C_6H_4NMe_2)_2$.—3. Boiling concentrated nitric acid forms $CO(C_6H_2(NO_2)_2.NMe.NO_2)_2$, whence hydroxylamine hydrochloride forms $CO(C_6H_2(NO_2)_2.NMeH)_2$ [c. 196°].—4. By heating with excess of *benzyl chloride* it is converted into $CCl_2(C_6H_4.NMe_2)_2$, a greyish-green powder, decomposed by water with production of $CO(C_6H_4NMe_2)_2$.— 5. *Aniline hydrochloride* at 150° forms phenyl-auramine $NPh:C(C_6H_4NMe_2)_2$ [171°]. — 6. *Phenyl-hydrazine* at 100° forms $CO(C_6H_4.NMe_2)_2$. *Aniline* at 150° also forms this ketone.—7. *Hydroxylamine* gives the oxim of tetra-methyl-di-amido-benzophenone.—8. Distillation over red-hot *zinc-dust* yields di-methyl-aniline and tetra-methyl-di-amido-di-phenyl-methane.—9. *Acetyl chloride* in the CS_2 solution forms $C_{17}H_{20}N_2SAcCl$, which forms a red alcoholic solution and a greenish-yellow solution in benzene. It begins to decompose at 160°.—10. *Benzoyl chloride* in CS_2 forms a similar compound $C_{17}H_{20}N_2SBzCl$, which is insol. water, but decomposed by solution in alcohol. — 11. Boiling with Ac_2O and NaOAc forms $C_{38}H_{46}N_4SO_4$, a dark-grey powder.—12. *Methyl iodide* appears to give $C_{17}H_{20}N_2SMeI$, which forms green plates with coppery lustre, decomposes at 108°, and yields a deep bluish-green aqueous solution with red fluorescence. It dyes silk green.—13. $CSCl_2$ acting on its CS_2 solution forms a black powder, probably $C_{17}H_{20}N_2SCSCl_2$. In chloroform solution, $CSCl_2$ forms white crusts of $CCl_2(C_6H_4NMe_2)_2CHCl_3$.

METHYL-AMIDO-THYMOQUINONE $C_{11}H_{15}NO_2$ *i.e.* $C_3H_7.C_6HMe(NHMe)O_2$. [74°]. From methylamine and thymoquinone in alcoholic solution (Zincke, *B.* 14, 97). Dark-violet laminæ (from very dilute alcohol). Volatile with steam. M. sol. water, v. e. sol. alcohol. The solutions are deep violet. Alcoholic HCl converts it into methylamine and oxythymoquinone.

Di-methyl-amido-thymoquinone $C_{12}H_{17}NO_2$ *i.e.* $C_3H_7.C_6HMe(NMe_2)O_2$. Prepared by mixing dimethylamine with thymoquinone in alcoholic solution (Schulz, *B.* 16, 899). Dark-coloured oil. Volatile with steam. Split up by heating with dilute HCl into oxythymoquinone and dimethylamine.

Di-methyl-di-amido-thymoquinone $C_{12}H_{18}N_2O_2$ *i.e.* $C_3H_7.C_6Me(NHMe)_2O_2$. [203°]. Formed, together with methyl-amido-thymoquinone, by treating a cold concentrated alcoholic solution of thymoquinone with methylamine (Zincke). Formed also by the action of methylamine on di-bromo-thymoquinone. Long reddish-violet needles (from alcohol). Decomposed by KOH or H_2SO_4 in alcoholic solution into methylamine and di-oxy-thymoquinone.

METHYL-AMIDO-TOLUENE *v.* METHYL-TOLUIDINE.

Methyl-di-amido-toluene *v.* METHYL-TOLYLENE-DIAMINE.

Methyl-tri-amido-toluene $C_8H_{13}N_3$ *i.e.* $C_6H_2Me(NH_2)_2(NHMe)$. The hydrochloride $B''H_2Cl_2aq$ is prepared by reducing the nitramine of di-nitro-methyl-*o*-toluidine with tin and HCl (Van Romburgh, *R. T. C.* 3, 400). It forms small crystals.

Di-methyl-amido-toluene sulphonic acid $C_9H_{13}NSO_3$ *i.e.* $NMe_2.C_6H_3Me.SO_3H$ [2:1:4 ?]. Formed by heating di-methyl-*o*-toluidine (1 pt.) with H_2SO_4 (4 pts.) at 180° to 210° (Michler a. Sampaio, *B.* 14, 2168). Large glittering prisms (from water); insol. alcohol, v. sol. hot water.—CaA'_2 (dried at 130°). Nodules.—BaA'_2 (dried at 130°). Laminæ; v. sol. hot water. — ZnA'_2: needles.

TETRA-METHYL-DI-AMIDO-DITOLYL $NMe_2.C_6H_3Me.C_6H_3Me.NMe_2$. *Tetra-methyl-tolidine.* [80°]. Formed by oxidising di-methyl-*o*-toluidine with MnO_2 and dilute H_2SO_4. Formed also by methylation of di-amido-ditolyl (Michler a. Sampaio, *B.* 14, 2170). White plates; sol. ether and hot alcohol, insol. water. —$B''H_2Cl_2$: white needles.—$B''H_2PtCl_6$: yellow crystalline pp.

Tetra-methyl-di-amido-ditolyl $C_{18}H_{24}N_2$ *i.e.* $NMe_2.C_6H_3Me.C_6H_3Me.NMe_2$. [190°]. Formed in small quantity by heating dimethyl-*o*-toluidine with H_2SO_4 (M. a. S.). Long needles; sol. hot alcohol, ligroïn, and ether, insol. water. Gives a green colouration with Fe_2Cl_6 and yellow colour with CrO_3.

Tetra-methyl-di-amido-ditolyl (?) $C_{18}H_{24}N_2$ *i.e.* $NMe_2.C_6H_3Me.C_6H_3Me.NMe_2$. [57°]. Prepared by heating dimethyl-*p*-toluidine with H_2SO_4 (Michler a. Pattinson, *B.* 14, 2167). White needles; sol. alcohol and ether, insol. water. —$B''H_2Cl_2PtCl_4$.

DI-METHYL-AMIDO-TOLYL-BUTANE $C_{13}H_{21}N$ *i.e.* $C_4H_9.C_6H_3Me.NMe_2$. [251°]. From amido-tolyl-butane and MeI (Effront, *B.* 17, 2339).—$B'_2H_2PtCl_6$.

DI-METHYL-AMIDO-TOLYL METHYL KETONE $C_{11}H_{15}NO$ *i.e.* [1:2:5]$C_6H_3(CH_3)(NMe_2).CO.CH_3$. [95°]. Flat yellowish prisms; e. sol. alcohol, ether, and hot water, nearly insol. petroleum-ether. Formed by methylation of amido-tolyl methyl ketone (Klingel, *B.* 18, 2699).

METHYL-α-AMIDO-*n*-VALERIC ACID $C_6H_{13}NO_2$ *i.e.* $CH_3.CH_2.CH_2.CH(NHMe).CO_2H$. Obtained by heating butyric aldehyde with conc. aqueous HCy, adding methylamine, and heating again. The nitrile then separates as an oil, which is hydrolysed by prolonged boiling with dilute HClAq (Menozzi a. Belloni, *G.* 17, 116). Long glistening needles (containing aq); decomposed partially at 110° with formation of a sublimate.

S a l t s.—CuA'_22aq: blue prisms.—$HA'HNO_3$: prisms, v. sol. water.

Methyl-α-amido-isovaleric acid $C_6H_{13}NO_2$ *i.e.* $(CH_3)_2CH.CH(NHMe).CO_2H$. Formed by boiling α-bromo-isovaleric acid with aqueous methylamine (Duvillier, *C. R.* 88, 425; *A. Ch.* [5] 21, 434). White crystalline powder; v. e. sol. water, m. sol. hot alcohol, insol. ether. Neutral in reaction. With cyanamide it forms a creatinin $C_7H_{13}N_3O$, crystallising in slender needles, v. sol. boiling alcohol (Duvillier, *C. R.* 95, 456).—$HA'HCl$. Crystallises with difficulty. — $H_2A'_2H_2SO_4$: prisms; v. sol. water. — $HA'HAuCl_4aq$: short trimetric prisms. The c o p p e r s a l t forms an intense blue solution.

Di-methyl-α-amido-isovaleric acid. *Methylo-iodide* of the *methyl ether.*

Pr.CH(NMe_3I).CO_2Me. Formed by heating MeI (4 pts.) with zinc amido-valerate (1 pt.) and ZnO (1 pt.) at 110° for 16 hrs. (Duvillier, *C. R.* 110, 640). Yields {Pr.CH(NMe_3Cl).CO_2H}$_2PtCl_4$4aq and Pr.CH(NMe_3Cl).CO_2HAuCl_3.

METHYLAMINE CNH_5 *i.e.* $CH_3.NH_2$. Mol. w. 31. (−6°) (Hofmann, *B.* 22, 701). S.G. $-\frac{10.8}{}$ ·699. H.F.p. 9,540. H.F.v. 8,380 (Thomsen, *Th.*). H.C. 256,900 (Müller, *Bl.* [2] 44, 609). *Heat of neutralisation* by HCl: 25,900 (Müller, *A. Ch.* [6] 15, 531). S. (gas) 1150 at 12·5°; 950 at 25°.

Occurrence.—1. In bone oil (Anderson, *A.* 80, 44).—2. In *Mercurialis annua* and *M. perennis* (Schmidt, *B.* 10, 2226; *A.* 193, 73; *cf.* Reichardt, *Z.* 1868, 734).—3. In herring-brine (Bocklisch, *B.* 18, 1922).—4. In crude wood spirit (G. Williams, *Chem. Gaz.* 1853, 409; Commaille, *J.* 1873, 686; Vincent, *C. R.* 77, 898).—5. In the product of the distillation of beet-root molasses (Duvillier a. Buisine, *A. Ch.* [5] 23, 317).—6. In the 'yolk' or '*suint*' of sheep. When an aqueous extract of this substance is allowed to stand for some time, and is then boiled, it gives off 4 pts. of NH_2Me for 95 pts. of NH_3 and 1 pt. of NMe_3 (Buisine, *C. R.* 104, 1292).

Formation.—1. Discovered by Wurtz, who obtained it by distilling methyl cyanate (or cyanurate) with potash (*C. R.* 28, 223, 323; *A. Ch.* [3] 30, 443).—2. By decomposing methyl-urea with potash (Wurtz).—3. In small quantity, together with $NHMe_2$ and NMe_3, by heating ammonia with MeI (Hofmann, *A.* 79, 19). Formed also by heating the methyl ethers of other inorganic acids with ammonia.—4. By heating wood spirit with ammonium chloride or iodide at 300° (Berthelot, *J.* 1852, 551; Girard, *Bl.* [2] 24, 121; *cf.* Weith, *B.* 8, 458). By heating methyl alcohol (3 pts.) with NH_4Cl (2 pts.) and HCl (1 pt.) at 207° for 30 hours Dusart a. Bardy converted one-third of the NH_3 into NH_2Me (*C. R.* 74, 188).—5. By heating methyl alcohol with ammoniacal $ZnCl_2$ (Gasiorowsky, *B.* 17, 639).—6. By heating morphine or codeïne with KOH (Wertheim, *A.* 73, 210; Anderson, *A.* 77, 374).—7. By distilling glycocoll with BaO (Cahours, *A.* 109, 28).—8. By the action of chlorine on theobromine or caffeïne (Rochleder a. Hlasiwetz, *J.* 1850, 434, 437).—9. In small quantity by reducing HCy with zinc and dilute H_2SO_4 (Mendius, *A.* 121, 129).—10. By passing a mixture of HCy and hydrogen over platinum-black at 110° (Debus, *A.* 128, 200).—11. By reducing nitro-methane with iron filings and dilute HOAc (Preibisch, *J. pr.* [2] 7, 480).—12. By digesting di-methyl-uric acid with HClAq for several hours at 170° (Hill a. Mabery, *Am.* 2, 310).

Preparation.—1. By distilling methyl cyanurate with aqueous KOH (Wurtz). The distillate is received in dilute HCl, and the methylamine hydrochloride dried and distilled with quicklime. 2. A mixture of acetamide (1 mol.) and bromine (1 mol.) is treated in the cold with a 10 p.c. solution of KOH till nearly decolourised. The solution of methyl-bromo-amide thus obtained is then run in a slow stream into a 30 p.c. solution of 3 mols. of KOH heated to 60°-70° and digested for 10 or 15 mins. till decolourised. The solution is then boiled and the methylamine received in HCl; the yield is 87 p.c. of the theoretical (Hofmann, *B.* 15, 765; 18, 2741).—3. Methyl nitrate (1 mol.) is heated in closed vessels at 100° with a solution of ammonia (1 mol.) in wood spirit. Besides the nitrate of mono-methyl-amine there is formed tetra-methyl ammonium nitrate together with small quantities of di- and tri-methylamine nitrates. At the end of the reaction the product is neutralised with sulphuric acid, heated to evaporate off the alcohol, and the residue decomposed by potash, and the bases received in hydrochloric acid. The hydrochlorides are treated with absolute alcohol to remove the ammonium chloride, and again decomposed, the bases being received in sulphuric acid. The sulphates are then treated with absolute alcohol in which mono-methyl-amine sulphate is insoluble. To remove the last traces of impurities the insoluble sulphate is again decomposed and converted into di-methyl-oxamide, which yields on decomposition pure mono-methyl-amine (Duvillier a. Buisine, *A. Ch.* [5] 23, 322; *cf.* Juncadella, *C. R.* 48, 342).—4. By the action of tin and HCl on chloropicrin (Wallach, *A.* 184, 51; *cf.* Geisse, *A.* 109, 282).—5. By heating dry ammonium methyl-sulphate at 300° and distilling the product with potash (Milner Morrison, *Pr. E.* 10, 275).

Properties.—Colourless gas with strong ammoniacal odour. Not solid at −75°. Turns red litmus blue. Fumes strongly with HCl. Rapidly absorbed by water and by charcoal. Of all known gases it is the most soluble in water. Burns in air with livid yellowish flame (difference from NH_3). The aqueous solution of methylamine is extremely caustic, and gives off the gas when boiled. It ppts. metallic salts, for the most part in the same manner as ammonia. Zinc hydroxide is, however, soluble in a large excess of methylamine. With cupric salts it gives a bluish-white pp. dissolving in excess and forming a deep-blue solution. With salts of Cd, Ni, and Co it forms pps. insoluble in excess (difference from NH_3). It ppts. lead nitrate but not lead acetate. With mercurous nitrate it gives a black pp.; with $HgCl_2$ a white pp.; with $AgNO_3$ it gives a pp. of Ag_2O soluble in excess. It dissolves AgCl. With chloride of gold it gives a brownish-yellow pp., soluble in excess. Platinic chloride gives a yellow crystalline pp.

Reactions.—1. Passage through a *red-hot tube* converts it into hydrogen, CH_4, ammonia, and HCy. No acetylene, benzene, or C_2H_4 is formed (Muller, *Bl.* [2] 45, 438). When an aqueous solution of methylamine is set on fire, HCy is found in the residue (Tollens, *Z.* [2] 2, 516).—2. Heated *potassium* forms hydrogen and KCy.—3. *Cyanogen chloride* forms methyl-cyanamide (Cahours a. Cloëz, *C. R.* 38, 354).—4. *Iodine* forms $MeNI_2$.—5. CO_2 forms methylamine methyl-carbamate.—6. According to Berthelot, heating with saturated HIAq yields ammonia and CH_4.—7. $COCl_2$ yields NHMe.COCl [90°].—8. Liquid MeCl, under pressure, forms NMe_4Cl and $NMeH_3Cl$ (Vincent a. Chappuis, *C. R.* 102, 436).—9. MeBr (1 mol.) in MeOH at 100° forms, chiefly, NMe_4Br. In like manner MeI forms NMe_4I (Duvillier a. Buisine, *C. R.* 90, 1426).—10. *Benzoic aldehyde* added to aqueous $NMeH_2$ forms PhCH:NMe, an oil (o. 180°) which yields benzyl-methylamine (185°) on reduction (Zaunschirm, *A.* 245, 281).—11. *o-Oxy-benzoic aldehyde* forms C_8H_9NO (229°) (Dennstedt a. Zimmer-

mann, *B.* 21, 1553).—12. '*Dicyanamidobenzoyl*' (*cf.* vol. i. p. 155) forms small needles of $C_{10}H_{10}N_4O$ (Griess, *B.* 18, 2420).—13. *Diazobenzene chloride* added to a cool 33 p.c. solution of methylamine forms $MeN(N_2Ph)_2$ [113°] which crystallises in yellow needles, v. sol. ether, m. sol. alcohol. It is reduced by Zn and HOAc to methylamine and phenylhydrazine. Boiling dilute H_2SO_4 gives nitrogen, aniline, MeOH, phenol, and some $PhN_2C_6H_4NH_2$ (Goldschmidt a. Badl, *B.* 22, 934). — 14. o-*Diazo-anisole chloride* forms yellow needles of the compound $MeN(N_2.C_6H_4OMe)_2$ [141°] (G. a. B.).—15. *p-Diazo-anisole chloride* forms $MeN(N_2C_6H_4OMe)_2$ [112°] (G. a. B.).—16. *p-Diazo-toluene chloride* forms $MeN(N_2C_6H_4Me)_2$ [147°].

Salts.—B'HCl. Large deliquescent laminæ (from water), may be sublimed. Sol. alcohol, insol. $CHCl_3$.—$B'HAuCl_4$ aq. Trimetric crystals (Topsoë, *J.* 1883, 618).—$B'HAuCl_4$. Monoclinic (T.). — $B'_2H_2PtCl_6$. Golden hexagonal scales (Lüdecke, *J.* 1880, 511). S. 2 at 14°. Insol. alcohol, not decomposed by boiling water (De Coninck, *Bl.* [2] 45, 131).—$B'_2H_2Cl_2PtBr_4$. Scarlet crystals (Maly a. Hinterberger, *M.* 3, 89).—B'_2PtCl_2. Insoluble green powder.—B'_4PtCl_2. V. e. sol. water.—$B'_2H_2IrCl_6$. Small hexagonal brownish-black plates (Vincent, *Bl.* [2] 43, 154). —$B'_8H_8Rh_2Cl_{14}$ (Vincent, *C. R.* 101, 322).—$B'_2H_2HgCl_4$. Monoclinic crystals, v. sol. water. —$B'HHgCl_3$. Rhombohedral crystals (T.).—$B'_2H_2CuCl_4$. Trimetric crystals.—$B'_2H_2PdCl_4$.—B'HBr. Large deliquescent plates (from alcohol), v. sol. water and alcohol.—B'HI.—$B'_5H_5I_5 3BiI_3$. Scarlet pp. (Kraut, *A.* 210, 312).—$B'_3H_3I_3 2BiI_3$. Crystalline pp. (K.).—$B'HNO_3$. Elongated trimetric prisms. Deliquescent, v. sol. water, sl. sol. cold alcohol. [100°] (Franchimont, *R. T. C.* 2, 338).—$B'_2H_2SO_4$. Deliquescent needles, insol. alcohol.—$B'HMeSO_4$. Crystals, v. e. sol. water (Claesson a. Lundvall, *B.* 13, 1701).—$B'HVO_3$ (Bailey, *C. J.* 45, 692).—$B'HVO_3 \frac{1}{2}$aq. Colourless acicular crystals (Ditte, *C. R.* 104, 1844).—$B'_2(H_2O)(V_2O_5)_2$ 4aq. Yellow powder (D.). — $B'_4(H_2O)_2(V_2O_5)_3$ 3aq (B.).—$B'_2H_2CO_3$. Formed, together with methyl-carbamic acid $NMeH.CO_2H$, by decomposing $CaCO_3$ with methylamine hydrochloride. Deposited in crystals from the liquid distillate. — $B'_2H_2C_2O_4$. Prisms, v. sol. water, insol. alcohol.—Benzene sulphonate [147°] (Norton a. Westenhoff, *Am.* 10, 129).—Valerate $NH_2Me2CMe_3CO_2H$? [81°]. (175°). From NH_2Me and tri-methyl-acetic acid at 150° (Franchimont a. Klobbie, *R. T. C.* 6, 234).

Acetyl derivative C_3H_7NO *i.e.* NMeAcH. *Methyl-acetamide.* [28°]. (206°). From EtOAc and aqueous methylamine at 150° (Hofmann, *B.* 14, 2725). — $NMeAcHHNO_3$. [58°]. Large hygroscopic crystals (Franchimont, *R. T. C.* 2, 341).

Di-acetyl derivative $C_5H_9NO_2$ *i.e.* $NMeAc_2$. (192°). A product of the action of Ac_2O on methyl-acetyl-urea (H.). Liquid, miscible with water. Split up by HCl into methylamine and acetic acid.

Tri-chloro-acetyl derivative $CCl_3.CO.NHMe$. [106°]. From CCl_3CO_2Et and aqueous methylamine (Franchimont a. Klobbie, *R. T. C.* 6, 234). White crystals, sl. sol. water and ether. Slowly attacked by pure HNO_3, which gives off N_2O.

Valeryl derivative $CMe_3.CO.NHMe$. [91°]. (204°). V.D. 3·98. From $Me_3C.COCl$ and NH_2Me. Methylamine and $Me_3C.CO_2Me$ yield only $(Me_3C.CO_2H)_2NH_2Me$. V. sol. water and alcohol (F. a. K.). Pure HNO_3 gives off N_2O.

Heptoyl derivative $C_6H_{13}.CO.NHMe$. [9°]. (266°). S.G. $\frac{15}{}$ ·895. Thick liquid (F. a. K.).

Benzoyl derivative $C_6H_5.CO.NHMe$. [78°]. Crystallises from alcohol (Romburgh, *R. T. C.* 4, 388).

o-*Amido-benzoyl derivative* $C_6H_4(NH_2).CO.NHMe$. [80°]. From isatoic acid and methylamine solution (Weddige, *J. pr.* [2] 36, 150). Thick prisms (from benzene), v. e. sol. alcohol and ether, sol. hot water. Ac_2O gives $C_6H_4(NHAc).CO.NHMe$ [172°]. BzCl forms $C_6H_4(NHBz).CO.NHMe$ [181°] (Körner, *J. pr.* [2] 36, 159).

Other alkoyl derivatives are described under the acids from which they are derived.

Methyl-di-chloro-amine $CH_3.NCl_2$. (60° uncor.). Pungent yellow liquid (Köhler, *B.* 12, 770).

Methyl-di-bromo-amine $CH_3.NBr_2$. Formed by the action of bromine and potash on methylamine hydrochloride (Hofmann, *B.* 15, 767). Extremely pungent liquid. Slowly converted into methylamine by HCl.

Methyl-di-iodo-amine $CH_3.NI_2$. Formed by the action of iodine on aqueous methylamine (Wurtz, *A. Ch.* [3] 30, 455). Prepared by adding iodine (1 g.) and water (50 g.) to methylamine hydrochloride, and then adding aqueous NaOH (Raschig, *A.* 230, 221). Brownish-red pp.; quickly becoming brick-red. Completely soluble in aqueous HCl, soon decomposing into methylamine and ICl. Ammonia forms $NMeH_2$ and NHI_2. Cold potash dissolves it, forming methylamine, KIO_3, and KI.

Methyl-nitro-amine $CH_3.NH.NO_2$. [38°]. Obtained by treating methyl chloroformate with methylamine, nitrating the resulting methyl methyl-carbamate $CH_3NH.CO.OMe$, and boiling the product with ammonia (Franchimont a. Klobbie, *R. T. C.* 7, 354; 8, 297). Formed also by decomposing $NO_2.NMe.CO.CO.NMe.NO_2$ with aqueous ammonia. Colourless needles, sol. alcohol. Strongly acid in reaction. Converted by KOH and MeI into crystalline $Me_2N.NO_2$.—$KMeN.NO_2$. Slender needles, sol. alcohol and water.

Dimethylamine C_2H_7N *i.e.* $(CH_3)_2NH$. Mol. w. 45. (7·2°) (Hofmann, *B.* 22, 702). S.G. $\frac{-5.8}{}$ ·687. S.V. 152·4 (Ramsay). H.F.p. 12,720 (Thomsen); 3,500 (Muller, *Bl.* [2] 44, 609). H.F.v. 10,980 (Thomsen, *Th.*). H.C. 42,600 (M.). *Heat of neutralisation* (by HCl): 23,980 (Müller, *A. Ch.* [6] 15, 531).

Occurrence.—In herring-brine (Bocklisch, *B.* 18, 1924).

Formation.—1. One of the products of the action of MeI on ammonia (Hofmann).—2. A mixture of mono-, di-, and tri- methyl-amine is obtained by heating methyl alcohol with ammoniacal $ZnCl_2$ at 200°–220° (Merz a. Gasiorowski, *B.* 17, 639).—3. In small quantity by heating the sulphite of aldehyde-ammonia in a sealed tube, or by distilling it with lime (Petersen, *A.* 102, 317).

Preparation.—1. The mixture of iodides obtained by heating ammonia with MeI is distilled with potash, and the evolved bases dried by KOH and condensed by a freezing mixture, the bases NMe_3, NMe_2H, and $NMeH_2$ being separated by means of oxalic ether (Hofmann, *Pr.* 12, 380).—2. The bases obtained from MeBr and NH_3 are treated with nitrous acid, and the dimethylnitrosamine decomposed by HCl and distilled over sodium (Hofmann).—3. Nitroso-dimethylaniline hydrochloride (2 pts.) is boiled with water (90 pts.) and aqueous NaOH (10 pts. of S.G. 1·25) (Baeyer a. Caro, *B.* 7, 964; 8, 616).

Properties.—Highly alkaline liquid or gas. Has not been solidified. If to an alcoholic solution of the base picryl chloride $C_6H_2(NO_2)_3Cl$ be added, and then H_2SO_4 followed by water, there is formed a characteristic yellow pp. of tri-nitro-di-methyl-aniline (Van Romburgh, *R. T. C.* 2, 106).

Reactions.—1. MeCl forms only NMe_4Cl and NMe_2HHCl (Vincent a. Chappuis, *C. R.* 102, 436).—2. SO_2Cl_2 forms oily $NMe_2.SO_2Cl$ (183°–187°) and $SO_2(NMe_2)_2$ (Behrend, *B.* 14, 1810).—3. *Cyanamide* heated with $NHMe_2$ at 110° forms di-methyl-guanidine (Tatarinoff, *C. R.* 89, 608). 4. *p-Diazotoluene chloride* forms $NMe_2.N_2C_7H_7$ [46°] (Goldschmidt a. Badl, *B.* 22, 935).

Salts.—B′HCl. V. sol. chloroform (difference from NH_4Cl and $NMeH_3Cl$ (Behrend, *B.* 15, 1611; *A.* 222, 119).—$B'HAuCl_4$. Monoclinic needles. — $B'_2H_2PtCl_6$. Trimetric needles. — $B'_2H_2IrCl_6$. Trimetric octahedra; $a:b:c = 1·969:1:1·954$ (Vincent, *Bl.* [2] 43, 154).—$B'_6Rh_2Cl_{12}$ 3aq. Large dark garnet-red prisms (Vincent, *Bl.* [2] 44, 513; *C. R.* 101, 322).—$B'_2H_2HgCl_4$. Monoclinic crystals (Topsoë, *J.* 1883, 618).—$B'HHg_2Cl_5$. Monoclinic crystals (T.). — $B'_2H_2Hg_5Cl_{12}$. Triclinic crystals. — $B'_2H_2SnCl_6$. Trimetric tables (Hjortdahl, *J.* 1882, 474).—$B'_3H_3CuCl_5$.—$B'_2H_2CuCl_4$. Crystals. —$B'HCuCl_3$. Monoclinic crystals (T.).—B′HBr. —$B'_2H_2PtBr_6$. Trimetric needles.—$B'_5H_5I_5 3BiI_3$. —$B'_3H_3I_3 2BiI_3$ (Kraut, *A.* 210, 314).—$B'HNO_3$. [74°]. Long hygroscopic needles or prisms. V. sol. alcohol (Franchimont, *R. T. C.* 2, 338; 3, 229). Decomposed by heat, yielding nitrogen, CO_2, and dimethylamine (Romburgh, *R. T. C.* 5, 246).—$B'HVO_3$ (Bailey, *C. J.* 45, 693).—$B'_4(H_2O)_2(V_2O_5)_3$ 4aq.—Benzene sulphonate [110°] (Norton, *Am.* 10, 129).—*p*-Toluene sulphonate [78°] (N.).

Acetyl derivative NMe_2Ac. (166°). S.G. $\frac{20}{}$ ·941. From dimethylamine and AcCl dissolved in ether (Franchimont, *R. T. C.* 2, 121, 342). Colourless liquid. Fuming HNO_3 forms in the cold $NMe_2.NO_2$ [57°].

Tri-chloro-acetyl derivative $CCl_3.CO.NMe_2$. [104°] (C.). S.G. $\frac{15}{}$ 1·441 (F. a. K.). From $CCl_3.CO.CCl_3$ and NMe_3 (Cloëz, *A. Ch.* [6] 9, 145).

Heptoyl derivative $C_6H_{13}.CO.NMe_2$. (243°). S.G. $\frac{15}{}$ ·894. Solidifies below −10° (Franchimont a. Klobbie, *R. T. C.* 6, 249). With HNO_3 it gives di-methyl-nitro-amine.

Valeryl derivative $CMe_3.CO.NMe_2$. (185°). S.G. $\frac{17}{}$ ·912. Liquid, v. sol. water. Not solidified at −17°. HNO_3 (S.G. 1·52) forms $NMe_2.NO_2$.

Benzoyl derivative $C_6H_5.CO.NMe_2$. [42°]. (256° uncor.). Crystals, v. sol. water. Split up by aqueous HCl at 200° into HOBz and $HNMe_2$ (Hallmann, *B.* 9, 846). Conc. HNO_3 gives $C_6H_4(NO_2).CO.NMe_2$ (Romburgh, *R. T. C.* 4, 385). With $COCl_2$ it forms deliquescent crystals of $C_6H_5.CCl_2.NMe_2$ [36°] decomposed by water into HCl and $C_6H_5.CO.NMe_2$.

Di-methyl-iodo-amine NMe_2I. From dimethylamine, iodine, and NaOH. Pale-yellow pp., which rapidly decomposes (Raschig, *A.* 230, 223).

Dimethylnitrosamine NMe_2NO (148° at 725 mm.). Formed by treating an aqueous solution of dimethylamine hydrochloride with potassium nitrite (E. Fischer, *B.* 8, 1587; Renouf, *B.* 13, 2169). Yellow oil. Volatile with steam. Reduced by zinc-dust and HOAc to di-methyl-hydrazine. Decomposed by boiling HCl into NMe_2H and nitrous acid.—B′HCl: white needles, decomposed by water or alcohol.

Di-methyl-nitro-amine $NMe_2.NO_2$. [57°]. From NMe_2Ac and HNO_3 (Franchimont). Large crystals.

Di-methyl-amine-tri-bromide Me_2NBr_3 2aq or $\begin{matrix} Me_2 \\ H_2 \end{matrix}\!\!>\!N\!<\!\!\begin{matrix} Br_3 \\ (OH)_2 \end{matrix}$. Formed, as a yellow pp., on adding an excess of bromine-water to a cold solution of dimethylamine—$2Me_2NH + 4Br + 2H_2O = C_2H_{10}NBr_3O_2 + Me_2NH_2Br$. Yellow powder. Sol. alcohol and ether, v. sl. sol. water. It is very unstable: on keeping over-night in a closed vessel it liquefies to a brown fluid containing free bromine; but under water it can be kept for several days. Alkalis and acids decompose it at once; thus HCl gives dimethylamine hydrochloride according to the equation $C_2H_{10}Br_3NO_2 + 2HCl = Me_2NH,HCl + 3Br + Cl + 2H_2O$ (Raschig, *B.* 18, 2249).

Trimethylamine C_3H_9N *i.e.* NMe_3. Mol. w. 59. (3·5°). S.G. $\frac{-5·2}{}$ ·662 (Hofmann, *B.* 22, 703). H.F.p. 15,870 (Thomsen, *Th.*); 14900 (Müller, *Bl.* [2] 44, 609). H.F.v. 13550. H.C. 577,600 (M.). *Heat of neutralisation* (by HCl) 17,900 (Müller, *A. Ch.* [6] 15, 531).

Occurrence.—In herring-brine (Hofmann, *C. J.* 5, 288; *cf.* Wertheim, *J.* 1851, 480). In the flowers of *Cratægus oxyacantha* (Wicke, *A.* 91, 121), *C. monogyna*, *Pyrus aucuparia*, and *P. communis* (Wittstein, *J.* 1854, 479). In the stinking goosefoot (*Chenopodium vulvaria*) (Dessaignes, *J.* 1851, 481); in *Arnica montana* (Hesse, *J.* 1864, 458); and in the seeds of the beech (Brandl a. Rakowiecki, *J.* 1864, 607). It also occurs in *Mercurialis annua* (E. Schmidt, *B.* 10, 2226). In human urine (Dessaignes, *A.* 100, 218), and in calves' blood which has stood 12 hours (Dessaignes, *J. Ph.* [3] 32, 43). In ergot of rye (Walz, *J.* 1852, 552; Ritthausen, *Rép. chim. pur.* 1863, 420; *cf.* Brieger, *H.* 11, 184). In small quantity in guano (Hesse, *J.* 1857, 402). In bone oil (Anderson, *A.* 80, 51). According to Ludwig (*Z.* 4, 96) it occurs in small quantity in several Austrian and Hungarian wines. In the product of the destructive distillation of putrid brain (Selmi, *G.* 6, 468) and of beet-root molasses (Vincent, *C. R.* 84, 1139; 85, 667; *J. Ph.* [4] 30, 132; Roscoe, *C. N.* 39, 107). In the putrefaction of yeast (A. Müller, *J.* 1857, 402) and of wheat dough (Sullivan, *J.* 1858, 231). In most of the cases here mentioned the trimethylamine is probably obtained from betaïne,

neurine, or lecithin, either by putrefactive decomposition or in the chemical treatment.

Formation.—1. Together with $NMeH_2$ and NMe_2H by the action of ammonia on MeI, and separated by treatment with oxalic ether, with which it does not react (Hofmann, *C. J.* 4, 304). 2. By the distillation of NMe_4OH (Hofmann, *A.* 93, 325).—3. By heating narcotine with KOH at 280° (Wertheim, *A.* 73, 208).—4. By heating extract of calamus root with alkali (Thoms, *B.* 21, 1912).—5. By passing coal gas through heated zinc-dust (Williams, *C. N.* 51, 15).

Preparation.—1. The residues in the preparation of sugar from beet-root are, after fermentation, subjected to dry distillation. The aqueous portion of the distillate is neutralised by H_2SO_4, ammonium sulphate separated by crystallisation, and, after evaporation, the trimethylamine expelled by an alkali. Commercial trimethylamine still contains methylamine, ethylamine, dimethylamine, propylamine, and isobutylamine. The proportion in which these bases are present varies greatly in different samples. To the aqueous solution of the bases oxalic ether is added, the primary bases being ppd. as di-alkyl-oxamides. The mother-liquor is distilled with addition of KOH and the dry bases dissolved in absolute alcohol. Oxalic ether is then added to the alcoholic solution, when the diamines are converted into di-alkyl-oxamic ethers, and the trimethylamine can be obtained by distillation (Vincent, *C. R.* 89, 238, 788; Duvillier a. Buisine, *C. R.* 89, 48, 709; 92, 250; *A. Ch.* [5] 23, 298; *cf.* Eisenberg, *B.* 13, 1669). 2. Perfectly pure trimethylamine is obtained by distilling NMe_4OH and rectifying over sodium (Hofmann, *B.* 22, 699).

Properties.—Gas with ammoniacal and fishy odour. Remains liquid at −75°. V. e. sol. water. When an aqueous solution is strongly cooled a hydrate NMe_3 7aq [4·3°] separates.

Reactions.—1. $KMnO_4$ oxidises it to CO_2 and oxalic acid (Wallach a. Claisen, *B.* 8, 1237).—2. At a *red heat* it is converted into HCy and NH_4Cy (Willm, *Bl.* [2] 41, 449). Passed with *hydrogen* through a *red-hot tube* it yields NH_3, cyanogen, hydrocarbons, and $CH_2(NMe_2)_2$ (Romeny, *B.* 11, 835).—3. CS_2 forms NMe_3CS_2, crystallising in white needles [125°]. This body is m. sol. chloroform and dilute alcohol, nearly insol. absolute alcohol, CS_2, and benzene. It splits up into its components, even at ordinary temperatures, but with dilute HCl it forms NMe_3CS_2HCl and $(NMe_3CS_2)_2H_3Cl_3$. Conc. HClAq splits it up into its components. Phosphoric acid forms $(NMe_3CS_2)_2H_3PO_4$ (Bleunard, *C. R.* 87, 1040).—4. *Glycol chlorhydrin* forms neurine chloride $NMe_3.ClCH_2.CH_2OH$.—5. *Chloro-acetic acid* forms betaïne $CH_2<{NMe_3 \atop CO}>O$.—6. *Dichlorhydrin* of glycerin forms 'sepine' chloride $C_3H_5Cl(OH).NMe_3Cl$ and 'aposepine' chloride $C_3H_5(OH)(NMe_3Cl)_2$ (Niemikovitch, *M.* 7, 249). — 7. *Hexa-chloro-acetone* forms $CCl_3.CO.NMe_2$ [104°] (Cloëz, *A. Ch.* [6] 9, 145). 8. When heated with aniline hydrochloride it yields a distillate of methyl-aniline.

Salts.—B′HCl: decomposes at 285°, giving off NMe_3 and MeCl, and leaving mono- and dimethylamine hydrochlorides. At 305° ammonia and methyl chloride are given off from the residue, and at 325° the whole has sublimed, the sublimate consisting of NH_4Cl and methylamine hydrochloride. This decomposition may be utilised for the manufacture of MeCl (Vincent, *C. R.* 84, 1139; 85, 666).—B′HBr: decomposed between 230° and 300° into NMe_3, ammonia, and MeBr.—B′HI: white scales, decomposed between 210° and 280° into NMe_3, ammonia, MeI, and a residue of NMe_4I.—$B'_2H_2PtCl_6$: orange regular crystals (Lüdecke, *J.* 1880, 512; Topsoë, *J.* 1883, 618). S. (alcohol) ·0362. More soluble than the di- and still more so than the mono-methylamine platinochloride (Eisenberg, *A.* 205, 139).—$B'_2H_2IrCl_6$: reddish-brown octahedra (Vincent, *Bl.* [2] 43, 155).—$B'HAuCl_4$: yellow monoclinic crystals. V. sl. sol. water, sol. alcohol. [220°] (Hesse, *J. pr.* 71, 480; Zay, *G.* 13, 420).—$B'_6H_6Rh_2Cl_{12}$ 9aq (Vincent, *C. R.* 101, 322).—$B'HCdCl_3$: trimetric crystals (Hjortdahl, *J.* 1882, 475).—$B'_2H_2HgCl_4$: monoclinic crystals (T.).—$B'HHgCl_3$: monoclinic crystals (T.).—$B'HHg_2Cl_5$: triclinic crystals (T.).—$B'HHg_5Cl_{11}$: rhombohedra (T.).—$B'HCuCl_3$ 2aq: monoclinic crystals.—$B'HCdBr_3$: six-sided hexagonal prisms.—$B'_2H_2PtBr_6$.—$B'_3H_3I_3$3BiI$_3$.—$B'_3H_3I_3$2BiI$_3$: six-sided crimson plates (Kraut, *A.* 210, 316).—$B'HNO_3$. [153°]. Long needles or prisms, v. sol. hot alcohol (Franchimont, *R. T. C.* 2, 338).—$B'_2H_2SO_4Al_2(SO_4)_3$ 24aq. [100°.] Large crystals (Reckenschufs, *A.* 83, 343).—$B'_6(H_2O)_3(V_2O_5)_5$ 7aq (Bailey, *C. J.* 45, 692).—$B'H_2C_2O_4$: plates (Loschmidt, *J.* 1865, 375).—Benzene sulphonate [89°] (Westenhoff, *Am.* 10, 129).

Tetra-methyl-ammonium hydroxide NMe_4OH. *Heat of neutralisation* (by HCl) 27,900 (Müller, *A. Ch.* [6] 15, 531). Obtained by digesting NMe_4I with moist Ag_2O (Hofmann, *Tr.* 1850, 93; *C. J.* 4, 321). White crystalline deliquescent mass, v. e. sol. water. Absorbs CO_2 with avidity. Its solution is strongly alkaline and caustic. Decomposed by heat into NMe_3 and MeOH (Hofmann, *B.* 14, 494). Neutralises acids, forming the following salts.

Iodide NMe_4I. S.G. $\frac{17}{}$ 1·827; $\frac{19·5}{}$ 1·831 (Clarke, *Am. S.* [3] 16, 401). The chief product of the action of MeI on ammonia and on mono-, di-, and tri- methylamine. Best obtained by heating a solution of NH_3 in methyl alcohol with MeI at 100°-120° (Lawson a. Collie, *C. J.* 53, 624). Dimetric prisms (from water). Sl. sol. water, almost insol. alcohol, insol. ether. Decomposes at a dull red heat into NMe_3 and MeI. Unites with iodoform forming red crystals of NMe_4I2CHI_3. When heated with liquefied NH_3, in which potassium has been dissolved, the products are KI, NMe_3, and ethane (Thompson a. Cundall, *C. J.* 53, 761). Unites with halogens, forming NMe_4I_3 (Welzien, *A.* 91, 41; 99, 1), NMe_4I_5 [130°], NMe_4I_9 [110°] (Geuther, *A.* 240, 68), NMe_4I_{11}, NMe_4ICl_2, NMe_4ICl_4, $(NMe_4I)_2Cl_6$ (W.), NMe_4IBr_2 [190°] (Dobbin a. Masson, *C. J.* 49, 851), and NMe_4ICl_2 [216°-220°]. The compound NMe_4I_5 is converted by ammonia into $NMe_4I_3NHI_2$, a dark-coloured explosive body (Stahlschmidt, *P.* 119, 421).—NMe_4HgI_3: small light-yellow prisms, m. sol. alcohol.—$(NMe_4I)_2$3HgI$_2$: lemon-yellow scales (Risse, *A.* 107, 223).—$(NMe_4I)_3$2BiI$_3$: amorphous scarlet pp. (Kraut, *A.* 210, 316).—NMe_4IHgCy_2: white crystals. On heating for a

long time at 200° it is converted into the isomeric $NMe_4CyHgICy$ (Claus a. Merck, *B.* 16, 2738).

Bromide NMe_4Br. S. 55·26 at 15°. Obtained by neutralising the hydroxide by HBr. Very deliquescent needles. Dissociates at 360° into NMe_3 and MeBr (Lawson a. Collie, *C. J.* 53, 625). Forms crystalline compounds with the halogens (Dobbin a. Masson, *C. J.* 49, 848).—$(NMe_4Br)_2PtBr_4$: regular octahedra (Topsoë).

Chloride NMe_4Cl. H.F. 27,500 (Müller, *Bl.* [2] 44, 192). Deliquescent crystals. Decomposed above 360° into NMe_3 and, doubtless, MeCl (L. a. C.).—$(NMe_4Cl)_2HgCl_2$: trimetric crystals (T.).—$NMe_4Cl5HgCl_2$: rhombohedra.—$(NMe_4Cl)_2CuCl_2$: trimetric crystals.—NMe_4AuCl_4: dimetric crystals.

Fluoride NMe_4F. From the hydroxide and HF. Radiating crystals. Decomposes at 180° into NMe_3 and MeF (L. a. C.).

Nitrate NMe_4NO_3. S. (94 p.c. alcohol) 3 at 11°. Obtained, together with $NMeH_3NO_3$, $NMe_2H_2NO_3$, and NMe_3HNO_3 by heating methyl nitrate with NH_3 dissolved in MeOH (Duvillier a. Buisine, *C. R.* 90, 872). The di- and tri-methylamine are formed in very small quantity (Duvillier a. Malbot, *C. R.* 100, 177). Formed also by treating NMe_4I with $AgNO_3$ (Lawson a. Collie, *C. J.* 53, 628). Needles or plates, v. sol. water, sl. sol. cold alcohol. Not attacked by boiling KOHAq. Above 300° it yields NMe_3, formic acid, $MeNO_2$, and NO (L. a. C.).

Nitrite NMe_4NO_2. From NMe_4I and $AgNO_3$. Deliquescent crystals. Decomposed above 300° into NMe_3, $MeNO_2$, Me_2O, NO, and oxygen (L. a. C.).

Sulphate $(NMe_4)_2SO_4$. [280°]. Deliquescent crystals. Decomposed above 280° into NMe_3 and NMe_4SO_4Me, which then undergoes further decomposition (L. a. C.).

Chromates $(NMe_4)_2CrO_4$: yellow trimetric crystals, v. e. sol. water (Hjortdahl, *J.* 1882, 475).—$(NMe_4)_2Cr_2O_7$: orange trimetric tables, v. sol. water.

Sulphite $NMe_4SO_3H\,x$aq. [180°]. Decomposes above 300°, yielding NMe_3, SO_2, MeOH, and other products (L. a. C.).

Sulphydrate NMe_4SH. Very deliquescent. Decomposes above 200° into NMe_3 and MeSH.

Phosphate. From NMe_4I and Ag_3PO_4. Forms a strongly alkaline solution. Decomposed at a high temperature into NMe_3, methyl alcohol, and HPO_3 (L. a. C.).

Vanadate NMe_4VO_3 (Bailey, *C. J.* 45, 693).

Carbonates $NMe_4.CO_3H$. H.F. 20,870 (Müller). Obtained by saturating a solution of the base with CO_2 (L. a. C.). Deliquescent crystals, decomposing above 180° into NMe_3, methyl alcohol, and CO_2.—$(NMe_4)_2CO_3$. H.F. 19,100. Obtained by acting on NMe_4I (2 mols.) with $Ag_2CO_3\,\frac{1}{10}Ag_2O$ (Müller, *Bl.* [2] 44, 191).

Oxalate $(NMe_4)_2C_2O_4$. Formed from NMe_4OH and oxalic acid, or from NMe_4I and silver oxalate. Deliquescent crystals, decomposed above 360° into NMe_3 and methyl oxalate, the latter being further resolved into Me_2O, CO, and CO_2.

Cyanide NMe_4Cy. Prisms. Sublimes at 226°. V. sol. water, m. sol. alcohol, insol. ether and chloroform (Claus a. Merck, *B.* 16, 2738).—$NMe_4CyHgCy_2$. [275° uncor.]. Yellow crystals.—$NMe_4CyAgCy$. [212° uncor.]. From AgCy and NMe_4I or NMe_4Cy (Thompson, *B.* 16, 2338). Long colourless prisms or slender needles; v. e. sol. water and alcohol, insol. ether. On dry distillation it yields NMe_3, acetonitrile, and methyl carbamine.

Ferrocyanides $(NMe_4)_2FeCy_6$13aq. Lamino-granular mass (Barth, *B.* 8, 1484).—$(NMe_4)_2H_2FeCy_6$2aq (E. Fischer, *A.* 190, 184).

Ferricyanide $(NMe_4)_3FeCy_6$3aq. From NMe_4I and silver ferricyanide (Bernheimer, *B.* 12, 408). Unstable hygroscopic prisms; sol. water, insol. alcohol.

Cobalticyanide $(NMe_4)_3CoCy_6$13aq. Yellow tables (C. a. M.).

Acetate NMe_4OAc. [c. 70°]. From NMe_4OH and HOAc. Deliquescent needles, decomposed at 200° into NMe_3 and MeOAc (L. a. C.).

Benzoate NMe_4OBz. [220°-230°]. Long deliquescent needles. Decomposed above 230° into NMe_3 and MeOBz (L. a. C.).

Cyanurate $NMe_4OC_3N_3(OH)_2$aq (Claus, *J. pr.* [2] 38, 225).

Picrate. [313°] (Lossen, *A.* 181, 374).

Trimethylamine iodo-methylo-iodide $NMe_3I.CH_2I$. From NMe_3 and methyleneiodide (Hofmann). Needles. Not attacked by NH_3. Moist silver oxide gives $NMe_3(OH).CH_2I$ and $NMe(OH).CH_2.OH$. It yields the platinum salt $PtCl_4(NMe_3Cl.CH_2I)_2$.

Trimethylamine ethylo-iodide $C_5H_{14}NI$ *i.e.* NMe_3EtI. From NMe_3 and EtI (Müller, *A.* 108, 1). Gives the following derivatives (Topsoë, *J.* 1883, 620).—$(NMe_3EtCl)_2HgCl_2$: trimetric crystals.—$NMe_3EtClHgCl_2$: monoclinic crystals.—$NMe_3EtCl(HgCl_2)_2$: trimetric crystals.—$(NMe_3EtCl)_2CuCl_2$: trimetric crystals.—Aurochloride $NMe_3EtAuCl_4$: dimetric crystals.—$(NMe_3EtCl)_2PtCl_4$: regular crystals.—Picrate [300°] (Lossen, *A.* 181, 374). The ethylo-hydroxide is decomposed on distillation into NMe_3, ethylene, and water. NMe_3EtCl on distillation yields MeCl, NMe_2Et, and NMe_3.

Trimethylamine ethylo-tri-iodide NMe_3EtI_3. [64°]. Regular crystals (Lüdecke, *A.* 240, 85).

Tri-methylamine ethylo-penta-iodide NMe_3EtI_5: [26°]; dark-green tables (Geuther, *A.* 240, 66).

Trimethylamine ethylo-ennea-iodide NMe_3EtI_9: [38°]; black-green crystals.

Trimethylamine bromo-ethylo-bromide $C_2H_4Br.NMe_3Br$. From NMe_3 and ethylene bromide at 45° (Hofmann, *C. R.* 47, 558). Needles, v. e. sol. hot alcohol. Ammonia as well as moist Ag_2O converts it into $C_2H_3.NMe_3OH$.—$(C_2H_4Br.NMe_3Cl)_2PtCl_4$. Octahedral crystals.—$C_2H_4Br.NMe_3I$ (Baeyer, *A.* 140, 312).

Trimethylamine iodo-ethylo-iodide $C_2H_4I.NMe_3I$. From neurine, HI, and phosphorus (Baeyer, *A.* 140, 309; 142, 324). Crystalline, sl. sol. cold water. Moist Ag_2O yields $C_2H_3.NMe_3OH$.—$(C_2H_4I.NMe_3Cl)_2PtCl_4$: octahedra.

Trimethylamine allylo-bromide $C_6H_{14}NBr$ *i.e.* $NMe_3C_3H_5Br$. Forms a dibromide $NMe_3C_3H_5Br_3$ [175°] of which the gold salt melts at 148° (Partheil, *B.* 22, 3317).

Trimethylamine bromo-allylo-bromide $NMe_3Br.CH_2.CH:CHBr$. [165°]. Formed from $NMe_3C_3H_5Br_3$ and alcoholic KOH. Colourless prisms, v. sol. water and alcohol, insol. ether,

gives a perbromide $NMe_3Br.CH_2.CHBr.CHBr_2$ crystallising in scales [156°].—Platinochloride $(C_3H_4Br.NMe_3Cl)_2PtCl_4$. [220°]. — Aurochloride $C_3H_4Br.NMe_3AuCl_4$. [181°].

Trimethylamine propylo-iodide NMe_3PrI. [190°] (Langeli, *G.* 16, 385).

Trimethylamine iodo-propylo-iodide $NMe_3I.C_3H_6I$. [151°]. From the allylo-iodide and HI at 100° (Partheil, *B.* 22, 3320). Colourless needles, sol. water and alcohol, insol. ether. Alcoholic KOH regenerates the allylo- compound.—$(C_3H_6I.NMe_3Cl)_2PtCl_4$. [237°].—Aurochloride $(C_3H_6I.NMe_3Cl)AuCl_3$. [135°].

Trimethylamine trimethenyl bromide

$$NMe_3Br.CH\Big<\begin{matrix}CH\\ \|\\ CH\end{matrix}$$

. From the bromo-allylo-bromide and alcoholic KOH.—Aurochloride $(NMe_3Cl.C_3H_3)AuCl_3$.

Dibromide $NMe_3Br.CH\Big<\begin{matrix}CHBr\\ |\\ CHBr\end{matrix}$. [187°].

From the preceding and Br. Colourless, somewhat hygroscopic crystals. Forms a platinochloride [232°] and an aurochloride [193°] both crystallising in tables.

Trimethylamine bromo-pentenyl bromide $C_5H_8BrNMe_3Br$. Formed from trimethylamine and di-bromo-amylene (valerylene bromide) (Ladenburg, *B.* 14, 231, 1342). With HI it forms $C_5H_8BrNMe_3I$. Silver chloride forms $C_5H_8BrNMe_3Cl$, whence $(C_5H_8BrNMe_3Cl)_2PtCl_4$ and $C_5H_8BrNMe_3ClAuCl_3$, both crystalline.

Trimethylamine isoamylo-triiodide $NMe_3C_5H_{11}I_3$. [80°]. From NMe_3 and $C_5H_{11}I$, the product being treated with iodine. Dark-brown prisms, nearly insol. water, v. sol. alcohol.

TRIMETHYLAMMELIDE *v.* vol. ii. p. 325.

DI-METHYL-AMMELINE *v.* vol. ii. p. 321.

METHYL-AMYL-ACETAL *v.* ALDEHYDE.

METHYL-ISOAMYL-ANILINE $C_{12}H_{19}N$ *i.e.* $C_6H_5NMe.C_5H_{11}$. (257°). S.G. $\frac{20}{}$ ·906. Obtained together with C_2H_4 and water by distilling $C_6H_5NMeEtC_5H_{11}OH$ (Hofmann, *A.* 79, 15). Formed also by heating dimethylaniline with isoamyl bromide (Claus a. Rautenberg, *B.* 14, 622).—$B'_2H_2PtCl_6$: crystalline pp.—$(B'HI)_23BiI_3$.

METHYL-AMYL-ARSINE *v.* *Organic compounds* of ARSENIC.

METHYL-AMYL-BENZENE *v.* AMYL-TOLUENE.

Di-methyl-isoamyl-benzene *v.* AMYL-XYLENE.

METHYL - ISOAMYL - BENZENE SULPHONIC ACID $CH_3.C_6H_3(C_5H_{11}).SO_3H$. From *p*-isoamyl toluene by sulphonation (Fittig a. Bigot, *A.* 141, 166).—KA'. The Ba salt is a deliquescent gummy mass.

Di-methyl-isoamyl-benzene sulphonic acid $(CH_3)_2.C_6H_2(C_5H_{11})SO_3H$. Formed by sulphonating isoamyl-xylene (F. a. B.). The K and Ba salts were not obtained in crystals.

METHYL-AMYL-CARBINOL *v.* HEPTYL ALCOHOL.

DI-METHYL AMYLENE DIKETONE $C_9H_{16}O_2$ *i.e.* $CEt_2(CO.CH_3)_2$. *Di-ethyl-acetyl-acetone.* (c. 203°). From $(CH_3.CO)_2CEtNa$ and EtI at 180° (Combes, *A. Ch.* [6] 12, 250). Liquid. Split up by KOH into $CH_3.CO_2K$ and $CH_3.CO.CHEt_2$.

Di-methyl amylene diketone $C_9H_{16}O_2$ *i.e.* $(CH_3.CO.CH_2.CH_2)_2CH_2$. *Di-acetyl-pentane.* [49°]. (212°–215° at 300 mm.). From the carboxylic ether and a dilute solution of KOH in MeOH (Kipping a. Perkin, *C. J.* 55, 337). V. sol. cold ether, alcohol, acetone, chloroform, and light petroleum. Cold conc. HNO_3 dissolves it without decomposition. Conc. H_2SO_4 forms a colourless oil $C_9H_{14}O$.

Di-oxim $(CH_3.C(NOH).CH_2.CH_2)_2CH_2$. [85°]. Colourless moss-like crystals; v. sol. cold water.

DI-METHYL-AMYLENE-DIKETONE CARBOXYLIC ACID $CO_2H.CHAc.CH_2.CH_2.CH_2.CH_2.CO.CH_3$. From its ether and KOH dissolved in MeOH. Liquid, miscible with water. Decomposed by heat into CO_2 and the diketone.

Ethyl ether EtA'. (240° at 200 mm.). Prepared from sodium aceto-acetic ether and $CH_3.CO.CH_2.CH_2.CH_2.CH_2Br$ (Kipping a. Perkin, *C. J.* 55, 333). Thick oil. Alcoholic NH_3 converts it into $Ac.CH_2.CH_2.CH_2.CH_2.C\Big<\begin{matrix}CMe\\ CO\end{matrix}\Big>NH$ [c. 235°], which forms monoclinic crystals; $a:b:c$ = ·7487:1: ·3997; β = 79° 11′. This 'dehydro-amide' yields an acetyl derivative $C_{10}H_{14}AcNO_2$, an oil, converted by boiling water into the amide $CH_3.CO.CH_2.CH_2.CH_2.CH_2.CH(COMe).CONH_2$, which melts between 200° and 228°.

METHYL AMYL ETHER *v.* METHYL AMYL OXIDE.

METHYL AMYL KETONE $C_7H_{14}O$ *i.e.* $CH_3.CO.CH_2.CH_2.CH_2.CH_2.CH_3$. (151°). S.G. $\frac{0}{}$ ·837. Formed by oxidising *sec*-heptyl alcohol obtained from *n*-heptane (Schorlemmer, *A.* 161, 279; 217, 149). Fragrant liquid. Unites with $NaHSO_3$. Yields on oxidation acetic and *n*-valeric acids. Formed also by dissolving heptinene $C_5H_{11}.C\vdots CH$ in conc. H_2SO_4, and distilling the product with water (Behal, *A. Ch.* [6] 15, 270).

Methyl isoamyl ketone $C_7H_{14}O$ *i.e.* $CH_3.CO.CH_2.CH_2.CH(CH_3)_2$. (144°). S.G. $\frac{0}{}$ ·828; $\frac{17}{}$ ·818 (Rohn, *A.* 190, 308); $\frac{0}{0}$ ·821 (Wagner, *J. R.* 16, 705).

Formation.—1. By heating a mixture of calcium hexoate with calcium acetate (Schmidt, *B.* 5, 604).—2. By the action of zinc isoamyl on acetyl chloride (Popoff, *A.* 145, 283).—3. By oxidising the corresponding heptyl alcohol (Grimshaw, *A.* 166, 169).—4. By boiling isobutyl-aceto-acetic acid with aqueous KOH: the yield being 70 p.c. (Purdie, *C. J.* 39, 467).

Properties.—Oil. Reduced by sodium to *sec*-heptyl alcohol and di-isopropyl-pinacone. CrO_3 oxidises it to acetic, isovaleric, and isohexoic acids. It combines with $NaHSO_3$.

Methyl amyl ketone $Me.CO.CHMePr$. (142°–147°). From methyl-propyl-aceto-acetic ether (E. J. Jones, *A.* 226, 293). Oil, smelling of peppermint.

Methyl amyl ketone $CH_3.CO.CHMePr$. (135°). S.G. $\frac{20}{}$ ·815. One of the products of the saponification of methyl-isopropyl-aceto-acetic ether (Van Romburgh, *R. T. C.* 5, 235). Does not combine with $NaHSO_3$. Does not give a solid phenyl-hydrazide.

Methyl amyl ketone $CH_3.CO.CH_2.CMe_3$. (125°–130°). Obtained by oxidising the alcohol $CMe_3.CH_2.CMe_2.OH$ (Butlerow, *A.* 189, 78). Oxidised by CrO_3 to acetic acid and $CMe_3.CO_2H$. Does not combine with $NaHSO_3$.

Methyl amyl ketone $CH_3.CO.CHEt_2$. (138°). S.G. $\frac{22}{}$ ·817. Obtained by boiling di-ethyl-aceto-

acetic ether with baryta-water (Frankland a. Duppa, *A.* 138, 212). Forms an oily compound with $NaHSO_3$.

Methyl amyl ketone $CH_3.CO.CMe_2Et$. *Methyl-amyl-pinacolin.* (132°). S.G. $\frac{0}{}$ ·812; $\frac{21}{}$ ·825. Obtained by the action of $ZnMe_2$ on $CMe_2Et.COCl$ (Wyschnegradsky, *A.* 178, 103). CrO_3 oxidises it to HOAc and $CMe_2Et.CO_2H$.

Methyl amyl ketone $CH_3.CO.C_5H_{11}$. (142°–146°). From *sec*-heptyl alcohol derived from petroleum heptane (90°). Gives acetic acid on oxidation (Schorlemmer, *A.* 166, 172).

Methyl isoamyl diketone $CH_3.CO.CO.C_5H_{11}$. *Methyl-isoamyl-glyoxal* (163°). S.G. $\frac{19}{4}$ ·8814. From methyl nitrosohexyl ketone (Otto a. Pechmann, *B.* 22, 2123). Oil, solidified by cold.

Phenyl-hydrazide. [100°]. White needles (from benzene-ligroïn).

Di-phenyl-di-hydrazide. [114°]. Needles (from dilute alcohol).

Di-oxim. [173°]. Needles.

Oxim-phenyl-hydrazide. [132°]. White needles (from benzene-ligroïn).

METHYL AMYL KETONE CARBOXYLIC ACID $CH_3.CO.CH_2.CH_2.CH_2.CH_2.CH_2.CO_2H$. [30°]. A product of the action of a boiling solution of KOH in MeOH upon dimethyl-amylene diketone carboxylic ether (Kipping a. Perkin, jun., *C. J.* 55, 338). Also from sodium-malonic ether and $CH_3.CO.CH_2.CH_2.CH_2.CH_2Br$, the resulting dicarboxylic acid being distilled. Crystalline plates, v. sol. water.—AgA′: colourless plates.

METHYL ISO-AMYL OXIDE $C_6H_{14}O$ *i.e.* $CH_3.O.C_5H_{11}$. Mol. w. 102. (92°). V.D. 3·74. S.V. 148·1 (Schiff). From MeONa and isoamyl iodide (Williamson, *C. J.* 4, 233).

METHYL-AMYL-PIPERIDINE $C_{11}H_{23}N$ *i.e.* $C_5H_9N(C_5H_{11})(CH_3)$. (190°–193°). Prepared by dry-distillation of the alkaline hydrate obtained by the action of moist Ag_2O on amyl-piperidine methylo-iodide (Schotten, *B.* 15, 422). Colourless fluid. Sl. sol. water. With MeI it forms a crystalline methylo-iodide.—B′HCl: hygroscopic salt.—$(B'HCl)_2PtCl_4$: sparingly soluble pp., melts at [140°].

METHYL AMYL SULPHIDE $CH_3.S.C_5H_{11}$. (137°). V.D. 58·6. From $NaSC_5H_{11}$ and MeI (Obermeyer, *B.* 20, 2924).

METHYL AMYL DI-THIO-CARBONATE $^{\times}CO(SMe)(SC_5H_{11})$. (c. 140°). From $Cl.CO.SC_5H_{11}$ and NaSMe (Schöne, *J. pr.* [2] 32, 244). Liquid, smelling like CS_2. With ammonia it gives HSC_5H_{11}, urea, and HSMe. Alcoholic potash forms K_2CO_3, methyl mercaptan, and HSC_5H_{11}.

METHYL-ANHYDRO-ACETONE-BENZIL *v.* vol. i. p. 463.

METHYL-ANILINE C_6H_5NHMe. Mol. w. 107. (193° uncor.) (Friswell a. Green, *B.* 19, 2035). S.G. $\frac{15}{}$ ·976. H.F. −5500. H.C.v. 973,000 (Petit, *C. R.* 107, 266). *Heat of neutralisation* (by HCl) 6,910 (Vignon, *C. R.* 106, 1722).

Formation.—1. Together with dimethylaniline from aniline and MeI or MeBr (Hofmann, *A.* 74, 150; *B.* 10, 591; *cf.* Kern, *B.* 10, 195).—2. Together with dimethylaniline by heating methyl alcohol with aniline and HCl at 200° under pressure (Girard, *Bl.* [2] 24, 120; *cf.* Poirrier a. Chappat, *J.* 1866, 903).—3. By heating aniline hydrobromide (or hydroiodide) with 10 p.c. more than the calculated quantity of methyl alcohol to 150° for 8 hours; the yield is 34 p.c. of the theoretical (Reinhardt a. Staedel, *B.* 16, 29; *cf.* Krämer a. Grodzky, *B.* 13, 1006).—4. By heating acetanilide with alcoholic sodium ethylate at 170°–200° under pressure (Seifert, *B.* 18, 1355).—5. By adding sodium to a solution of acetanilide in xylene, treating the resulting sodium-acetanilide with MeI and boiling the product (C_6H_5NMeAc) with alcoholic potash (Hepp, *B.* 10, 327).—6. From its formyl derivative (Pictet a. Crépieux, *B.* 21, 1108).—7. By boiling diazobenzene-methyl-anilide (100 g.) with conc. HCl (200 c.c.), making alkaline with NaOH, and distilling with steam; yield 40 g. (Friswell a. Green, *B.* 19, 2035).

Purification.—By the action of MeOH and HCl on aniline a mixture of bases is obtained. On adding dilute H_2SO_4 aniline sulphate separates, and the bases liberated from the filtrate may then be heated with AcCl. On pouring the product into water the acetyl derivative of methyl-aniline separates in long needles, while dimethyl-aniline hydrochloride remains in solution. The acetyl derivative may be quickly saponified by boiling with conc. HClAq (Hofmann, *B.* 7, 523). The mixture of bases may also be treated with nitrous acid, whereby a diazo-benzene salt, phenyl-methyl-nitrosamine, and nitroso-dimethylaniline are formed. The nitrosamine, being insoluble in water and acids, separates as a yellow oil, and may be reconverted by tin and HCl into methyl-aniline (Noelting a. Boasson, *Bl.* [2] 28, 2).

Properties.—Oil. Its aqueous solution is not coloured by bleaching-powder. With NaOBr it gives a yellow pp. (Denigès, *C. R.* 107, 662). With $CuSO_4$ it forms a compound $B'(CuSO_4)_2 4CuO$ (Lachovitch, *M.* 9, 514).

Estimation.—1. It is treated with a mixture of Ac_2O (1 vol.) and di-methyl-aniline (10 vols.), water is added after the reaction, and the solution titrated with phenol-phthaleïn. The di-methyl-aniline does not interfere with the reaction, and the mixture of it with the acetic anhydride keeps well (Giraud, *Bl.* [3] 2, 142).—2. In a mixture of aniline, methylaniline, and dimethylaniline the aniline is first determined by diazotisation and ppn. by (β)-naphthol disulphonic acid (*R.*) and NaCl. Another portion of the mixed bases (2 g.) is mixed with Ac_2O (4 g.), and, after 30 minutes water (50 c.c.) is added. The liquid is boiled to decompose the excess of Ac_2O, and the acid solution titrated with Na_2CO_3 using phenol-phthaleïn as indicator. The amount of Ac_2O found plus that required by the aniline previously determined is then subtracted from the amount taken, and gives a measure of the methylaniline present (Reverdin a. De la Harpe, *B.* 22, 1004).—3. In a mixture of mono- and di-methylaniline the amount of the former present may be known by observing the rise of temperature on mixing with an equal volume of Ac_2O.

Reactions.—1. HNO_3 gives off red fumes containing CO_2, and forms tetra-nitro-methyl-aniline (Van Romburgh, *R. T. C.* 2, 31).—2. $NaNO_2$ added to a solution of its hydrochloride forms phenyl-methyl-nitrosamine $C_6H_5.NMe.NO$, a yellow oil solidifying when cooled as needles [12°–15°]. It gives no reaction with gallic acid (Reverdin a. De la Harpe, *B.* 22, 1006).—3. Boiling *sulphur* forms methenyl-amido-phenyl mercap-

tan and crystalline $C_8H_7NS_2$ [89°] (360°) (Möhlau a. Krohn, *B.* 21, 59).—4. A solution of methyl-aniline sulphate saturated with SO_2 forms with an aqueous solution of *alloxan* small yellowish prisms of $CO<\begin{matrix}NH.CO\\NH.CO\end{matrix}>C(OH).SO_3NH_2PhMe2aq$ (Pellizzari, *A.* 248, 148).—5. An aqueous solution of alloxan forms $(C_4H_2N_2O_4)(NHPhMe)$, a compound crystallising in white scales, with a hydrochloride crystallising in prisms.—6. *Diazobenzene chloride* and aqueous NaOAc form PhNMe.N:NPh, a yellowish oil, decomposed by dilute H_2SO_4 into diazobenzene sulphate (or phenol) and methyl-aniline, and by $SnCl_2$ and HCl into phenyl-hydrazine and methyl-aniline (Nölting a. Binder, *B.* 20, 3017).—7. *p-Nitro-diazobenzene chloride* and NaOAc form $C_6H_4(NO_2).N:N.C_6H_4NHMe$ crystallising in red needles [134°], v. sol. hot alcohol (N. a. B.).—8. *Bromo-acetophenone* forms $C_6H_5.CO.CH_2.NPhMe$ in the cold, and on boiling it gives phenyl-indole and phenyl-methyl-indole (Cullmann, *B.* 21, 2595).

Salts.—$B'_2H_2PtCl_6$. Yellow scales. Decomposed by boiling water (De Coninck, *Bl.* [2] 45, 131).—$B'HCdBr_3$. Trimetric crystals (Hjortdahl, *J.* 1882, 522).—$B'_2H_2SnBr_6$. Monoclinic crystals.—$B'HSO_4Me$. Needles (Claesson a. Lundvall, *B.* 13, 1703).

Formyl derivative $C_6H_5NMeCHO$. [12·5°] (N. a. L.). (250°) (N. a. L.); (256°) (Pictet a. Crépieux, *B.* 21, 1108). S.G. $\frac{18}{4}$ 1·097. From sodium formanilide and MeI (Norton a. Livermore, *B.* 20, 2273). Formed also from methyl-aniline and the hydrochloride of formimido-ether (Pinner, *B.* 16, 1652). Oil; could not be solidified by Pictet. When boiled with 12½ p.c. nitric acid it yields dinitromethylaniline.

Acetyl derivative C_6H_5NMeAc. '*Exalgine*.' [101·5°] (Kamensky, *A.* 214, 236). (256°) (P. a. C.). Formed from sodium-acetanilide and MeI (Hepp, *B.* 10, 328; Hofmann, *B.* 10, 599). Formed also by the action of acetyl bromide on dimethylaniline (Staedel, *B.* 19, 1947). White needles and tablets, sl. sol. cold water, v. sol. dilute alcohol. As a medicine it has an energetic action on the cerebro-spinal system (Dujardin-Beaumetz, *C. R.* 108, 571; *cf.* Giraud, *C. R.* 108, 749). It is a good antiseptic. Boiling nitric acid forms (4, 2, 1)-di-nitro-methyl-aniline.

Thio-acetyl derivative $CH_3.CS.NPhMe$. [59°]. (290°). From the acetyl derivative and sulphide of phosphorus (Wallach, *B.* 13, 528). Monoclinic plates (from $CHCl_3$). Insol. water and alkalis, sol. alcohol and ether.

Propionyl derivative $CH_3.CH_2.CO.NPhMe$. [58·5°]. From sodium propionanilide and MeI (Norton a. Allen, *B.* 18, 1998). With boiling HNO_3 (100 pts. of S.G. 1·029) it yields (4, 2, 1)-di-nitro-methyl-aniline.

Oxalyl derivative $(CO.NPhMe)_2$. (250°). Forms oxalic acid, alcohol, and methylaniline (Norton a. Livermore, *B.* 20, 2273). Boiling nitric acid converts it into di-nitro-methylaniline [177°].

Benzoyl derivative C_6H_5NMeBz. [63°]. From methyl-aniline and BzCl (Hepp, *B.* 10, 329). Formed also by heating di-methyl-aniline with benzoyl chloride at 180° (Hess, *B.* 18, 685). Large monoclinic crystals; insol. water, but v. sol. other solvents. Gives a mono-nitro- derivative [136°].

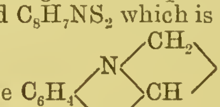
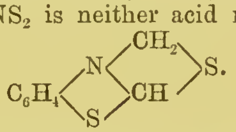
Nitrosamine PhMeN.NO. [12°–15°]. From methylaniline hydrochloride and aqueous $NaNO_2$ (Hepp, *B.* 10, 329; Fischer, *A.* 190, 151; Reverdin a. De la Harpe, *B.* 22, 1006). Yellow oil, solidified by cold. Reduced by tin and HCl to methylaniline. Gaseous HCl passed into its solution in alcohol-ether forms the isomeric $[4:1]NO.C_6H_4.NHMe$ [118°] which crystallises from water in prisms, v. sol. alcohol, and is converted by heating with aqueous NaOH into *p*-nitrosophenol and methylamine (Fischer a. Hepp, *B.* 19, 2991).

Di-methyl-aniline $C_6H_5NMe_2$. Mol. w. 121. [2°–2·5°] (Friswell a. Green, *private communication*). (193°). S.G. $\frac{20}{4}$ ·9575. $\mu_D = 1·559$ (Brühl, *A.* 235, 14). S.H. (9°–82°) ·443 (Schiff, *G.* 17, 286). *Heat of neutralisation* (by HCl) 6,810 (Vignon, *C. R.* 106, 1722). Formed by heating aniline with MeI or MeCl.

Preparation.—1. Aniline hydrobromide (or hydroiodide) is heated with (2 mols. + 10 p.c. excess of) methyl alcohol to 150° for 8 hours; the yield is 95 p.c. of the theoretical (Reinhardt a. Staedel, *B.* 16, 29; *cf.* Lauth, *Bl.* 7, 448).—2. Aniline (18 pts.) saturated with HCl is mixed with a further quantity (75 pts.) of aniline and methyl alcohol (75 pts.). The mixture is heated at 230° in closed vessels until the internal pressure falls. The use of a comparatively small quantity of HCl avoids the formation of toluidine and allows of the use of iron vessels. The HCl is sometimes replaced by H_2SO_4 (Schoop, *Chem. Zeit.* 11, 253).

Purification.—Dimethylaniline can be separated from methyl-aniline by the methods described under methyl-aniline. It can also be purified by freezing (Hübner, *A.* 224, 347).

Reactions.—1. When its vapour is passed through a *red-hot* tube it forms benzonitrile (25 p.c.), carbazole, NH_3, benzene, and HCy (Nietzki, *B.* 10, 474).—2. When heated in a current of HCl at 180° the products are MeCl and aniline (Lauth, *B.* 6, 677).—3. With *sodium hypobromite* it gives a greenish-yellow pp. in the cold and a red pp. on heating (Denigès, *C. R.* 107, 662).—4. *Bromine* (1 mol.) at 115° forms methyl-violet and naphthalene (Brunner a. Brandenburg, *B.* 11, 697).—5. By *nitration* with a mixture of equal volumes of ordinary conc. HNO_3 and water at 0° di-nitro-di-methyl-aniline $C_6H_3(NO_2)_2.NMe_2$ [4:2:1] is formed (yield 116 p.c.). If the mixture is allowed to get warm another di-nitro-di-methyl-aniline [probably 5:3:1] is formed (yield 15 p.c.). By further nitration of the first isomeride by boiling it with fuming nitric acid tri-nitro-phenyl-methyl-nitramide $C_6H_2(NO_2)_3NMe(NO_2)$ [6:4:2:1] is produced. By the same treatment the second isomeride is converted into di-nitro-phenyl-methyl-nitramide $C_6H_3(NO_2)_2NMe(NO_2)$ [5:3:1 ?] (Mertens, *B.* 19, 2123; *cf.* Romburgh, *R. T. C.* 2, 31). When nitrated in presence of a large excess of H_2SO_4 (20 pts.) it yields as chief product the *m*-nitro-derivative whilst the *p*-nitro-derivative is formed in smaller quantity (Groll, *B.* 19, 198; Nölting, *B.* 19, 545).—6. Combines with *aluminium chloride* with great evolution of heat forming long prisms [88°] (H. Giraud, *Bl.* [3] 1, 691).

Heated in sealed tube with 5 pts. of aluminium chloride for 10 hours at 250° no change is effected. Heated in air with excess of aluminium chloride it yields a tetra-methyl benzidine $(CH_3)_2NC_6H_4.C_6H_4N(CH_3)_2$, small needles [195°]. This base is split at 180° by action of HCl gas into methyl chloride and benzidine [118°].—7. *Nitric oxide* passed for 12 days into a solution of dimethylaniline (500 g.) in absolute alcohol (510g.) forms $NMe_2.C_6H_4.N{:}N.C_6H_4.NMe_2$. After 3 or 4 weeks' passage of the gas there are formed a base $C_{16}H_{22}N_2$ [173°] and a violet colouring matter $C_{16}H_{23}N_3O_3$ (?) (Lippmann a. Lange, *B.* 13, 2136). 8. *Nitrous acid* forms nitroso-di-methyl-aniline (*q. v.*).—9. By heating with *sulphur* there is formed a compound $C_8H_7NS_2$ which is converted by HNO_3 into a base  of which the nitrate $B'HNO_3$ crystallises in colourless needles and the platinochloride $B'_2H_2PtCl_6$ in plates (Möhlau a. Krohn, *B.* 21, 65). The compound $C_8H_7NS_2$ is neither acid nor basic and appears to be  It melts at 89° and forms prisms, insol. water, and volatile with steam. On heating with sulphur it is converted into methenyl-amido-phenyl mercaptan. 10. *Chloride of sulphur* forms tetra-methyl-di-amido-di-phenyl disulphide $S_2(C_6H_4NMe_2)_2$ (Hannimann, *B.* 10, 403).—11. Heated with *persulphocyanic acid* it gives $S(C_6H_4NMe_2)_2$ with simultaneous formation of thiocyanic acid, CS_2, H_2S, and NH_3 (Tursini, *B.* 17, 586).—12. Mixed with CS_2 and then treated with zinc-dust and HCl it gives tetra-methyl-di-amido-di-phenyl-methane [90°] and thioformic paraldehyde [212°] (Wiernik, *B.* 21, 3204).—13. *Oxidising agents* give rise to penta-methyl-tri-amido-tri-phenyl-carbinol (methyl violet) (O. a. E. Fischer, *B.* 11, 2099).—14. $COCl_2$ forms $CO(C_6H_4NMe_2)_2$ and, at 120°, $NMe_2.C_6H_3(CO.C_6H_4NMe_2)_2$.—15. CCl_4 gives at 180°C. $(C_6H_4NMe_2)_4$ (Hannimann, *B.* 10, 1689). 16. *Chloroform* at 230° yields $CH(C_6H_4NMe_2)_3$ (Hanimann, *B.* 10, 1235).—17. *Chloral hydrate* in presence of $ZnCl_2$ forms $CCl_3.CH(OH).C_6H_4NMe_2$ (Knöfler a. Boessneck, *B.* 20, 3195).—18. *Furfuraldehyde* in presence of zinc chloride yields $C_4H_3O.CH(C_6H_4NMe_2)_2$ which crystallises in pale-yellow needles [83°] and is a strong base (O. Fischer, *A.* 206, 141).—19. With *heptoic aldehyde* and $ZnCl_2$ it also forms a condensation-product (Auger, *Bl.* [2] 47, 42).—20. *Benzoic aldehyde* and $ZnCl_2$ forms $C_6H_5.CH(C_6H_4NMe_2)_2$ (O. Fischer, *B.* 10, 1624).—21. When treated in the cold with *acetyl bromide* it becomes hot and yields acetyl-mono-methyl-aniline (Staedel, *B.* 19, 1947).—22. *Heptoyl chloride* in presence of $ZnCl_2$ forms a base [72·5°] (278° at 15 mm.) (Krafft, *B.* 19, 2987).—23. By heating with *benzoyl chloride* at 190°, benzoyl-methyl-aniline is formed with splitting off of MeCl (Hess, *B.* 18, 685; *cf.* Michler, *B.* 9, 1899).—24. *Benzoic acid* (1 mol.) and P_2O_5 at 200° forms di-methyl-amido-benzophenone [38°] (O. Fischer, *A.* 206, 88).—25. *Phthalic anhydride* in presence of $ZnCl_2$ forms di-methyl-aniline phthaleïn.—26. *Benzotrichloride* forms 'malachite green' $(NMe_2.C_6H_4)_2CCl.C_6H_5$. The same body is formed by the action of Bz_2O or BzCl in presence of P_2O_5.—27. *Orthoformic ether* and $ZnCl_2$ form $CH(C_6H_4NMe_2)_3$.—28. *Vanillin* and $ZnCl_2$ form $C_{21}H_{28}N_2O_2$ [136°] (Fischer a. Schmidt, *B.* 17, 1895).—29. A blue compound is obtained by the oxidation of dimethylaniline with *chloranil* or other chlorinated quinone. It appears to have the same constitution whichever chloro-quinone is used, as on reduction it always gives a leuco-base of the formula $C_{16}H_{20}N_2$ and melting-point [173°]. The latter forms glistening plates, sl. sol. cold alcohol, v. sol. hot alcohol, benzene, and ether. It forms the salts: $B''H_2Cl_2$: colourless crystals.—$B''H_2Cl_2PtCl_4$: fine needles.—$B''Me_2Cl_2$: crystals, sol. water, sl. sol. alcohol; with wet Ag_2O it gives an alkaline fluid (Meister, Lucius, a. Brüning, *B.* 13, 212, 2100; Wichelhaus, *B.* 14, 1952).—30. *Acetone* saturated with SO_2 forms $(C_3H_6O)(SO_2)(NMe_2Ph)$ crystallising in lustrous plates, v. sol. water and alcohol, insol. acetone (Boessneck, *B.* 21, 1906). Acetone and $ZnCl_2$ at 150° forms $CMe_2(C_6H_4NMe_2)_2$ [83°] (Doebner, *B.* 12, 810).—31. Di-methylaniline dissolved in a saturated solution of SO_2 and mixed with an aqueous solution of *alloxan* forms $(C_4H_2N_2O_4)(NMe_2Ph)H_2SO_3$ 4aq crystallising in monoclinic plates; $a{:}b{:}c = 1·3399{:}1{:}·3394$; $\beta = 93°\ 23'$ (Pellizzari, *A.* 248, 148; *G.* 18, 329).—32. A saturated aqueous solution of *alloxan* forms a compound $C_{12}H_{13}N_3O_4$aq crystallising in colourless needles, sl. sol. water, decomposing at 250° (Pellizzari, *G.* 17, 409). The compound forms a crystalline hydrochloride, nitrate, and oxalate, and yields a silver salt $C_{12}H_{12}AgN_3O_4$. It is decomposed by alkalis forming a compound $C_{11}H_{12}N_2O_3$, decomposing at 281°.—33. *s-Trinitrobenzene* forms a compound $NMe_2PhC_6H_3(NO_2)_3$ [108°] which crystallises in long dark violet needles, sl. sol. alcohol (Hepp, *A.* 215, 358).—34. *Tri-nitro-toluene* forms a corresponding body (H.).—35. *Tri-nitro-aniline* forms $NMe_2PhC_6H_3(NO_2)_2(NH_2)$ [141°] (Hepp).

Salts.—Dimethylaniline is apparently less basic than aniline, for if a mixture of the bases is treated with an insufficient quantity of cold aqueous HCl the base left uncombined is chiefly dimethylaniline (Morley, *C. J.* 51, 580).—$B'H_2SO_4$. [80°]. Sol. water, insol. ether and benzene. H.F. 8400. The normal sulphate could not be formed. At 190° the acid sulphate splits up into CO_2 and the sulphonic acid (Vignon, *C. R.* 107, 263).—$B'_2H_2HgCl_4$. [149°]. Large tables or prisms; sol. hot water and hot alcohol. Prepared by adding aqueous $HgCl_2$ to an alcoholic solution of dimethylaniline (Klein, *B.* 11, 1741).—$B'_2Hg_2OCl_2$. Formed together with the preceding. Small needles or glistening leaflets; m. sol. hot water and hot alcohol, insol. cold water, v. sol. benzene. On heating to 100° a blue colouring matter is formed.—B'_2HgCl_2 (Leeds, *J.* 1882, 504).—$B'_2H_2SnCl_4$. Large monoclinic crystals (Hjortdahl, *J.* 1882, 523).—$B'_2H_2PtCl_6$. Tables.—$B'_2H_2PtCl_6$ 2aq (Reinhardt a. Staedel, *B.* 16, 29).—$B'_2H_2PtBr_6$. Brownish-red monoclinic needles.—$BiI_3 2B'HI$ (Kraut, *A.* 210, 324).—$(BiI_3)_2 3B'HI$.—$(BiI_3)_3 4B'HI$.—$(BiI_3)_5 6B'HI$.—$BiI_3 B'HI$.—$B'_2H_4FeCy_6$. Laminæ; sl. sol. cold water, being less soluble than the methylaniline

and aniline ferrocyanides (Fischer, *A.* 190, 184).— $B'_2H_4FeCy_6$ 2aq (Eisenberg, *A.* 205, 266).

Methylo-iodide $C_6H_5NMe_3I$. *Phenyl-tri-methyl-ammonium iodide.* S. (alcohol) 2·2 at 8°. The combination of $PhNMe_2$ and MeI takes place rapidly (Lauth, *Bl.* 7, 448). It may also be obtained by shaking a mixture of aniline (1 mol.) with MeI (3 mols.) and KOH (2 mols.) dissolved in water (Pawlinoff, *J. R.* 13, 448; *Bl.* [2] 37, 493). Plates (from alcohol). Converted by moist Ag_2O into $C_6H_5NMe_3OH$ a deliquescent, crystalline, caustic base. When the methylo-iodide is distilled it splits up into NMe_2Ph and MeI, but these recombine in the receiver. If, however, a current of HCl be passed through the retort NMe_2PhHCl condenses in the receiver, while MeI escapes and may be condensed in a second colder receiver (Merill, *J. pr.* [2] 17, 286). When treated in a sealed tube with a solution of potassium in anhydrous liquefied ammonia it yields KI, NMe_3, and possibly benzene (Thompson a. Cundall, *C. J.* 53, 761). Boiling conc. KOHAq slowly decomposes $PhNMe_3I$ into di-methylaniline, KI, and MeOH (Claus a. Rautenberg, *B.* 14, 621). The methylo-iodide gives rise to the following derivatives:—$PhNMe_3I_3$. [115°]. Brown trimetric plates (Geuther, *A.* 240, 69).—$PhNMe_3I_5$. [87°] (Dafert, *M.* 4, 500). Lustrous green monoclinic needles; $a:b:c = 1·794:1:1·251$; $\beta = 69°\ 43'$. — $PhNMe_3I_7$. [65°]. Violet-black plates.—$PhNMe_3IZnI_2$. Trimetric crystals (Hjortdahl).—$PhNMe_3ClHgCl_2$. [188°]. S. ·36 at 6·2°. Needles (Hübner, *A.* 224, 352).—$(PhNMe_3Cl)_2PtCl_6$. Orange needles (from water). S. ·33 at 7·4°.—$(PhNMe_3)_2Cr_2O_7$. Prisms. S. ·5.—$(PhNMe_3)_2Cr_3O_{10}$. Monoclinic crystals (Hjortdahl).

Ethylo-iodide B'EtI. [125°]. Identical with methyl-ethyl-aniline-methylo-iodide; KOH splits off dimethylaniline (Claus a. Howitz, *B.* 17, 1325).—$PhNMe_2EtI_3$. [81°]. Dark-violet hexagonal rhombohedra (Geuther).—$PhNMe_2EtI_5$. [50°]. Lustrous bluish-green plates. — $PhNMe_2EtI_7$. [45°]. Violet-black plates.

References. — Bromo-, Bromo-di-nitro-, Chloro-, Chloro-nitro-, Iodo-di-, Nitro-, and Nitroso-di-methylaniline.

DIMETHYLANILINE - AZYLINE *v. Di-methyl-amido-benzene-*azo-*dimethylaniline.*

DI - METHYL - ANILINE - PHTHALEÏN *v.* Tetra-methyl-di-amido-di-phenyl-phthalide.

METHYLANILINE SULPHONIC ACID *v.* Methylamidobenzene sulphonic acid.

o-**DIMETHYLANISIDINE** *v.* *o*-Dimethyl-amido-phenol.

METHYL-ANISOL is the *methyl ether* of Cresol.

(*B.* 1)-**METHYL-ANTHRACENE** $C_{15}H_{12}$ *i.e.*

$C_6H_4\left\langle{CH \atop CH}\right\rangle C_6H_3Me\left[{6 \atop 5}\ 1\right]$. Mol. w. 192. [203°] (Börnstein); [200°] (Birukoff). Formed by distilling *erythro*-oxy-methyl-anthraquinone with zinc-dust (Birukoff, *B.* 20, 2070). Formed also by boiling *iso*-methylanthraquinone with zinc-dust and ammonia, and splitting off water from the resulting methyl-hydroxanthranol by boiling with xylene (Börnstein, *B.* 15, 1821). White plates.—$B'C_6H_2(NO_2)_3OH$: red needles. Gives on oxidation methyl-anthraquinone [167°] and the corresponding anthraquinone carboxylic acid. Forms a di-bromo-methyl-anthracene [148°].

Hexahydride $C_{15}H_{18}$. [c. 65°]. Formed by reducing the dilactone of benzophenone di-carboxylic acid with phosphorus and hydric iodide (Graebe a. Juillard, *A.* 242, 256). Plates. V. sol. alcohol, ether, and chloroform. Passed through a red-hot tube it yields a hydrocarbon [195°]. On oxidation it yields methylanthraquinone [154°].

(*B.* 2)-Methyl-anthracene

$C_6H_4\left\langle{CH \atop CH}\right\rangle C_6H_4Me\left[{6 \atop 5}\ 2\right]$. [200°]. Occurs in coal-tar oil, and hence is present in crude anthracene and phenanthrene (Japp a. Schultz, *B.* 10, 1049).

Formation.—1. By passing di-tolyl-methane through a red-hot tube (Weiler, *B.* 7, 1181).—2. By passing di-tolyl-ethane through a red-hot tube (O. Fischer, *B.* 7, 1191; 8, 675).—3. Apparently occurs among the products obtained by passing vapour of oil of turpentine through a red-hot tube (Schultz, *B.* 10, 84).—4. By the action of zinc-dust at high temperatures on chrysophanic acid $C_{15}H_8O_2(OH)_2$, on emodin $C_{15}H_7O_2(OH)_3$ (Liebermann, *B.* 8, 970; *A.* 183, 163), on aloïn (in small quantity) (E. Schmidt, *B.* 8, 1275; *Ar. Ph.* [3] 8, 496), on the acid [4:1]$CH_3.C_6H_4.CO.C_6H_4.CO_2H$ (Gresly, *A.* 234, 238), on abietic acid (colophony), on gum benzoïn (Ciamician, *B.* 11, 273), on chrysarobin (Liebermann a. Seidler, *A.* 212, 34), and on methyl-quinizarin (Nietzki, *B.* 10, 2013).—5. By boiling phenyl xylyl ketone $C_6H_5.CO.C_6H_3Me_2$[1:2:4] for a long time (Elbs, *J. pr.* [2] 35, 472). The isomeric $C_6H_5.CO.C_6H_3Me_2$[1:2:5] condenses on boiling to the extent of 10 to 20 p.c. to (*B.* 2)-methyl-anthracene; dehydrating agents either stop the reaction or split off benzoic acid.

Properties.—Yellowish plates (from alcohol). Sublimes in large white plates, exhibiting blue fluorescence. Sl. sol. alcohol, ether, and HOAc, v. sol. $CHCl_3$, benzene, and CS_2. Chromic acid in HOAc oxidises it to anthraquinone carboxylic acid [282°]. Conc. HNO_3 added to its alcoholic solution forms methyl-anthraquinone. Bromine in CS_2 forms a di-bromo- derivative [156°] (Fischer), which yields, on further bromination, a tetra-bromo- derivative crystallising from toluene in needles. The picric acid compound melts at [93°] (Gresly).

Di-methyl-anthracene $C_{16}H_{14}$ *i.e.*

$C_6H_4\left\langle{CH \atop CH}\right\rangle C_6H_2Me_2$. [71°]. (above 360°). V.D. 7·19. One of the products obtained by passing benzyl-mesitylene through a red-hot tube. Separated from the di-methyl-anthracene [218°] which accompanies it in smaller quantity, by crystallisation from toluene, in which the compound, melting at 71°, is extremely soluble. Further purified by means of its picric acid compound (Louise, *Bl.* [2] 44, 180; *A. Ch.* [6] 6, 191). White needles, v. e. sol. cold benzene and toluene, m. sol. HOAc and alcohol. On oxidation with CrO_3 in HOAc it yields di-methyl-anthraquinone [158°]. The picric acid compound forms long red needles. Forms a grey compound with nitro-anthracene.

Di-methyl-anthracene $C_6H_4\left<\begin{matrix}CH\\ \vert\\ CH\end{matrix}\right>C_6H_2Me_2$. [219°]. One of the products of the passage of benzyl-mesitylene through a red-hot tube (Louise, *Bl.* [2] 44, 178). Rhomboidal plates, insol. cold alcohol, sl. sol. ether, ligroïn, and acetic acid, v. sol. hot benzene and toluene. Forms small colourless leaflets when sublimed. Br in CS_2 forms a crystallised bromo- derivative. The picric acid compound crystallises in red needles. CrO_3 in HOAc oxidises it to a di-methyl-anthraquinone [170°]. Forms a green compound with nitro-anthracene.

Di-methyl-anthracene

$C_6H_4\left<\begin{matrix}CH\\ \vert\\ CH\end{matrix}\right>C_6H_2Me_2\left[{1 \atop 6}:2:4\right]$? [220°–226°].

Obtained by distilling with zinc-dust the tri-oxy-di-methyl-anthraquinone derived from *m*-xylene carboxylic acid, gallic acid, and H_2SO_4 (Birukoff, *B.* 20, 871). Plates. Oxidised by CrO_3 to a di-methyl-anthraquinone [112°].

Di-methyl-anthracene $C_6H_4\left<\begin{matrix}CH\\ \vert\\ CH\end{matrix}\right>C_6H_2Me_2$. [216°]. Obtained by treating a mixture of toluene (3 pts.), CS_2 (3 pts.), and chloroform (1 pt.) with $AlCl_3$ (2 pts.) (Elbs a. Wittich, *B.* 18, 348). With chromic acid it gives a quinone [162°]. Probably identical with the isomeride [219°].

Di-methyl-anthracene $C_6H_4\left<\begin{matrix}CH\\ \vert\\ CH\end{matrix}\right>C_6H_2Me_2$. [203°]. From $[2:4:1]C_6H_3Me_2.CO.C_6H_4.CO_2H[1:2]$ by heating with red-hot zinc-dust (Gresly, *A.* 234, 238). Plates. Possibly identical with the isomeride [220°–226°].

Di-methyl-anthracene

$C_6H_4\left<\begin{matrix}CH\\ \vert\\ CH\end{matrix}\right>C_6H_2Me_2\left[\begin{matrix}1 & 3\\ 6 & 4\end{matrix}\right]$. [246°]. Formed by reduction of di-methyl-anthraquinone [183°] with zinc-dust and NH_3. White plates, with bluish-green fluorescence. Its picrate forms garnet-red needles, decomposed by alcohol (Elbs a. Eurich, *B.* 20, 1363).

Di-methyl-anthracene

$C_6H_3Me\left<\begin{matrix}CH\\ \vert\\ CH\end{matrix}\right>C_6H_3Me$. [200°]. Formed from coal-tar xylene by chlorination at boiling temperature, and subsequently heating the resulting $[3:1]C_6H_4(CH_3)(CH_2Cl)$ with water at 210° (Van Dorp, *B.* 5, 674). White fluorescent plates. Yields on oxidation with chromic acid a quinone [153°]. Br gives a di-bromo-di-methyl-anthracene [154°]. Perhaps identical with the following isomeride.

Di-methyl-anthracene

$C_6H_3Me\left<\begin{matrix}CH\\ \vert\\ CH\end{matrix}\right>C_6H_3Me$. [225°] (A.); [232°] (F. a. C.). Occurs in coal-tar (Zincke a. Wachendorff, *B.* 10, 1481). Formed from toluene, $AlCl_3$, and acetylene tetra-bromide (Anschütz, *A.* 235, 172). Prepared by acting on toluene with methylene chloride in presence of $AlCl_3$ (Friedel a. Crafts, *Bl.* [2] 41, 323; *A. Ch.* [6] 11, 266). Scales. With CrO_3 in HOAc it gives dimethyl-anthraquinone [160°], which forms an orange solution in H_2SO_4. The picric acid compound crystallises in slender needles.

Di-methyl-anthracene

$C_6H_3Me\left<\begin{matrix}CH\\ \vert\\ CH\end{matrix}\right>C_6H_3Me$. [244°]. From tetra-methyl-anthracene dihydride,

$C_6H_3Me\left<\begin{matrix}CHMe\\ CHMe\end{matrix}\right>C_6H_3Me$ by distillation over red-hot zinc-dust (Anschütz, *A.* 235, 320), Greenish-yellow laminæ (from benzene); m. sol. benzene, sl. sol. alcohol. Gives on oxidation di-methyl-anthraquinone [236°].

s-**Di-methyl-anthracene dihydride** $C_{16}H_{16}$ *i.e.* $C_6H_4\left<\begin{matrix}CMeH\\ CMeH\end{matrix}\right>C_6H_4$. [181°]. From ethylidene bromide, benzene, and $AlCl_3$ (Anschütz, *A.* 235, 305). Yellow laminæ (from alcohol). Sublimes in yellow needles. V. sol. benzene, CS_2, and ether, sl. sol. cold alcohol and glacial HOAc. Distillation over red-hot zinc-dust gives anthracene. Oxidation gives anthraquinone. Bromine in HOAc gives $C_6H_4\left<\begin{matrix}CMeBr\\ CMeBr\end{matrix}\right>C_6H_4$, which crystallises from toluene in needles.

Picrate $C_{16}H_{16}C_6H_2(NO_2)_3OH$. [174°].

u-**Di-methyl-anthracene dihydride** $C_6H_4\left<\begin{matrix}CH_2\\ CMe_2\end{matrix}\right>C_6H_4$. [56°]. Formed by the action of HI and red phosphorus on dimethyl-anthron $C_6H_4\left<\begin{matrix}CO\\ CMe_2\end{matrix}\right>C_6H_4$ at 150° (Hallgarten, *B.* 21, 2508). White crystals, sol. ether, benzene, and HOAc.

Tri-methyl-anthracene $C_6H_4\left<\begin{matrix}CH\\ \vert\\ CH\end{matrix}\right>C_6HMe_3$ $\left[{1 \atop 6}:2:3:5\right]$. [236°] (W.); [243°] (G.). Obtained by distilling 'ψ-cumene-phthaloylic' acid $C_6H_2Me_3.CO.C_6H_4.CO_2H$ with zinc-dust (Gresly, *A.* 234, 239). Formed also by distilling tri-oxy-di-methyl-anthraquinone [244°] over zinc-dust (Wende, *B.* 20, 868). Exhibits green fluorescence.

Tri-methyl-anthracene $C_{17}H_{16}$ *i.e.*

$\left[2:5:{1 \atop 6}\right]$ $C_6H_2Me_2\left<\begin{matrix}CH\\ \vert\\ CH\end{matrix}\right>C_6H_3Me$ $\left[{1 \atop 6}:3\right]$. [227°].

Formed by boiling di-*p*-xylyl-ketone $C_6H_3Me_2.CO.C_6H_3Me_2$ for six hours, H_2O being eliminated. Colourless plates, with bluish-green fluorescence. Sublimes below 100°; slightly volatile with alcohol. V. sl. sol. cold alcohol, v. sol. ether. By CrO_3 and acetic acid it is oxidised to tri-methyl-anthraquinone [184°] (Elbs a. Olberg, *B.* 19, 409; *J. pr.* [2] 35, 483).

Tetra-methyl-anthracene $C_{18}H_{18}$. [c. 280°]. A small quantity (·3 g.) is formed from *m*-xylene (100 g.), Al_2Cl_6, and acetylene tetrabromide (Anschütz, *A.* 235, 173). CrO_3 gives a substance (tetra-methyl-anthraquinone?) which forms needles [c. 300°].

Tetra-methyl-anthracene (?). [280°]. From *o*-xylene, Al_2Cl_6, and acetylene tetrabromide (Anschütz, *A.* 235, 175). Fluorescent needles.

Tetra-methyl-anthracene (?). [280°]. Formed similarly from *p*-xylene (A.).

Tetra-methyl-anthracene $C_{14}H_6Me_4$. [163°]. Formed by the action of methylene chloride in presence of $AlCl_3$ on *m*-xylene, and in smaller

quantity on ψ-cumene (Friedel a. Crafts, *A. Ch.* [6] 11, 268). Crystallises from benzene. Gives a dark-red crystalline compound with picric acid. Conc. H_2SO_4 gives a yellow solution. CrO_3 in HOAc oxidises it to tetra-methyl-anthraquinone [206°].

Tetra-methyl-anthracene dibromide $C_6H_3Me{<}\begin{smallmatrix}CBrMe\\CBrMe\end{smallmatrix}{>}C_6H_3Me$. From the corresponding tetra-methyl-anthracene dihydride by bromination (Anschütz, *A.* 235, 321). Yellow needles; decomposes when heated.

Tetra-methyl-anthracene dihydride $MeC_6H_3{<}\begin{smallmatrix}CMeH\\CMeH\end{smallmatrix}{>}C_6H_3Me$. [171°]. Obtained by the action of ethylidene chloride on toluene in presence of Al_2Cl_6 (Anschütz, *A.* 235, 317). Pale-yellow trimetric laminæ; $a:b:c = {\cdot}675:1:{\cdot}924$ (from alcohol and HOAc); v. sol. benzene, sl. sol. HOAc, v. sl. sol. alcohol. Distillation over red-hot zinc-dust gives di-methyl-anthracene [244°]. Oxidation gives di-methyl-anthraquinone [236°].

Picrate $C_{18}H_{20}C_6H_2(NO_2)_3OH$. [165°]. Red glistening needles.

Hexa-methyl-anthracene $C_{14}H_4Me_6$. [c. 220°]. One of the products of the action of methylene chloride on ψ-cumene in presence of $AlCl_3$ (Friedel a. Crafts, *A. Ch.* [6] 11, 272). Not volatile at 440°. The alcoholic solution gives with picric acid a brownish-black pp. [203°]. Conc. H_2SO_4 forms a red solution, becoming colourless after absorbing moisture.

References.—Di-bromo-methyl-anthracene and Amido-methyl-anthracene dihydride and dibromide.

DI-METHYL-ANTHRACHRYSONE *v.* Tetra-oxy-di-methyl-anthraquinone.

DI-METHYL-ANTHRACYL-AMINE *v.* Di-methyl-anthramine.

DI-METHYL-ANTHRAFLAVIC ACID *v.* Di-oxy-di-methyl-anthraquinone.

METHYL-ANTHRAGALLOLS *v.* (1:2:3)-Tri-oxy-methyl-anthraquinones.

DI-METHYL-ANTHRAMINE $C_{14}H_9.NMe_2$. *Di-methyl-anthracylamine.* [155°]. Formed by heating the methylo-hydrate. Thin golden plates. Soluble in alcohol with a green fluorescence.

Salts.—B'HCl: colourless plates, decomposed by water.—$B'_2H_2Cl_2PtCl_4$: yellow pp.

Methylo-iodide B'MeI. [215° uncor.]. Formed by heating anthramine with methyl iodide at 100°. Flat needles, sol. hot water, sl. sol. cold, nearly insol. alcohol.

Methylo-chloride-platinum salt $B'_2Me_2Cl_2PtCl_4$: yellow crystalline pp.

Methylo-hydrate B'Me(OH): strongly alkaline. Formed by the action of Ag_2O on the iodide; on boiling the aqueous solution it decomposes into di-methyl-anthramine and methyl alcohol (Bollert, *B.* 16, 1636).

METHYL-ANTHRANILIC ACID *v.* Amido-toluic acid.

(B. 1)-METHYL-ANTHRAQUINONE $C_{15}H_{10}O_2$ *i.e.* $C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_3Me\left[\begin{smallmatrix}6&\\5&1\end{smallmatrix}\right]$. Mol. w. 222. [154°] (Graebe); [167°] (Birukoff); [176°] (Börnstein). Formed by oxidising (*B.* 1)-methyl-anthracene with CrO_3 and HOAc (Birukoff, *B.* 20, 2070). Formed also by oxidising (*B.* 1)-methyl-anthracene hexahydride (Graebe, *A.* 242, 256). The same, or the following, methyl-anthraquinone is a by-product in the preparation of anthraquinone (Wachendorff a. Zincke, *B.* 10, 1485; Börnstein, *B.* 15, 1820). Small needles (from dilute HOAc). V. e. sol. alcohol and benzene.

(B. 2)-Methyl-anthraquinone $C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_3Me\left[\begin{smallmatrix}6&\\5&2\end{smallmatrix}\right]$. [163°] (F.); [172°] (E.); [177°] (Römer a. Link, *B.* 16, 695).

Formation.—1. By warming an alcoholic solution of (*B.* 2)-methyl-anthracene with nitric acid, ppg. with water, and subliming (O. Fischer, *B.* 8, 675).—2. In small quantity by boiling phenyl *m*-xylyl ketone (Elbs, *J. pr.* [2] 35, 471). 3. By warming $[4:1]CH_3.C_6H_4.CO.C_6H_4.CO_2H$ with H_2SO_4 at 170° for ten minutes (Gresly, *A.* 234, 239).

Properties.—Yellow needles. Sublimes in almost colourless needles. V. sol. alcohol, benzene, and HOAc (R. a. L.); according to Fischer, however, it is sl. sol. these solvents. Conc. H_2SO_4 forms a blood-red solution which becomes violet on heating. When heated with zinc-dust it yields methyl-anthracene [203°]. With fuming H_2SO_4 it yields a disulphonic acid, which on fusion with potash forms di-oxy-methyl-anthraquinone (methyl-alizarin) [252°] (Fischer).

Isomeride of Methyl-anthraquinone *v.* Methanthrene.

Di-methyl-anthraquinone $C_{16}H_{12}O_2$ *i.e.* $C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_2Me_2\left[\begin{smallmatrix}1\\6\end{smallmatrix}:2:4\right]$? [158°]. Obtained by oxidising the corresponding di-methyl-anthracene [71°]. Formed also by heating benzoyl-mesitylenic acid $C_6H_5.CO.C_6HMe_2CO_2H$ with P_2O_5 and subliming the product (Louise, *A. Ch.* [6] 6, 193, 228; *Bl.* [2] 44, 181). Yellow acicular prisms (from chloroform-acetone) or needles (by sublimation). Insol. water, sl. sol. alcohol, sol. chloroform and acetone. With zinc-dust and KOH it gives an intense red colour. This di-methyl-anthraquinone ought theoretically to be identical with those melting at 180° and 112° (*v. infra*).

Di-methyl-anthraquinone $C_{16}H_{12}O_2$. [170°]. Obtained by oxidising di-methyl-anthracene [219°] with CrO_3 in HOAc (Louise, *A. Ch.* [6] 6, 189; *Bl.* [2] 44, 180). Yellow needles (from alcohol). With zinc-dust and KOH it gives a characteristic red tint, which disappears on heating.

Di-methyl-anthraquinone

$$C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_2Me_2\left[\begin{smallmatrix}1\\6\end{smallmatrix}:3:4\right].\quad [183°].$$

Obtained by heating *o*-xylyl-phenyl-ketone-carboxylic acid (o-xyloyl-o-benzoic acid) $[3:4:1]C_6H_3Me_2.CO.C_6H_4.CO_2H[1:2]$ with conc. H_2SO_4. By HNO_3 (S.G. 1·2) at 220° it is oxidised to anthraquinone-di-carboxylic acid [340°] (Elbs a. Eurich, *B.* 20, 1361).

Di-methyl-anthraquinone

$$C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_2Me_2\left[\begin{smallmatrix}1\\6\end{smallmatrix}:2:4\right].\quad [180°].$$

Formed by heating *m*-xylyl-phenyl-ketone-o-carboxylic acid (*m*-xyloyl-o-benzoic acid) $[2:4:1]C_6H_3Me_2.CO.C_6H_4.CO_2H[1:2]$ with conc. H_2SO_4; the yield is 60 to 70 p.c. of the theoretical (Gresly, *A.* 234, 240; Elbs a. Günther, *B.* 20, 1364). Small needles, sl. sol. benzene

and alcohol. By dil. HNO_3 it is oxidised to anthraquinone *m*-di-carboxylic acid [above 330°]. Reduced by zinc-dust and ammonia to a hydrocarbon [85°] which forms with picric acid reddish-brown scales [135°].

Di-methyl-anthraquinone

$C_6H_4<^{CO}_{CO}>C_6H_2Me_2\left[{}^{1}_{6}:2:5\right]$. [118°]. Formed by warming $[4:1:x]C_6H_3Me_2.CO.C_6H_4.CO_2H[2:1]$ with conc. H_2SO_4 at 120° (Gresly, *A.* 234, 240).

Di-methyl-anthraquinone

$C_6H_4<^{CO}_{CO}>C_6H_2Me_2\left[{}^{1}_{6}:2:4\right]$? [112°]. Obtained by oxidising the di-methyl-anthracene [220°–226°] (Birukoff, *B.* 20, 871).

Di-methyl-anthraquinone

$C_6H_4<^{CO}_{CO}>C_6H_2Me_2$. [162°]. Obtained by oxidising di-methyl-anthracene [216°] (Elbs a. Wittich, *B.* 18, 348).

Di-methyl-anthraquinone

$C_6H_3Me<^{CO}_{CO}>C_6H_3Me$. [236°]. Formed by oxidation of di-methyl-anthracene [244°]. Pale-yellow needles, sl. sol. HOAc, v. sl. sol. alcohol (Anschütz, *A.* 235, 321).

Di-methyl-anthraquinone

$C_6H_3Me<^{CO}_{CO}>C_6H_3Me$. [155°]. Obtained by oxidising the di-methyl-anthracene occurring in coal-tar xylene (Wachendorff a. Zincke, *B.* 10, 1482). Small light-yellow needles (from dilute alcohol). May be sublimed. M. sol. alcohol, ether, and HOAc.

Di-methyl-anthraquinone

$C_6H_3Me<^{CO}_{CO}>C_6H_3Me$. [160°]. Obtained by oxidising the di-methyl-anthracene formed from toluene, methylene chloride, and $AlCl_3$ (Friedel a. Crafts, *A. Ch.* [6] 11, 266). Forms an orange solution in H_2SO_4. Probably identical with the preceding.

Tri-methyl-anthraquinone

$C_6H_4<^{CO}_{CO}>C_6HMe_3$. [Me:Me:Me = 1:2:4]. [161°]. Formed by warming ψ-cuminoyl-benzoic acid $C_6H_2Me_3.CO.C_6H_4.CO_2H$ for a short time with conc. H_2SO_4 (Gresly, *A.* 234, 240). Needles.

Tri-methyl-anthraquinone

$\left[2:5:{}^{1}_{6}\right]C_6H_2Me_2<^{CO}_{CO}>C_6H_3Me\left[{}^{1}_{6}:3\right]$. [184°]. Formed by oxidation of the tri-methyl-anthracene obtained from di-*p*-xylyl ketone (Elbs a. Olberg, *B.* 19, 409).

References. — Amido-, Nitro-, and Oxy-methyl-anthraquinones.

METHYL-ANTHRAQUINONE CARBOXYLIC ACID $C_{16}H_{10}O_4$ *i.e.* $C_6H_3Me<^{CO}_{CO}>C_6H_3.CO_2H$. [246°]. Occurs among the products of the oxidation of coal-tar di-methyl-anthracene by CrO_3 in HOAc (Wachendorff a. Zincke, *B.* 10, 1483). Small needles (by sublimation); v. sol. hot alcohol.

Di-methyl-anthraquinone carboxylic acid $C_{17}H_{13}O_4$ *i.e.* $C_6H_4<^{CO}_{CO}>C_6H_2Me_2.CO_2H$. [240°]. Formed by heating ψ-cuminoyl-benzoic acid $C_6H_2Me_3.CO.C_6H_4.CO_2H[2:1]$ with fuming H_2SO_4 (Gresly, *A.* 234, 241). Small needles. V. sol. alkalis, sl. sol. alcohol and benzene. May be sublimed.

DI-METHYL-ANTHRARUFIN *v.* Di-oxy-di-methyl-anthraquinone.

DI-METHYL-ANTHRONE $C_{16}H_{14}O$ *i.e.* $C_6H_4<^{CO}_{CMe_2}>C_6H_4$. [94°]. Formed by the action of MeI and KOHAq on anthranol (Hallgarten, *B.* 21, 2508). Transparent crystals, v. sol. benzene, ether, sl. sol. petroleum ether. Converted by the action of HI and red phosphorus into di-methyl-anthracene dihydride.

METHYL-ARBUTIN *v.* Arbutin.

METHYL ARSENATE Me_3AsO_4. (214°). S.G. $\frac{14}{}$ 1·559. Formed from Ag_3AsO_4 and MeI (Crafts, *Bl.* [2] 14, 99).

METHYL ARSENITE Me_3AsO_3. (129°). S.G. $\frac{10}{4}$ 1·428. V.D. 6·01. From $AsCl_3$ and NaOMe (Crafts, *Bl.* [2] 14, 104). When arsenious acid is dissolved in aqueous NaOH and treated with alcoholic MeI the product is not mono-methyl arsenite but methane arsonic acid $CH_3.AsO(OH)_2$ (Klinger, *A.* 249, 149; *cf.* vol. i. p. 317).

METHYL-ARSINE *v. Organic* Arsenic compounds.

METHYL-ATROLACTIC ACID *v.* Oxy-tolyl-propionic acid.

METHYL-ATROPIC ACID *v.* Phenyl-crotonic acid.

METHYL-AURIN $C_{20}H_{16}O_3$ aq. A by-product in the preparation of aurin (Zulkowsky, *A.* 194, 131; 202, 210; *M.* 3, 476). Brick-red crystals with green lustre (from 60 p.c. alcohol). Its alcoholic solution is yellowish-red, and becomes crimson on addition of alkalis. It loses aq at 100°, but does not melt below 200°. HCl added to its dilute alcoholic solution ppts. $C_{23}H_{25}ClO_4$ as red crystals with blue reflex. On heating with water in sealed tubes at 245° methyl-aurin is split up into *p*-cresol and di-oxy-benzophenone. Alkaline $KMnO_4$ oxidises methyl-aurin to $C_{16}H_{14}O_3$. Potash-fusion forms *p*-oxy-benzoic acid. Zinc-dust and HOAc reduce it to methyl-leucaurin $C_{20}H_{18}O_3$, which crystallises in long colourless needles. H_2SO_4 forms red crystals of $(C_{20}H_{16}O_3)_2H_2SO_4$ which are blue by reflected light. Bromine in HOAc forms crystals of $C_{20}H_{12}Br_4O_3HBr$ aq, which have a steel-blue reflex.

METHYL-AZELAÏC ACID *v.* Octane di-carboxylic acid.

METHYL-DIAZO- COMPOUNDS *v. Di*-Azo-compounds.

TETRA-METHYL-TETRAZONE $C_4H_{12}N_4$ *i.e.* $(CH_3)_2N.N:N.N(CH_3)_2$. (130°). Prepared by the oxidation of dimethyl-hydrazine in ethereal solution with HgO (Renouf, *B.* 13, 2173). Oily fluid. Explodes with violence if heated above 130°. Alkaline in reaction. Reduces $AgNO_3$ to a silver mirror. It is decomposed by boiling aqueous acids into dimethylamine, methylamine, formic acid, and nitrogen.

S a l t s. — The picrate $B'C_6H_2(NO_2)_3OH$ forms yellow prisms. V. sol. water, sl. sol. alcohol. The other salts are also easily soluble in water.

METHYL-*iso*-BARBITURIC ACID $C_5H_6N_2O_3$. Formed by treating nitro-methyl-uracil

$CO<\begin{smallmatrix}NMe.CH\\NH\ .CO\end{smallmatrix}>C.NO_2$ with tin and HCl (Lehmann, *A.* 253, 80). Needles, v. sol. cold water.

Di-methyl-barbituric acid *v. Di-methyl derivative* of BARBITURIC ACID, vol. i. p. 439.

METHYL-BENZAMIDES *v. Benzoyl derivatives* of METHYLAMINES.

METHYL-BENZENE *v.* TOLUENE.

Di-methyl-benzene *v.* XYLENE.

Tri-methyl-benzene *v.* ψ-CUMENE, MESITYLENE, and HEMIMELLITHENE.

Tetra-methyl-benzene *v.* DURENE.

Penta-methyl-benzene $C_{11}H_{16}$ *i.e.* C_6HMe_5. Mol. w. 148. [52°]. (231° i.V.). V.D. 5·27 (calc. 5·12). H.F. 31,900. H.C. 1,554,100 (Stohmann, Kleber, a. Langbein, *J. pr.* [2] 40, 83). One of the products of the action of MeCl on benzene or toluene in presence of $AlCl_3$ (Friedel a. Crafts, *A. Ch.* [6] 1, 472; Ador a. Rilliet, *B.* 12, 332). Formed also in like manner by the action of MeCl and $AlCl_3$ on tri-methyl-benzenes at 100°–110°; the fraction (220°–235°) on crystallisation from alcohol deposits C_6Me_6 first, and the penta-methyl-benzene remaining in the mother-liquor may then be purified by means of its sulphamide (Jacobsen, *B.* 20, 896). Penta-methyl-benzene is a by-product in the formation of tetramethyl-benzene by the action of MeI and $AlCl_3$ on ψ-cumene (Claus, *J. pr.* [2] 38, 231).

Properties.—Flat prisms; v. e. sol. alcohol.

Reactions. — 1. *Bromine* in $CHCl_3$ forms C_6Me_5Br. [163°] (292° i.V.) (F. a. C.; Jacobsen, *B.* 20, 898).—2. $AgNO_3$ and vapour of Br forms di-bromo-*c*-durene [202°] (Gottschalk, *B.* 20, 3288).—3. $ClSO_3H$ forms the sulphone and sulphochloride (Jacobsen).—4. Cold conc. H_2SO_4 does not form the corresponding sulphonic acid, but yields *c*-tetra-methyl-benzene sulphonic acid and hexa-methyl-benzene (J.).—5. $KMnO_4$ forms benzene penta-carboxylic acid (F. a. C.).—6. Fuming *nitric acid* forms di-nitro-*c*-tetra-methyl-benzene [178°] (Gottschalk, *B.* 20, 3287). Dilute nitric acid acting on its solution in benzene produces tetra-methyl-benzoic acid [165°].—7. Heating with $AlCl_3$ forms isodurene, C_6Me_6, and other hydrocarbons (Jacobsen, *B.* 18, 340).—8. $Cl.CONH_2$ and $AlCl_3$ convert C_6HMe_5 dissolved in CS_2 into the amide of penta-methyl-benzoic acid (Jacobsen, *B.* 22, 1219).

Picric acid compound $C_6HMe_5C_6H_2(NO_2)_3OH$. [131°]. Golden-yellow prisms.

Hexa-methyl-benzene $C_{12}H_{18}$ *i.e.* C_6Me_6. Mol. w. 162. [164°] (F. a. C.); [166°] (J.). (264°). S. (95 p.c. alcohol) ·2 at 0°. V.D. 5·73 (calc. 5·61) (F. a. C.); 5·58 (H.). H.C.v. 1,709,600. H.C.p. 1,712,200. H.F. 36,800 (Stohmann, Kleber, a. Langbein, *J. pr.* [2] 40, 84).

Formation.—1. The final product of the action of MeCl on benzene or toluene in the presence of $AlCl_3$ (Friedel a. Crafts, *A. Ch.* [6] 1, 467; *C. R.* 91, 257; Ador a. Rilliet, *B.* 12, 332).—2. From o-di-chloro-benzene, MeCl, and $AlCl_3$ at 100° (Friedel a. Crafts, *A. Ch.* [6] 10, 411).—3. A by-product in the formation of (1,2,3,4)-tetra-methyl-benzene by the action of MeI and $AlCl_3$ on ψ-cumene (Claus, *J. pr.* [2] 38, 231).—4. By heating dimethylaniline methylo-iodide at 330° (Hofmann, *B.* 5, 721).—5. Said to be a product of the action of fused $ZnCl_2$ on sugar (*C. J.* 38, 863; *D. P. J.* 237, 146).—6. Formed as a by-product in the preparation of cumidine by heating xylidine hydrochloride with methyl alcohol; also in small quantity by the action of methyl alcohol at a high temperature on aniline hydrochloride (Hofmann, *B.* 13, 1729).—7. By dropping methyl alcohol upon strongly-heated $ZnCl_2$ (Le Bel a. Greene, *Am.* 2, 21).—8. By pouring acetone upon fused $ZnCl_2$ (H. Greene, *C. R.* 87, 931).—9. By shaking crotonylene CMe:CMe with H_2SO_4 (3 pts.) diluted with water (1 pt.) (Favorsky, *J. pr.* [2] 37, 384; Lwoff a. Almédingen, *Bl.* [2] 37, 493).—10. Together with other products by the prolonged action of conc. H_2SO_4 upon durene (Jacobsen, *B.* 19, 1211).—11. A product of the action of cold conc. H_2SO_4 on penta-methyl-benzene (Jacobsen, *B.* 20, 901).

Properties.—Colourless plates (from alcohol) or prisms (from benzene); insol. water, sl. sol. cold, v. sol. hot, alcohol, v. sol. benzene. Forms iridescent plates on sublimation. Does not dissolve in conc. H_2SO_4.

Reactions. — 1. *Bromine* at 100° yields $C_{12}H_{12}Br_6$ [255°] (F. a. C.); [227°] (H.).—2. $KMnO_4$ oxidises it at a low temperature to mellitic acid.—3. Dilute *nitric acid* yields *c*-tetra-methyl-benzene dicarboxylic acid (Jacobsen, *B.* 22, 1216).—4. When heated with $AlCl_3$ at 200° a gas is given off and penta-methyl-benzene, durene (Friedel a. Crafts, *C. R.* 100, 692), isodurene, tri-methyl-benzenes, xylenes, toluene, and benzene are formed (Jacobsen, *B.* 18, 339).—5. PCl_5 forms hexa-chloro-hexa-methyl-benzene (*q. v.*).

Picric acid compound $C_6Me_6C_6H_2(NO_2)_3OH$. [169°]. Golden plates.

METHYL-BENZENE CARBOXYLIC ACID *v.* TOLUIC ACID.

Di-methyl-benzene carboxylic acid *v.* MESITYLENIC and DI-METHYL-BENZOIC ACIDS.

Tri-methyl-benzene carboxylic acid *v.* ψ-CUMINIC ACID.

Methyl-benzene dicarboxylic acid *v.* UVITIC ACID, METHYL-ISOPHTHALIC ACID, METHYL-TEREPHTHALIC ACID, and TOLUENE DICARBOXYLIC ACID.

Di-methyl-benzene dicarboxylic acid *v.* DI-METHYL-ISOPHTHALIC and DI-METHYL-TEREPHTHALIC ACIDS.

Tri-methyl-benzene dicarboxylic acid $C_6HMe_3(CO_2H)_2$. Obtained by oxidising $C_6HMe_3.CO.C_6H_5$ with $KMnO_4$ in alkaline solution (Ador a. Meyer, *J.* 1879, 562). Needles (from water).—BaA″aq. Slender needles; almost insol. water.

Tetra-methyl-benzene dicarboxylic acid $C_6Me_4(CO_2H)_2$ [6:5:4:3:2:1]. [249°]. Formed by boiling C_6Me_6 with dilute HNO_3 (Jacobsen, *B.* 22, 1215). Small needles (from hot water) or prisms (from alcohol). Yields *c*-durene when distilled with lime.—BaA′₂2aq.

DI-METHYL-BENZENE GLYCOL *v.* DI-ω-OXY-XYLENE.

METHYL-BENZENE SULPHINIC ACID *v.* TOLUENE SULPHINIC ACID.

Tri-methyl-benzene sulphinic acid $C_6H_2Me_3(SO_2H)$ [1:3:4:6]. [98°]. Long needles (from water).—NaA′.—BaA′₂. S. 5 at 7°. Thin plates.—AgA′ (Radloff, *B.* 11, 32).

METHYL-BENZENE SULPHONIC ACID *v.* TOLUENE SULPHONIC ACID.

Di-methyl-benzene sulphonic acid *v.* XYLENE SULPHONIC ACID.

c-Tri-methyl-benzene sulphonic acid $C_6H_2Me_3(SO_3H)$ [1:2:3:5]. *Hemimellithene sulphonic acid.* Formed by sulphonation of hemimellithene (Jacobsen, *B.* 15, 1858; 19, 2517). Crystallises from dilute H_2SO_4 in six-sided plates or tables (containing aq).—NaA′aq: tables, v. sol. hot, m. sol. cold, water.—*BaA′$_2$: brittle plates, v. sl. sol. water.

Amide $C_6H_2Me_3SO_2NH_2$. [196°]. Prisms or needles. Less soluble in alcohol than the amide of ψ-cumene sulphonic acid.

Isomerides *v.* ψ-CUMENE SULPHONIC ACID and MESITYLENE SULPHONIC ACID.

Tetra-methyl-benzene sulphonic acid *v.* DURENE SULPHONIC ACID.

Penta-methyl-benzene sulphonic acid $C_6Me_5SO_3H$. Obtained by treating penta-methylbenzene with $ClSO_3H$ and treating the product with NaOH to convert the $C_6Me_5SO_2Cl$ first formed into $C_6Me_5SO_3Na$ (Jacobsen, *B.* 20, 899). In the action of $ClSO_3H$ on C_6Me_5H a sulphone [98·5°], crystallising from petroleum-ether in needles, is also formed. The free acid, liberated by shaking the sodium salt with light petroleum and H_2SO_4, at once undergoes hydrolysis, C_6HMe_5 dissolving in the petroleum.

Salts.—A′Na: tables (from neutral aqueous solution) or plates (from hot, dilute, NaOH); sl. sol. cold water, m. sol. hot water, insol. cold, dilute NaOH.—A′K: plates (from hot water).—A′$_2$Ba: plates, v. sl. sol. hot water.—A′$_2$Ca: plates.—A′Ag: plates, v. sl. sol. cold, m. sol. hot, water.—A′$_2$Cu: greenish-white tables; sl. sol. water.

Chloride. [82°]. Plates (from EtOH), or prisms (from Et_2O); v. sol. EtOH and Et_2O.

Amide. [186°]. Prisms; v. e. sol. hot, m. sol. cold, EtOH; insol. water. $KMnO_4$ produces a sulphamic acid [c. 265°].

METHYL - BENZGLYCOCYAMIDINE *v.* BENZCREATININE.

METHYL-BENZGLYCOCYAMINE *v.* BENZCREATIN.

TETRA-METHYL-BENZIDINE *v.* TETRA-METHYL-DI-*p*-AMIDO-DIPHENYL.

METHYL-BENZIL *v.* PHENYL TOLYL DIKETONE.

METHYL-BENZOIC ACID *v.* TOLUIC ACID.

Di-methyl-benzoic acid $C_9H_{10}O_2$ *i.e.* $C_6H_3Me_2.CO_2H$ [6:2:1]. *m-Xylene c-carboxylic acid.* [97°-99°]. Formed by fusing potassium *m*-xylene c-sulphonate with sodium formate (Jacobsen, *B.* 11, 21). Short needles (from water). Forms *m*-xylene when distilled with lime.

Di-methyl-benzoic acid $C_6H_3Me_2.CO_2H$ [4:2:1]. *m-Xylene i-carboxylic acid. Xylylic acid. Xyloic acid.* [126°]. (267°) at 727 mm.

Formation.—1. By the oxidation of ψ-cumene by dilute nitric acid, being separated from the accompanying $C_6H_3Me_2CO_2H$ [5:2:1] through the greater solubility of its Ca salt (Fittig a. Laubinger, *A.* 151, 269).—2. By treating bromo-*m*-xylene with sodium and CO_2 (Kekulé, *A.* 137, 186).—3. By warming its nitrile with H_2SO_4 (85 p.c.) and heating the resulting amide with conc. HClAq at 170° (Birukoff, *B.* 20, 871; *A.* 240, 286).—4. By heating its diphenylamide with HClAq (*v. infra*).—5. By decomposing its chloride (*v. infra*) with water.

Properties.—Slender needles (from water) or monoclinic prisms (from alcohol). May be sublimed. Almost insol. cold water, sl. sol. hot water, v. sol. hot alcohol. Gives *m*-xylene when heated with lime. Chromic acid mixture oxidises it to $C_6H_3Me(CO_2H)_2$ [3:1:4].

Salts.—CaA′$_2$2aq: monoclinic prisms, v. sol. water.—BaA′$_2$8aq?—AgA′.

Chloride $C_6H_3Me_2.COCl$. [25·5°]. (235°). Formed by passing $COCl_2$ into *m*-xylene containing $AlCl_3$, and heating to 100° (Ador a. Meyer, *B.* 12, 1968).

Amide $C_6H_3Me_2.CONH_2$. [180°]. Formed by warming the nitrile with H_2SO_4 (85 p.c.). Formed also by the action of $NH_2.COCl$ on *m*-xylene in presence of $AlCl_3$ (Gattermann, *A.* 244, 53). Formed also by passing gaseous HCNO and HCl gas into *m*-xylene containing $AlCl_3$ on the water-bath (Gattermann a. Rossolymo, *B.* 23, 1196). Long shining needles (from water). Almost insol. cold water, v. sol. alcohol.

Anilide $C_6H_3Me_2.CONHPh$. [138·5°]. Crystals, v. sl. sol. hot water.

Diphenylamide $C_6H_3Me_2.CONPh_2$. [142°]. Formed from *m*-xylene and $NPh_2.COCl$ in presence of $AlCl_3$ (Lellmann a. Bonhöffer, *B.* 20, 2120). Monoclinic crystals, v. e. sol. hot alcohol, HOAc, and chloroform, sl. sol. hot ether, v. sl. sol. hot petroleum-ether.

Nitrile $C_6H_3Me_2CN$. [25°]. (224°). S.G. $\frac{12}{}$ ·9871 (Hinrichsen, *B.* 21, 3082). V.D. 4·64.

Formation.—1. By heating the formyl derivative of *m*-xylidine with zinc-dust; the yield being about 12 p.c. (Gasiorovsky a. Merz, *B.* 18, 1012).—2. By distilling the corresponding $PO(OC_6H_3Me_2)_3$ with KCy; the yield being 15 p.c. (Kreysler, *B.* 18, 1713).—3. From *m*-xylidine by Sandmeyer's reaction (Birukoff, *B.* 20, 871). *Properties.*—Triclinic crystals (from dilute alcohol). Volatile with steam. Yields benzyl-di-methyl-amine on reduction.

Amidoxim $C_6H_3Me_2C(NH_2):NOH$. [178°]. *Xylenyl-amidoxim.* Formed by the action of hydroxylamine on the nitrile at 85° (E. Oppenheimer, *B.* 22, 2443). White needles, v. sol. alcohol, ether, chloroform, and hot water, sl. sol. cold water. *Reactions.*—1. EtI acting on its Na derivative forms $C_6H_3Me_2.C(NH_2):NOEt$ which crystallises in white needles, [172°], v. sol. alcohol, ether, chloroform, benzene, and boiling water, sl. sol. cold water. Excess of HCl converts the ethyl derivative into $C_6H_3Me_2CCl:NOEt$, a yellow aromatic oil.—2. *Chloral* forms a compound $CCl_3.CHO(C_6H_3Me_2.C(NH_2):NOH)$ [112°] crystallising in white scales, sol. alcohol and ether but decomposed by water and dilute acids. 3. $ClCO_2Et$ acting on the amidoxim in chloroform forms $C_6H_3Me_2.C(NH_2):NOCO_2Et$ [143°] which crystallises in white needles, v. sol. alcohol, ether, and chloroform, sl. sol. ligroïn. It is converted by heat into $C_6H_3Me_2.C\langle{}^{N.O}_{NH}\rangle CO$ which crystallises in needles [182°], v. sol. alcohol and ether.—4. *Potassium cyanate* acting on the hydrochloride of the amidoxim forms $C_6H_3Me_2.C(NOH).NH.CO.NH_2$ [153°] which crystallises from dilute alcohol in white scales, and forms an unstable platinochloride.—5. *Phenyl cyanate* at 100° reacts forming

$C_6H_3Me_2.C(NOH).NH.CO.NHPh$ [138°] which crystallises from alcohol in light-yellow scales, sol. acids, alcohol, ether, chloroform, benzene, and hot water.—6. *Phenyl thio-carbimide* at 100° forms $C_6H_3Me_2.C(NOH).NH.CS.NHPh$ [150°], sol. alcohol, ether, benzene, boiling water, and acids.—7. Heating with Ac_2O forms the azoxim $C_6H_3Me_2.C\ll^{N.O}_{N}\gg C.CH_3$ [89°].—8. *Succinic anhydride* forms the azoxim $C_6H_3Me_2.C\ll^{N.O}_{N}\gg C.CH_2.CH_2.CO_2H$ which forms long white needles, [112°], v. sol. alcohol, ether, benzene, $CHCl_3$, and hot water, and yields crystalline salts.

Acetyl derivative of the *amidoxim* $C_6H_3Me_2.C(NOAc)NH_2$. [189°]. Small white needles, v. sol. alcohol and chloroform, sl. sol. ether (Oppenheimer, *B.* 22, 2445).

Benzoyl derivative of the *amidoxim* $C_6H_3Me_2C(NOBz)NH_2$. [158°]. White crystals, v. sol. alcohol, ether, and chloroform, sl. sol. water and ligroïn. Converted by heat into $C_6H_3Me_2.C\ll^{N.O}_{N}\gg C.C_6H_5$, which crystallises in faintly yellow scales, v. sol. alcohol, ether, and chloroform, volatile with steam (Oppenheimer, *B.* 22, 2444).

Di-methyl-benzoic acid $C_6H_3Me_2.CO_2H$ [5:2:1]. *p-Xylene carboxylic acid.* [132°]. (268° i.V.).

Formation.—1. From bromo-*p*-xylene by treatment with $ClCO_2Et$ and sodium-amalgam, the resulting ether being then saponified (Jacobsen, *B.* 14, 2111).—2. By oxidation of methyl xylyl ketone $CH_3.CO.C_6H_3Me_2$ [1:2:5] by dilute HNO_3 or by $KMnO_4$ (Claus, *B.* 18, 1858; 19, 3183).—3. From its amide.

Properties.—Large needles (from alcohol); v. sl. sol. hot water, v. e. sol. alcohol. Volatile with steam. Yields $C_6H_3Me(CO_2H)_2$ [2:5:1] on oxidation.

Salts.—CaA'_2 2aq: crusts, m. sol. water.—BaA'_2 4aq: small needles.

Amide $C_6H_3Me_2.CONH_2$. [186°]. Formed by the action of $Cl.CO.NH_2$ (or of HNCO and HCl) on *p*-xylene in presence of $AlCl_3$ (Gattermann, *A.* 244, 54; *B.* 23, 1199). Colourless needles (from water); m. sol. hot water; v. e. sol. alcohol.

Di-methyl-benzoic acid $C_6H_3Me_2.CO_2H$ [3:2:1]. o-*Xylene c-carboxylic acid. Hemimellithylic acid.* [144°]. Formed by the oxidation of hemi-mellithene $C_6H_3Me_3$ [3:2:1] by dilute nitric acid (Jacobsen, *B.* 19, 2518). Prisms (from hot alcohol) or plates (from dilute alcohol). Volatile with steam; v. sl. sol. hot water, insol. cold water. Yields o-xylene when distilled with lime. CaA'_2 aq. Long prisms, m. sol. cold water.

Di-methyl-benzoic acid $C_6H_3Me_2.CO_2H$ [4:3:1]. o-Xylene *i*-carboxylic acid. [165°]. Obtained by boiling its amide for 2 days with caustic potash solution. Formed also, together with the isomeric *m-xylene i-carboxylic acid* [126°] (*v. supra*), by oxidising ψ-cumene with dilute HNO_3 (Fittig a. Laubinger, *A.* 151, 275). Its ether is formed by the action of sodium-amalgam on a mixture of bromo-o-xylene and $ClCO_2Et$ (Jacobsen, *B.* 17, 2374). Prisms (from alcohol); almost insol. cold water, v. sl. sol. boiling water, v. e. sol. alcohol. Gives o-xylene when distilled with lime. Gives $C_6H_3Me(CO_2H)_2$ [3:4:1] on oxidation with dilute nitric acid.—CaA'_2 3½aq. Needles.—BaA'_2 4aq. Needles, v. sol. water.

Amide $C_6H_3Me_2.CONH_2$. [131°]. Formed by the action of $NH_2.COCl$ on o-xylene in presence of ACl_3 (Gattermann, *A.* 244, 52). Long shining needles (from water). The amide obtained from o-xylene, gaseous cyanic acid, HCl, and $AlCl_3$ melts at 165° (Gattermann a. Rossolymo, *B.* 23, 1199).

Diphenylamide $C_6H_3Me_2.CONPh_2$. [136°]. From $NPh_2.COCl$, o-xylene, and $AlCl_3$ (Lellmann a. Bonhöffer, *B.* 20, 2119). Small prisms; v. sol. hot alcohol, sl. sol. ether and ligroïn.

Nitrile $C_6H_3Me_2.CN$. (232°). V.D. 4·61. Formed by fusing potassium o-xylene sulphonate with KCy (Jacobsen, *B.* 11, 23). Formed also by heating the corresponding xylenyl phosphate $PO(OC_6H_3Me_2)_3$ with KCy, the yield being 20 p.c. (Kreysler, *B.* 18, 1711). Liquid, miscible with alcohol and ether.

Di-methyl-benzoic acid $C_6H_3Me_2.CO_2H$ [5:3:1] is described as MESITYLENIC ACID.

Di-methyl-benzoic acid $C_6H_3Me_2.CO_2H$? *Lauroxylic acid.* [155°]. Produced by the action of dilute nitric acid on laurene $C_{11}H_{16}$ (Fittig, Köbrich, a. Jilke, *A.* 145, 151). Hard nodules (from alcohol). Nearly insol. cold, sl. sol. boiling, water, v. sol. alcohol. Yields acetic acid on oxidation with chromic acid mixture.—BaA'_2 4aq. Concentrically-grouped needles, v. sol. water.—CaA'_2 4aq.—AgA'. White pp.; may be crystallised from water.

Tri-methyl-benzoic acid *v.* ψ-CUMINIC ACID. Another **tri-methyl-benzoic acid**, *Hemimellithene carboxylic acid*, is described as *c*-CUMINIC ACID.

Tetra-methyl-benzoic acid $C_6HMe_4CO_2H$ [5:4:3:2:1]. [165°] (G.); [150°] (C.). (c. 270°). Formed by oxidising penta-methyl-benzene, dissolved in benzene, with dilute nitric acid (Gottschalk, *B.* 20, 3286). Formed also by oxidising tetra-methyl-phenyl methyl ketone or tetra-methyl-phenyl-acetic acid with $KMnO_4$ (Claus, *J. pr.* [2] 38, 234). Needles (G.), m. sol. hot water, v. e. sol. alcohol, ether, benzene, CS_2, and chloroform (C.). Its alkaline salts are very soluble. The Ag salt is v. sl. sol. water. The cupric salt forms light-green plates.—BaA'_2 2aq. Plates or nodules, v. sol. water and alcohol (G.).—BaA'_2 6aq (C.).—CaA'_2 3aq (C.).—NaA' 3aq.

Tetra-methyl-benzoic acid $C_6HMe_4.CO_2H$ [6:4:3:2:1]. Formed by oxidising the corresponding $C_6HMe_4.CO.CH_3$ with $KMnO_4$ (Claus a. Foecking, *B.* 20, 3103). Yellow liquid, not solidified at 0°.

Tetra-methyl-benzoic acid $C_6HMe_4.CO_2H$ [6:5:3:2:1]. [109°] (C. a. F.); [112°] (G.). Formed by oxidising the corresponding $C_6HMe_4.CO.CH_3$ with $KMnO_4$ (Claus a. Foecking, *B.* 20, 3103). Formed also by boiling its amide for several days with alcoholic potash (G.). Plates.

Amide $C_6HMe_4.CONH_2$. [173°]. From durene, $ClCONH_2$, and $AlCl_3$ (Gattermann, *A.* 244, 55). Shining plates (from dilute alcohol).

Tetra-methyl-benzoic acid $C_6HMe_4.CO_2H$. [179°]. From durene, $COCl_2$, and $AlCl_3$, the product being decomposed by water (Jacobsen, *B.* 22, 1223). Also from $C_6HMe_4.CO.C_6H_5$ and $KMnO_4$ (Meyer a. Ador, *J.* 1879, 562). Must be identical with one of the three preceding acids,

probably with that of Gottschalk. Large plates (from dilute alcohol), v. sl. sol. cold water. Volatile with steam. May be distilled. Conc. HClAq at 210° yields durene and CO_2.—CaA'_2. Short prisms, sl. sol. hot water.—BaA'_2 4aq. Small plates (from hot water).

Methyl ether $C_6HMe_4.CO_2Me$. [59°]. (260° i.V.). Plates (Jacobsen, *B.* 22, 1223). Saponified by alcoholic potash at 210°.

Nitrile $C_6HMe_4.CN$. [77°]. Formed by distilling tetra-methyl-benzoic acid with $PbCy_2$ (Jacobsen, *B.* 22, 1224). Needles, v. e. sol. alcohol. Split up by HCl at 215° into durene and CO_2. A crystalline nitrile $C_6H(CH_3)_4.CN$ [69°], (260°), probably identical with the last is formed by the isomeric change of the carbamine derived from duridine (*q. v.*) by distillation. It is very stable towards HCl, by which it is not saponified to the acid, but at 250° it decomposes with formation of tetra-methyl-benzene (Hofmann, *B.* 17, 1914).

Amide $C_6HMe_4.CONH_2$. [173°]. Formed by passing gaseous cyanic acid and HCl into durene containing $AlCl_3$ at 100° (Gattermann a. Rossolymo, *B.* 23, 1199). It is probably the amide of the acid [179°], but has not been fully examined.

Penta-methyl-benzoic acid $C_6Me_5.CO_2H$. [210·5°]. Formed from penta-methyl-benzene, $COCl_2$, and $AlCl_3$ at 0°; after a fortnight the product is exposed to moist air and then treated with water (Jacobsen, *B.* 22, 1220). Needles (from water) or prisms (from 70 p.c. alcohol); v. sl. sol. cold, sl. sol. hot, water, v. e. sol. hot alcohol. Volatile with steam. May be distilled. With H_2SO_4 it yields C_6Me_6 and *c*-durene (prehnitene). HNO_3 forms di-nitro-*c*-durene. Fuming HClAq at 200° yields CO_2 and penta-methyl-benzene. — CaA'_2. Prisms; m. sol. water.—BaA'_2 2aq. Plates; sol. hot water.

Methyl ether MeA'. [67·5°]. (300° i.V.). Plates; v. sol. alcohol.

Amide $C_6Me_5.CONH_2$. [206°]. From C_6HMe_5, chloro-formamide, and $AlCl_3$. Plates; sl. sol. hot, v. sl. sol. cold, water.

Nitrile $C_6(CH_3)_5.CN$. [170°] (J.); [168°] (H.). (292°) (H.); (295°) (J.). Formed from the carbamine C_6Me_5NC by intra-molecular transformation by heating it a few degrees above its melting-point (Hofmann, *B.* 18, 1825). Large white needles; sol. alcohol and ether, insol. water. It is remarkably stable, and could not be saponified by treatment with acids or alkalis. By heating with HI at 220°–230° it yields penta-methyl-benzene, NH_3, and CO_2. Conc. HClAq at 215° also yields C_6HMe_5.

METHYL-BENZOIC ALDEHYDE *v.* Toluic aldehyde.

Di-methyl-benzoic aldehyde $C_6H_3Me_2.CHO$ [4:2:1]. *m-Xylobenzaldehyde. Xylylic aldehyde.* [-8°]. (216°). Formed by oxidising di-methyl-benzyl alcohol with $K_2Cr_2O_7$ and H_2SO_4 (Hinrichsen, *B.* 21, 3085; 22, 121). Separated by K_2CO_3. Colourless oil, volatile with steam. HNO_3 oxidises it to di-methyl-benzoic acid [126°].

Di-methyl-benzoic aldehyde $C_6H_3Me_2.CHO$ [5:3:1]. (221°). Formed from mesitylene by treatment in CS_2 with CrO_2Cl_2, followed by water (Étard, *C. R.* 97, 909). The yield is almost the theoretical quantity. Yields mesitylenic acid on oxidation.

Tri-methyl-benzoic aldehyde. *Phenyl hydrazide* $Me_3C_6H_2.CH:N_2HPh$. [129°]. Formed by the action of tri-methyl-benzoic aldehyde on a solution of phenyl-hydrazine in dilute HOAc (Rudolph, *A.* 248, 100). Colourless needles, very sensitive to light; v. sol. ether, hot alcohol, and petroleum ether.

DI-METHYL-BENZOÏN $C_{16}H_{16}O_2$ *i.e.* [4:1] $C_6H_4Me.CO.CH(OH).C_6H_4Me$ [1:4]. [89°]. *p-Toluoïn.* Prepared by boiling 10 pts. of *p*-toluic aldehyde (from *p*-xylene) with 2 pts. of KCy and 30 pts. of 50 p.c. alcohol, and shaking the mass, after cooling, till the yellow product separates (Stierlin, *B.* 22, 380; *cf.* Grimaux a. Lauth, *Bl.* 7, 233). Pale-yellow prisms (from dilute alcohol); sl. sol. hot water, v. sol. alcohol, ether, and benzene. Fuming H_2SO_4 gives a beautiful green colour.

Acetyl derivative $C_{16}H_{15}AcO_2$. [100°]. White crystals; v. sol. alcohol and ether.

Benzoyl derivative $C_{16}H_{15}BzO_2$. [119°]. White crystals; v. sol. alcohol and ether.

METHYL-BENZONITRILE *v. Nitrile* of Toluic acid.

Di-methyl-benzonitrile *v. Nitrile* of Di-methyl-benzoic acid.

METHYL-BENZOPHENONE *v.* Phenyl tolyl ketone.

Di-methyl-benzophenone *v.* Phenyl xylyl ketone and Di-tolyl-ketone.

TRI-METHYL-BENZOQUINONE CARBOXYLIC ACID *v.* ψ-Cumoquinone carboxylic acid.

METHYL-BENZOYL-ACETIC ACID *v.* α-Benzoyl-propionic acid.

Di-methyl-benzoyl-acetic acid [5:2:1] $C_6H_3Me_2.CO.CH_2.CO_2H$. *Xylyl methyl ketone carboxylic acid.* [132°]. Formed, together with di-methyl-benzoic acid, by oxidising xylyl ethyl ketone with very dilute $KMnO_4$ (Claus a. Fickert, *B.* 19, 3183). Needles; sl. sol. water, v. sol. alcohol and ether.—NaA'aq: crusts; v. sol. water.—CaA'_2 $2\frac{1}{2}$aq: needles; sl. sol. cold water. —BaA'_2 4aq: prisms; sl. sol. cold water.—AgA'.

TETRA-METHYL-BENZOYL-BENZOIC ACID $C_6HMe_4.CO.C_6H_4.CO_2H$ [2:1]. *Duroyl-benzoic acid.* [c.260°]. Formed by heating phthalic anhydride with durene in presence of $AlCl_3$ (Friedel a. Crafts, *A. Ch.* [6] 14, 454; *C. R.* 92, 833). Insol. water, v. sol. alcohol, ether, and benzene. May be crystallised from HOAc. The Pb, Cu, and Ag salts are insol. water.—$^{\times}$KA': minute needles; v. sol. cold water.—$^{\times}$NaA'; v. sl. sol. alcohol.—$^{\times}NH_4A'$: needles.—BaA'_2 aq: groups of needles; v. sl. sol. water.—CaA'_2 aq: needles; v. sl. sol. water.

METHYL-BENZOYL-ETHYL-HYDROXYLAMINE *v.* Hydroxylamine derivatives.

TRI-METHYL-BENZOYL-PROPIONIC ACID *v.* ψ-Cumyl-ethyl-ketone-carboxylic acid.

METHYL-DIBENZYL *v.* Phenyl-tolyl-ethane.

METHYL-BENZYL-ACETIC ACID *v.* Phenyl-*iso*-butyric acid.

DI-METHYL-BENZYL ALCOHOL $C_9H_{12}O$ *i.e.* [4:2:1] $C_6H_3Me_2.CH_2OH$. *Xylyl alcohol.* [22°]. (232°). Formed by adding KNO_2 to a solution of dimethyl-benzyl-amine sulphate (Hinrichsen, *B.* 21, 3085). Colourless liquid, with aromatic odour, volatile with steam. Oxidised by chromic acid mixture to di-methyl-benzoic aldehyde.

Acetyl derivative $C_9H_{11}OAc$. (230°-234°).

Benzoyl derivative $C_9H_{11}OBz$. (333°). Yellow oil (Hinrichsen, *B.* 22, 123).

Penta-methyl-benzyl alcohol $C_{12}H_{18}O$ *i.e.* $C_6Me_5CH_2OH$. *Mellityl alcohol.* [160·5°]. Obtained by saponifying its acetyl derivative with alcoholic potash (Jacobsen, *B.* 22, 1217). Dimetric prisms, insol. water, v. sol. alcohol.

Acetyl derivative $C_6Me_5.CH_2OAc$. [85°]. (310°). Obtained by the action of KOAc and HOAc on the chloride $C_6Me_5.CH_2Cl$, which is got by heating hexamethyl-benzene with PCl_5 at 140° (Jacobsen). Plates or prisms (from alcohol); v. sol. ether, m. sol. alcohol at 0°, insol. water.

o-METHYL-BENZYL-AMINE [2:1]$C_6H_4Me.CH_2.NH_2$. *o-Tolyl-methyl-amine. Xylylamine.* (202°). Formed by heating methyl-benzyl-phthalimide (derived from ω-bromo-o-xylene) with conc. HClAq in sealed tubes at 200° (Strassmann, *B.* 21, 577). Liquid, which absorbs moisture and CO_2 from the air.—$B'_2H_2PtCl_6$: yellow needles.—B'HCl: needles (from alcohol). —Picrate $B'C_6H_3N_3O_7$: long yellow needles, decomposing above 170°.

Acetyl derivative $C_6H_4Me.CH_2NHAc$. [69°]. Formed by heating the hydrochloride with NaOAc and Ac_2O. Crystallises from alcohol.

m-**Methyl-benzyl-amine** [3:1]$C_6H_4Me.CH_2NH_2$. (202°). Formed by heating ω-bromo-*m*-xylene with potassium phthalimide, and decomposing the product with conc. HClAq at 190° (Brömme, *B.* 21, 2700). Colourless liquid, miscible with alcohol and ether. Absorbs CO_2 from the air.—B'HCl: needles. $B'_2H_2PtCl_6$. [212°]. Golden plates.—Sulphate [248°].—$B'_2H_2C_2O_4$. [172°]. Plates, v. sol. water.—Picrate [156°].

Acetyl derivative $C_6H_4Me.CH_2.NHAc$. (235°-240°). Oil.

Benzoyl derivative $C_6H_4Me.CH_2.NHBz$. [69°]. White plates (from alcohol), v. sol. chloroform, HOAc, and benzene.

p-**Methyl-benzyl-amine** [4:1]$C_6H_4Me.CH_2NH_2$. Formed by treating an alcoholic solution of the amide of thio-*p*-toluic acid with zinc and HClAq (Paterno a. Spica, *B.* 8, 441).

m-(?)-**Methyl-benzyl-amine** $C_6H_4Me.CH_2NH_2$. *Xylylamine.* (196°). Formed, together with di-methyl-di-benzyl-amine and tri-methyl-tri-benzyl-amine by heating ω-chloro-xylene with alcoholic NH_3 at 116° (Pieper, *A.* 151, 129). Oil, smelling like herring-brine. Is either the *m*-compound or a mixture. Lighter than water. Absorbs CO_2 from the air.—B'HCl. [185°]. Needles; v. sol. water and alcohol.—$B'_2H_2PtCl_6$.

Di-*m*-(?)-methyl-di-benzyl-amine $C_{16}H_{19}N$ *i.e.* $(C_6H_4Me.CH_2)_2NH$. Formed as above (Pieper). Oil smelling like herring-brine. Lighter than water. Decomposes above 210°.—B'HCl. [198°]. Needles; sl. sol. cold water, v. sol. hot water and alcohol.—B'HBr. [196°].

Tri-*m* (?)-methyl-tri-benzyl-amine $C_{24}H_{27}N$ *i.e.* $(C_6H_4Me.CH_2)_3N$. Formed as above (Pieper). Oil; sl. sol. alcohol. Cannot be distilled. With bromine water it yields $(C_6H_4Me.CH_2)_2NH$ and $C_6H_4Me.CHO$.—B'HCl. [212°] (P.); [204°] (Jannasch, *A.* 142, 303). Needles; sl. sol. cold alcohol, insol. water and ether. Heated in a current of dry HCl it yields $(C_6H_4Me.CH_2)_2NH$ and $C_6H_4Me.CH_2Cl$.—$B'HNO_3$. [122°] (J.).

Di-methyl-benzyl-amine $C_9H_{13}N$ *i.e.* [4:2:1]$C_6H_3Me_2.CH_2NH_2$. (219°). *Xylyl-methyl-amine. Xylobenzyl-amine.* Formed by reducing with sodium the nitrile of the corresponding di-methyl-benzoic acid dissolved in alcohol (Hinrichsen, *B.* 21, 3083; 22, 122). Liquid, sl. sol. water, v. sol. alcohol and ether. Readily absorbs CO_2 and moisture from the air. Nitrous acid converts it into the corresponding alcohol. —B'HCl. [210°]. Needles or plates.—$B'_2H_2PtCl_6$. [228°].—$B'HHgCl_3$. [205°].—Nitrate [158°].—Sulphate [254°].—Picrate [223°].—$B'CdI_2$.—$B'_2H_2I_2CdI_2$.

Benzoyl derivative $C_9H_{12}BzN$. [98°]. Needles, v. sl. sol. water, v. e. sol. alcohol and benzene.

Di-methyl-benzyl-amine *v.* BENZYL-DI-METHYL-AMINE.

METHYL-BENZYL-ANILINE $C_6H_5NMe.CH_2Ph$. (306°) (N.); (above 360°) (S.). From methyl-aniline and benzyl chloride (Noelting, *J.* 1883, 702; Stebbins, *A. C. J.* 7, 42). Pale-yellow oil.

p-**METHYL-BENZYL-BENZOIC ACID** $C_{15}H_{14}O_2$ *i.e.* [4:1]$C_6H_4Me.CH_2.C_6H_4.CO_2H$. [134°]. Formed from $C_6H_4Me.CO.C_6H_4.CO_2H$ by reducing with zinc-dust and ammonia, filtering, diluting with water, adding HCl, dissolving the pp. in NH_4Cl, and re-ppg. with acid (Gresly, *A.* 234, 235). Long needles (from alcohol); v. sol. alcohol, HOAc, and benzene, almost insol. water. —BaA'_2: plates, v. sol. water.

Di-methyl-benzyl-benzoic acid $C_{16}H_{16}O_2$ *i.e.* [4:2:1]$C_6H_3Me_2.CH_2.C_6H_4CO_2H$[1:2]. [158°]. Obtained by reducing $C_6H_3Me_2.CO.C_6H_4.CO_2H$ with zinc-dust and ammonia (Gresly, *A.* 234, 237). Small needles (from alcohol).—BaA'_2aq. Plates (from dilute alcohol), sl. sol. water.

METHYL-BENZYL BROMIDE *v.* ω-BROMO-XYLENE.

DI-METHYL-BENZYL-CARBAMIC ETHER $C_{12}H_{17}NO_2$ *i.e.* [6:4:2:1]$C_6H_2Me_3.NH.CO_2Et$. *Mesityl-carbamic ether.* [62°]. From mesidine and $ClCO_2Et$ (Eisenberg, *B.* 15, 1016). Long needles (from water). Volatile with steam.

METHYL-BENZYL-CARBINOL *v.* PHENYL-*iso*-PROPYL ALCOHOL.

PENTA-METHYL-BENZYL CHLORIDE $C_6Me_5CH_2Cl$. [99°]. (c. 285°). Formed by heating C_6Me_6 (40 g.) with PCl_5 (50 g.) at 140° (Jacobsen, *B.* 22, 1217). Plates (from alcohol-ether); v. e. sol. ether, sl. sol. alcohol.

TRI-METHYL-BENZYL CYANATE [6:4:2:1]$C_6H_2Me_3N.CO$. (219°). From tri-methyl-benzyl-carbamic ether and P_2O_5 (Eisenberg, *B.* 15, 1017). Pungent liquid.

METHYL-BENZYL-GLYOXIM *v.* BENZYL-METHYL-GLYOXIM.

DI-ω-METHYL-DI-BENZYLIDENE-ETHYLENE-DIAMINE $C_{18}H_{20}N_2$ *i.e.* $C_2H_4(N:CMe.C_6H_5)_2$. [c. 104°]. Formed by heating ethylene-diamine (1 mol.) with acetophenone (2 mols.) to 120°. White needles. V. sol. alcohol and benzene, sl. sol. ether. It is readily decomposed into its constituents, especially by acids (Mason, *B.* 20, 273).

METHYL BENZYL KETONE *v.* BENZYL-METHYL-KETONE.

Methyl benzyl diketone $C_{10}H_{10}O_2$ *i.e.* $CH_3.CO.CO.CH_2C_6H_5$. (176°). S.G. $\frac{14}{4}$ 1·0721. This ketone is formed by distilling its monoxim $CH_3.CO.C(NOH).CH_2.C_6H_5$ with $FeCl_3$ and dilute HCl (H. Müller *a.* Pechmann, *B.* 22, 2133). Thick yellow oil, smelling like honey.

Di-phenyl-dihydrazide $CH_3.C(N_2HPh).C(N_2HPh).CH_2C_6H_5$. [173°]. Almost colourless flat silky needles.

Mono-oxim $CH_3.CO.C(NOH).CH_2C_6H_5$. *Isonitroso-benzyl-acetone.* [81°]. Formed by the action of nitrous acid on barium benzyl-acetoacetate (Ceresole, *B.* 15, 1876, 3072; 16, 836). Needles, insol. ligroïn. May be sublimed. Dissolves in aqueous alkalis forming yellow solutions. With NaOEt and benzyl chloride it gives $CH_3.CO.C(NOCH_2Ph).CH_2.C_6H_5$, a thick yellow oil, volatile with steam.

Di-oxim $CH_3.C(NOH).C(NOH).CH_2.C_6H_5$. *Methylbenzylacetoximic acid.* [181°]. Formed by adding an alcoholic solution of hydroxylamine hydrochloride to an alcoholic solution of the mono-oxim (Schramm, *B.* 16, 181, 2188). Small needles. With Ac_2O it yields a di-acetyl derivative $CH_3.C(NOAc).C(NOAc).CH_2C_6H_5$ [80°].

METHYL-BENZYL-MALONIC ACID *v.* Benzyl-methyl-malonic acid.

o-**METHYL-BENZYL-PHTHALAMIC ACID** $C_{16}H_{15}NO_3$ *i.e.* $[1:2]C_6H_4Me.CH_2.NH.CO.C_6H_4.CO_2H[2:1]$. *o-Xylyl-phthalamic acid.* [156°]. Formed by boiling o-methyl-benzyl-phthalimide with aqueous NaOH and ppg. the solution with HCl (Strassmann, *B.* 21, 576). Slender needles.—AgA′.

m-**Methyl-benzyl-phthalamic acid** $[1:3]C_6H_4Me.CH_2.NH.CO.C_6H_4.CO_2H[2:1]$. [131°]. Formed in like manner from *m*-methyl-benzyl-phthalimide (Brömme, *B.* 21, 2700). Slender needles (from hot alcohol).—AgA′: v. sol. boiling water.

o-**METHYL-BENZYL-PHTHALIMIDE** $[1:2]C_6H_4Me.CH_2.N{<}{}^{CO}_{CO}{>}C_6H_4$. [149°]. Obtained by heating ω-bromo-*o*-xylene with potassium phthalimide at 200°; the yield being 76 p.c. of the theoretical amount (Strassmann, *B.* 21, 576). White hexagonal crystals (from alcohol), insol. water. With conc. HClAq at 200° it forms methylbenzyl-amine (202°). Aqueous NaOH converts it into o-methyl-benzyl-phthalamic acid.

m-**Methyl-benzyl-phthalimide** $[1:3]C_6H_4Me.CH_2.N{<}{}^{CO}_{CO}{>}C_6H_4$. *m-Xylyl-phthalimide.* [118°]. Formed in like manner by heating ω-bromo-*m*-xylene with potassium phthalimide at 190° (Brömme, *B.* 21, 2700). Slender hexagonal needles (from hot alcohol), v. sol. ether, chloroform, and alkalis.

METHYL-BENZYL-PIPERIDINE *v.* Benzyl-methyl-piperidine.

METHYL BENZYL SULPHIDE $C_8H_{10}S$ *i.e.* $CH_3.S.CH_2C_6H_5$. (195°–198°). Formed by heating benzyl chloride with $Pb(SMe)_2$ at 100° (Obermeyer, *B.* 20, 2926).

o-**Methyl-benzyl thiocarbimide** C_9H_9NS *i.e.* $[2:1]C_6H_4Me.CH_2.N:CS$. *o-Xylyl thiocarbimide.* (256°). Formed by boiling an ethereal solution of o-methylbenzyl-amine with CS_2 and $HgCl_2$ (Strassmann, *B.* 21, 578). Oil, smelling strongly like horse-radish.

Di-methyl-benzyl thiocarbimide $C_{10}H_{11}NS$ *i.e.* $[4:2:1]C_6H_3Me_2.CH_2.N:CS$. *Xylobenzyl mustard oil.* Formed by heating the corresponding urea $(C_6H_3Me_2.CH_2.NH)_2CO$ with syrupy phosphoric acid (Hinrichsen, *B.* 22, 123).

METHYL-BENZYL-THIO-UREA $CH_3.NH.CS.NH.CH_2.C_6H_5$. [74°]. Formed by exposing an alcoholic solution of benzylamine mixed with methyl thiocarbimide for some days to the air (Dixon, *C. J.* 55, 619). White octahedra, v. sol. hot benzene and hot alcohol, m. sol. ether. Gives a black pp. with ammoniacal $AgNO_3$, but the aqueous or alcoholic solution is not desulphurised by prolonged boiling with alkaline lead tartrate.

Methyl-di-benzyl-ψ-thio-urea *v.* Di-benzyl-methyl-ψ-thio-urea.

o-**Methyl-benzyl-thio-urea** $C_9H_{12}N_2S$ *i.e.* $[2:1]C_6H_4Me.CH_2.NH.CS.NH_2$. *o-Xylyl thio-urea.* [167°]. Formed by evaporating a solution of potassium sulphocyanide and *o*-methyl-benzyl amine hydrochloride, and heating the residue to 140° (Strassmann, *B.* 21, 578). White needles (from water), m. sol. hot water. Turns red in air.

m-**Methyl-benzyl-thio-urea** $[3:1]C_6H_4Me.CH_2.NH.CS.NH_2$. [112°]. Prepared in the same way as the preceding body, using $[3:1]C_6H_4Me.CH_2NH_2$ (Brömme, *B.* 21, 2700).

Di-*m*-methyl-di-benzyl-thio-urea $C_{17}H_{20}N_2S$ *i.e.* $(C_6H_4Me.CH_2.NH)_2CS$. [97°]. Prepared by boiling *m*-methylbenzyl-amine with alcoholic CS_2 (B.). Needles; insol. water, acids, and alkalis.

Tetra-methyl-di-benzyl-thio-urea $C_{19}H_{24}N_2S$ *i.e.* $(C_6H_3Me_2.CH_2.NH)_2CS$. *Dixylobenzylsulphourea.* [177°]. From (4, 2, 1)-di-methyl-benzyl-amine and alcoholic CS_2 (Hinrichsen, *B.* 22, 123). Glittering needles (from hot alcohol).

o-**METHYL-BENZYL-UREA** $C_9H_{12}N_2O$ *i.e.* $[2:1]C_6H_4Me.CH_2.NH.CO.NH_2$. *o-Xylyl-urea.* [173°]. Formed from *o*-methylbenzyl-amine sulphate and potassium cyanate (Strassmann, *B.* 21, 578). Radiating moss-like crystals (from alcohol), insol. water.

m-**Methyl-benzyl-urea** $[3:1]C_6H_4Me.CH_2.NH.CO.NH_2$. [148°]. Long needles from alcohol (Brömme, *B.* 21, 2700).

Di-*m*-methyl-di-benzyl-urea $(C_6H_4Me.CH_2.NH)_2CO$. [137°]. Formed from *m*-methylbenzyl-amine and $COCl_2$ in ethereal solution (B.). Slender needles (from alcohol or ether).

Di-methyl-benzyl-urea $C_{10}H_{14}N_2O$ *i.e.* $[4:2:1]C_6H_3Me_2.CH_2.NH.CO.NH_2$. *m-Xylobenzyl-urea.* [184·5°]. Formed by mixing concentrated solutions of (4, 2, 1)-di-methyl-benzyl-amine hydrochloride and potassium cyanate (Hinrichsen, *B.* 22, 122). Slender needles (from alcohol); m. sol. water from which it separates as a flocculent pp.

METHYL-BISMUTHINE *v.* *Bismuth methide* under Bismuth, organic derivatives.

METHYL BORATES.

Tri-methyl-borate Me_3BO_3. (72°) (E. a. B.); (65°) (S.). S.G. $\frac{0}{}$ ·955 (E. a. B.); ·940 (S.). V.D. 3·66 (E. a. B.). Prepared by heating B_2O_3 with methyl alcohol at 100° in sealed tubes, and distilling. The distillate is freed from MeOH by shaking with conc. H_2SO_4, and the upper

layer is then rectified (Schiff, *Bl.* [2] 5, 372; 6, 36). Formed also by the action of BCl_3 on dry methyl alcohol; the upper layer of the product being rectified (Ebelmen a. Bouquet, *A. Ch.* [3] 17, 59; *A.* 60, 251) Colourless mobile liquid, sol. alcohol and ether. Burns with a green flame (greener than that of Et_3BO_3). Decomposed by water into boric acid and MeOH.

Methyl metaborate $MeBO_2$. A thick liquid, formed by heating Me_3BO_3 with B_2O_3. When heated, it begins to decompose at 160° giving off Me_3BO_3, and at 250° there remains a mass of the composition MeB_3O_5, which becomes vitreous on cooling.

An acid methyl borate $Me_2B_4O_7$ was described by Ebelmen (*A. Ch.* [3] 16, 137) as obtained by treating B_2O_3 with dry MeOH, and as being a vitreous mass, readily decomposed by water into boric acid and MeOH. It was probably a mixture of Me_3BO_3 and $MeBO_2$.

METHYL-BORNYL-UREA *v.* Bornyl-methyl-urea.

TRI-METHYL-BRAZILIN $C_{16}H_{11}Me_3O_5\frac{3}{4}aq.$ Formed in the preparation of tetra-methyl-brazilin (*v. infra*). Crystalline, sol. dilute alcohol. Its solution in aqueous NaOH is colourless and gives a brown pp. with $FeCl_3$.

Acetyl derivative $C_{16}H_{10}AcMe_3O_5$. [97°].

Tetra-methyl-brazilin $C_{16}H_{10}Me_4O_5$. [139°]. Formed by the action of NaOEt and MeI on brazilin (Schall a. Dralle, *B.* 20, 3365; 21, 3009). Snow-white crystals. Bromine in HOAc forms $C_{16}H_9BrMe_4O_5$ [181°] and crystalline di-bromo-tetra-methyl-brazilin dibromide $C_{16}H_8Br_4Me_4O_5$.

METHYL-BROMACETOL *v.* αα-Di-bromo-propane.

METHYL BROMIDE CH_3Br. *Bromo-methane.* Mol. w. 95. (4·5°). S.G. $\frac{\cdot8}{\cdot8}$ 1·7331; $\frac{2\cdot2}{2\cdot2}$ 1·7235 (Perkin); $\frac{0}{0}$ 1·732 (Merrill). V.D. (H=1) 95. M.M. 4·644 at 1·5° (Perkin, *C. J.* 45, 454). H.F.p. 14,790. H.F.v. 14,210 (Thomsen). S.V. 55·7 (Lossen, *A.* 254, 68).

Preparation.—Methyl alcohol (800 grms.) and amorphous phosphorus (133 grms.) are put into a retort. Bromine (800 grms.) is slowly run in. After some hours the retort is heated and the product condensed in a receiver surrounded by a freezing mixture. It is washed with dilute potash, dried over calcic chloride and distilled (Merrill, *J. pr.* 126, 296; *cf.* Pierre, *J. Ph.* [3] 13, 156; Bunsen, *A.* 46, 44).

Properties.—Colourless, mobile liquid, with burning taste and pleasant smell resembling chloroform. Burns with greenish-brown smoky flame. Miscible with alcohol, ether, chloroform, and CS_2. Poured into cold water a white ice-like mass is formed. It is approximately $CH_3Br, 20aq.$ At 5° it begins to split up with evolution of methyl bromide gas.

METHYL-BROMO-ACETOACETIC ETHER *v.* Bromo-aceto-acetic acid.

METHYL-BROMO-ACETOL *v.* Di-bromo-propane.

METHYL α-BROMO-ALLYL OXIDE C_4H_7BrO *i.e.* $CH_3.O.CH_2.CBr:CH_2$. (116°). S.G. $\frac{10}{}$ 1·35. Formed by the action of NaOH on $CH_3.O.CH_2.CHBr.CH_2Br$ (Henry, *B.* 5, 455).

METHYL BROMO-ALLYL SULPHIDE C_4H_7BrS *i.e.* $CH_3.S.CH_2.CH:CHBr$. Formed by heating $Pb(SMe)_2$ with *s*-tri-bromo-propane in ethereal solution at 150° (Obermeyer, *B.* 20, 2925). Decomposes at 120°–130°. Combines with Br (1 mol.).

METHYL-BROMO-AMINE *v.* Methylamine.

METHYL-DI-BROMO-ANTHRACENE *v.* Di-bromo-methyl-anthracene.

METHYL-DI-BROMO-ATROLACTIC ACID *v.* Di-bromo-oxy-tolyl-propionic acid.

METHYL BROMO-BUTYL KETONE *v.* Acetyl-butyl bromide.

TRI-METHYL-BROMO-ETHYL-AMMONIUM BROMIDE *v.* Trimethylamine *bromo-ethylo-bromide.*

METHYL-BROMO-ISATIN *v. Methyl derivative of Bromo-*Isatin, p. 71.

METHYL-BROMO-ISATOÏD *v. Bromo-methyl-isatoïd*, p. 71.

METHYL BROMOPROPYL KETONE $CH_3.CO.CH_2.CH_2.CH_2Br$. *Acetyl-propyl bromide.* (118°) at 90 mm. (P.); (106°) at 60 mm. (L.). Formed by treating acetyl-propyl alcohol (*q. v.*) with a saturated aqueous solution of HBr (Colman a. Perkin, jun., *C. J.* 55, 357; Lipp, *B.* 22, 1196). Colourless mobile liquid with penetrating odour. Turns brown in light. Sl. sol. cold water, quickly decomposed by hot water, dissolving as acetyl-propyl alcohol. Forms a crystalline compound with $NaHSO_3$. NaOEt and KOH act on it, forming a light ethereal oil C_5H_8O (113°), probably methylene-furfurane tetrahydride.

METHYL-BROMO-STYRENE *v.* Bromo-tolyl-ethylene.

METHYL-BRUCINE *v. Methylo- compounds of* Brucine, vol. i. p. 637.

METHYL-BUTENYL TRICARBOXYLIC ACID *v.* Pentane tricarboxylic acid.

METHYL BUTENYL KETONE *v.* Allyl-acetone.

METHYL ISOBUTYL ACETAL *v.* Aldehyde.

METHYL-BUTYL-ACETIC ACID *v.* Heptoic acid.

Methyl-di-butyl-acetic acid *v.* Hendecoic acid.

METHYL-BUTYL-ACETYLENE *v.* Heptinene.

METHYL-ISOBUTYL-ANILINE $C_{11}H_{17}N$ *i.e.* $C_6H_5NMe.CH_2Pr$. (235°) (Noelting, *J.* 1883, 702).

METHYL-ISOBUTYL-BENZENE *v. Iso-*Butyl-toluene.

METHYL-BUTYL-CARBINOL *v.* Hexyl alcohol.

Di-methyl-butyl-carbinol *v.* Heptyl alcohol.

METHYL ISOBUTYL CARBONATE $C_6H_{12}O_3$ *i.e.* $CH_3O.CO.OC_4H_9$. (143·6° cor.). S.G. $\frac{27}{}$ ·95 (Röse, *A.* 205, 230).

DI-METHYL-BUTYLENE-DIKETONE $C_8H_{14}O_2$ *i.e.* $CH_3.CO.CH_2.CH_2.CH_2.CH_2.CO.CH_3$. *Di-acetyl-butane.* [44°]. Obtained by heating its dicarboxylic ether with NaOMe in MeOH (Marshall a. Perkin, jun., *C. J.* 57, 241). Crystalline mass, sl. sol. water, v. sol. other menstrua. Combines with $NaHSO_3$. Reacts with phenyl-hydrazine and with hydroxylamine. Boiling alcoholic potash condenses it forming methyl-penta-methenylyl trihydride methyl ketone

$$CH_3.C\Big\langle\begin{matrix}C(CO.CH_3)\\CH_2.CH_2\end{matrix}\Big\rangle CH_2.$$

DI-METHYL-BUTYLENE-DIKETONE CARBOXYLIC ETHER $C_{11}H_{18}O_4$ *i.e.* $CH_3.CO.CH_2.CH_2.CH_2.CH(CO_2Et).CO.CH_3$. *αω-*

di-acetyl-n-valeric ether. (195°–200°) at 100 mm. Obtained by distilling the corresponding di-carboxylic ether (di-acetyl-adipic ether) with potash, neutralising the residue with H_2SO_4, extracting with ether, washing the ether with water, drying and evaporating (Perkin, jun., *C. J.* 57, 229). Colourless oil, v. sol. ether and alcohol, sl. sol. water. Its alcoholic solution is coloured violet by $FeCl_3$. On hydrolysis it yields acetyl-valeric acid and acetic acid.

Di-methyl-butylene-diketone dicarboxylic ether $C_{14}H_{22}O_6$ *i.e.* $CH_3.CO.CH(CO_2Et).CH_2.CH_2.CH(CO_2Et).CO.CH_3$ *Ethylene-diaceto-acetic ether. Di-acetyl-adipic ether.* Formed by the action of sodium (46 g.) on aceto-acetic ether (260 g.) and ethylene bromide (190 g.), dissolved in alcohol (Perkin, jun., *C. J.* 57, 215). It may be purified by conversion into the yellow flocculent di-sodium compound $(Ac.CNa(CO_2Et).CH_2)_2$, decomposing this with very dilute HCl, and extracting with ether. Thick oil, miscible with alcohol and ether, sl. sol. dilute aqueous KOH. $FeCl_3$ colours its alcoholic solution intense violet-red. Combines with great difficulty with $NaHSO_3$. Decomposed by heat into di-methyl-butylene-diketone carboxylic ether, and the two ethers

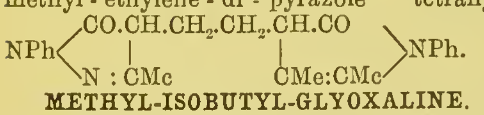
$C(CH_3) : C.CO.CH_3$
$\quad|\qquad\quad|$
$CO_2Et.CH.CH_2.CH_2$

and

$C(CH_3) : C.CO_2Et$
$\quad|\qquad\quad|$
$CO_2Et.CH.CH_2.CH_2$

. Alcoholic *ammonia* converts the dicarboxylic ether into the **di-imide** $(CH_3.C(NH).CH(CO_2Et).CH_2)_2$ [174°] which is reconverted by warming with dilute HCl into the original ketonic ether.

Phenyl hydrazide $(CH_3.C(N_2HPh).CH(CO_2Et).CH_2)_2$. [c. 145°]. Formed by heating di-methyl-butylene-diketone carboxylic ether with phenyl-hydrazine on the water-bath (Perkin, jun., a. Obremsky, *B.* 19, 2049; Perkin, jun., *C. J.* 57, 221). Plates or needles (from MeOH), v. sol. conc. HClAq, insol. alkalis, v. sl. sol. ether. At 200° it gives off EtOH (2 mols.), forming di-oxy-di-phenyl-di-methyl-ethylene-di-pyrazole tetrahydride



METHYL-ISOBUTYL-GLYOXALINE. *Methylo-iodide* $C_9H_{17}N_2I$ *i.e.* $N_2C_3H_2MeC_4H_9MeI$. [170°]. Formed by treating isobutyl-glyoxaline (glyoxal-isoamyline) with MeI in MeOH (Radziszewsky a. Szul, *B.* 17, 1294). Trimetric prisms (from alcohol).

METHYL-n-BUTYL KETONE $CH_3.CO.C_4H_9$. (127°). S.G. $\frac{0}{}$ ·830. Formed by the oxidation of *sec*-hexyl alcohol (Erlenmeyer a. Wanklyn, *A.* 135, 144; Schorlemmer, *A.* 161, 263). Combines with $NaHSO_3$. Gives on oxidation acetic, *n*-butyric, and valeric acids (Wagner, *B.* 18, 2267).

Methyl isobutyl ketone $CH_3.CO.CH_2Pr$. (115°). S.G. $\frac{0}{0}$ ·8195; $\frac{19}{0}$ ·8034 (Wagner, *J. R.* 16, 703). A product of the distillation of potassium isovalerate with NaOAc (Williamson, *A.* 81, 86). Formed by the action on valeryl chloride of $ZnMe_2$ followed by water. Formed also by boiling isopropyl-aceto-acetic ether with baryta-water (Frankland a. Duppa, *A.* 145, 82). Combines with $NaHSO_3$. Yields on oxidation acetic, isobutyric, and isovaleric acids.

Methyl sec-butyl ketone $CH_3.CO.CHMeEt$. (118° i.V.). S.G. $\frac{14.5}{4}$ ·8181. Formed by boiling methyl-ethyl-acetoacetic ether with dilute KOH or baryta-water (Wislicenus, *A.* 219, 307; Wagner, *J. R.* 16, 711). Oil, smelling of peppermint. Oxidised by chromic acid mixture to methyl ethyl ketone and HOAc. Sodium reduces it to the corresponding hexyl alcohol and methyl *sec*-butyl pinacone [249°].

Methyl tert-butyl ketone $CH_3.CO.CMe_3$. *Pinacoline.* (105·3°) (Schiff, *B.* 19, 562). S.G. $\frac{0}{}$ ·8265; $\frac{16}{}$ ·800.

Formation.—1. By distilling pinacone with dilute sulphuric acid (Fittig, *A.* 114, 56).—2. By the action of $CMe_3.COCl$ on $ZnMe_2$, followed by water (Butlerow, *A.* 174, 125).—3. By the dry distillation of calcium isobutyrate (Barbaglia a. Gucci, *B.* 13, 1572).

Properties.—Liquid, smelling of peppermint, nearly insol. water. Sodium-amalgam forms the corresponding hexyl alcohol. Combines with $NaHSO_3$. Chlorine forms pungent $C_6H_{10}Cl_2O$ crystallising in needles [51°], (178°).

Oxim $CH_3.C(NOH).CMe_3$. [75°]. Slender needles, very volatile with steam (Janny, *B.* 15, 2780). May be sublimed. Sl. sol. cold, v. sol. hot, water. Has a camphor-like smell and taste. Not decomposed by acids.

Methyl isobutyl diketone $C_7H_{12}O_2$ *i.e.* $CH_3.CO.CO.CH_2.CH(CH_3)_2$. *Acetyl isovaleryl. Diketoheptane.* (138°). S.G. $\frac{22}{4}$ ·908. Formed by distilling its mono-oxim with dilute H_2SO_4 (Otte a. Pechmann, *B.* 22, 2122). Yellow oil with irritating smell, becoming fruity when diluted. Sl. sol. water.

Mono-oxim $CH_3.CO.C(NOH).CH_2Pr$. *Nitroso-isobutyl-acetone.* [42°]. Formed by adding $NaNO_2$ (10 g.) to a solution of isobutyl-aceto-acetic ether (27 g.) in water (300 c.c.) and KOH (8 g.), and extracting with ether (Treadwell a. Westenberger, *B.* 15, 2786). White plates, v. sol. alcohol and ether, sl. sol. cold water, dissolves in alkalis.

Dioxim $CH_3.C(NOH).C(NOH).CH_2Pr$. [c. 172°]. Small white shining plates (from dilute alcohol) (O. a. P.).

Oxim-phenylhydrazide $C_{13}H_{19}N_3O$ *i.e.* $CH_3.C(N_2HPh).C(NOH).CH_2Pr$. [151°]. Almost colourless needles.

Phenylhydrazide $C_{13}H_{18}N_2O$. [98°]. Almost colourless needles.

Diphenylhydrazide $C_{19}H_{24}N_4$ *i.e.* $CH_3.C(N_2HPh).C(N_2HPh).CH_2Pr$. [116·5°]. Almost colourless needles.

METHYL-n-BUTYL KETONE CARBOXYLIC ACID $C_7H_{12}O_3$ *i.e.* $CH_3.CO.CH_2.CH_2.CH_2.CH_2.CO_2H$. *ω-Acetyl-valeric acid.* [42°]. A product of the hydrolysis of di-methyl-butylene-diketone carboxylic ether by a solution of KOH in methyl alcohol (Perkin, jun., *C. J.* 57, 231). Colourless crystals, v. sol. water, alcohol, and ether. Its **ammonium salt** is very soluble.—AgA′: leafy masses (from hot water). The **cupric salt** forms minute spherules.

METHYL-ISOBUTYL-KETONE SULPHONIC ACID $CH_3.CO.C_4H_8(SO_3H)$. The **sodium salt** of this acid is slowly formed by the action of a

saturated solution of $NaHSO_3$ on mesityl-oxide. It is easily soluble in water and alcohol, melts at 95°, is not attacked by Na_2CO_3, but by NaOH it gives mesityl-oxide (Pinner, *B.* 15, 592).

METHYL BUTYL KETOXIM *v. Oxim* of METHYL BUTYL KETONE.

METHYL n-BUTYL OXIDE $C_5H_{12}O$ *i.e.* $CH_3.O.C_4H_9$. (70·3°). S.G. $\frac{0}{0}$ ·7635. S.V. 127·2. C.E. (0°–10°) ·00125 (Dobreiner, *A.* 243, 3).

Methyl isobutyl oxide $CH_3.O.CH_2Pr$. (60°). One of the products of the action of $NaOCH_2Pr$ on methylene iodide or iodoform (Gorboff, *J. pr.* [2] 41, 238, 254). Oil. Conc. HIAq yields MeI and isobutyl iodide.

METHYL-ISOBUTYL-PHENOL $C_{11}H_{16}O$ *i.e.* $C_6H_3(CH_3)(C_4H_9).OH$[1:3:6]. (236°). *Isobutyl-o-cresol.* Formed by the action of nitrous acid on methyl-isobutyl-phenyl-amine (Effront, *B.* 17, 2324). Oil. V. sol. alcohol and ether, nearly insol. water.

Isomeride *v. Methyl ether* of ISOBUTYL-PHENOL.

METHYL-ISOBUTYL-PHENYL-AMINE $C_6H_3(CH_3)(C_4H_9)NH_2$[1:3:6]. *Isobutyl-tolyl-amine or toluisobutylamine.* (243°). Formed by heating *o*-toluidine hydrochloride with isobutyl alcohol at 200°–300° (Effront, *B.* 17, 2317). Colourless liquid. Volatile with steam. Miscible with alcohol and ether, nearly insol. water.

Salts.—B'HCl. Long thin needles, sl. sol. cold water, v. sol. hot water.—B'HBr: long soluble needles.—$B'_2H_2SO_4$: needles, sl. sol. cold water.—$B'_2H_2C_2O_4$: silvery needles, insol. ether.

Formyl derivative $C_{11}H_{15}.NH(COH)$. [106°]. Colourless tables, v. sol. alcohol and ether, nearly insol. cold water.

Acetyl derivative $C_{11}H_{15}.NHAc$. [162°]. Colourless plates, sparingly sol. hot water, easily in alcohol.

Benzoyl derivative $C_{11}H_{15}.NHBz$. [168°]. Small white needles, insol. cold water, v. sl. sol. hot.

METHYL-ISOBUTYL-PHENYL-AMINE $C_6H_3(CH_3)(C_4H_9)NH_2$[1:5:6]. (244°). Formed by heating *o*-toluidine with isobutyl alcohol and $ZnCl_2$ at 270°–280° (Effront, *B.* 17, 2339). Colourless liquid. Volatile with steam.

Salts.—B'HCl. Plates.—$B'_2H_2SO_4$: plates.—$B'_2H_2C_2O_4$: easily sol. ether.

Formyl derivative $C_{11}H_{15}.NH(CHO)$. [105°]. White plates, v. sol. alcohol and ether, nearly insol. water.

Acetyl derivative $C_{11}H_{15}.NHAc$. [141°]. Long silky needles.

Benzoyl derivative $C_{11}H_{15}.NHBz$. [142°]. Silvery plates.

METHYL - ISOBUTYL - PHENYL - DI - METHYL-AMINE $C_6H_3(CH_3)(C_4H_9)NMe_2$[1:3:6]. *Dimethyl-toluisobutylamine.* (250°). Colourless liquid. Formed by methylation of methyl-isobutyl-phenyl-amine.—$B'_2H_2Cl_2PtCl_4$ (Effront, *B.* 17, 2339).

DI-METHYL-DI-BUTYL-DI-PHENYL-THIO-UREA *v.* DI-BUTYL-DI-TOLYL-THIOUREA.

METHYL-BUTYL-PINACONE *v.* DI-OXY-DODECANE.

DI-METHYL-DI-ISOBUTYL-PYRAZINE $C_{14}H_{24}N_2$ *i.e.* $N\lessgtr\begin{matrix}CMe:C(C_4H_9)\\C(C_4H_9).CMe\end{matrix}\gtrless N$. *Di-isobutyl-ketine.* (243°). Formed by reducing the oxim of methyl isobutyl diketone $Me.CO.C(NOH).C_4H_9$ with tin and HCl (Lang, *B.* 18, 1364; Oeconomides, *B.* 19, 2526; Wolff, *B.* 20, 433). Yellow oil.—$B'H_2PtCl_6$: orange needles.

DI-METHYL-ISOBUTYL-PYRIDINE $C_{11}H_{17}N$ *i.e.* $N\lessgtr\begin{matrix}CMe:CH\\CMe.CH\end{matrix}\gtrless C.C_4H_9$. *Isobutyl-lutidine.* (210°–213°). S.G. $\frac{18}{}$ ·8961. Formed by distilling its carboxylic acid with lime (Engelmann, *A.* 231, 65). Oil, smelling of violets. Tastes bitter. More soluble in cold water than in hot water.—$B'_2H_2PtCl_6$. [209°]. Yellow crystalline pp.—$B'_2H_2Cr_2O_7$. Yellow plates, v. sol. boiling water.—Picrate [115°]. Yellow needles.

Hexahydride $C_{11}H_{23}N$ *i.e.* $NH\lessgtr\begin{matrix}CHMe:CH_2\\CHMe.CH_2\end{matrix}\gtrless CH.C_4H_9$. *s-Isobutyl-lupetidine. Di-methyl-isobutyl-piperidine.* (198°) at 720 mm. Formed by reducing di-methyl-isobutyl-pyridine in alcoholic solution with sodium (Jaeckle, *A.* 246, 47). Oil. With $NaNO_2$ and HCl it yields a nitroso- compound.—B'HCl. [184°]. Prisms, v. sol. water and alcohol.—B'HBr. Prisms. The platinochloride and chromate could not be crystallised.

DI-METHYL-ISOBUTYL-PYRIDINE DI-CARBOXYLIC ACID $C_{13}H_{17}NO_4$ *i.e.* $N\lessgtr\begin{matrix}CMe:C(CO_2H)\\CMe.C(CO_2H)\end{matrix}\gtrless C.C_4H_9$. [273°]. Formed by boiling its diethyl ether with alcoholic, and afterwards with aqueous, potash (Engelmann, *A.* 231, 57). Long monoclinic prisms (containing 2aq). Decomposed by fusion. M. sol. cold, v. sol. hot, alcohol.—CaA″3aq. Small four-sided pyramids, v. sol. water.—BaA″5aq.—$H_2A''HCl$. M. sol. cold water.

Mono-ethyl ether HEtA″. [135°]. Formed by boiling the di-ethyl ether with alcoholic potash. Long prisms, v. sol. water and alcohol.—$Ba(EtA'')_2 5aq$.—HEtA″HCl 2aq: thick prisms.

Di-ethyl ether Et_2A''. (312°–318°). Formed by passing nitrous acid gas into an alcoholic solution of its dihydride. Thick oil.—$Et_2A''HCl$: long needles, decomposed by water into HCl and Et_2A''.—$(Et_2A'')_2H_2PtCl_6$. [208°]. Cubes.

Dihydride of the diethyl ether $NH\lessgtr\begin{matrix}CMe:C(CO_2H)\\CMe:C(CO_2H)\end{matrix}\gtrless CH.C_4H_9$. [100°]. Formed by warming acetoacetic ether with isovaleric aldehyde-ammonia in alcohol (E.). Long prisms, v. sol. alcohol, ether, and benzene.

METHYL ISOBUTYL SULPHATE $C_5H_{12}SO_4$ *i.e.* $(CH_3)(C_4H_9)SO_4$ appears to be formed by the action of methyl alcohol on $C_4H_9O.SO_2Cl$, the product of the action of isobutyl alcohol on SO_2Cl_2 (Behrend, *J. pr.* [2] 15, 34). Decomposed by water into HOMe and $C_4H_9O.SO_2.OH$.

DI-METHYL-ISOBUTYRYL-ACETIC ETHER *v.* DI-ISOPROPYL-KETONE CARBOXYLIC ETHER.

METHYL-CAFFEÏC ACID *v.* CAFFEÏC ACID.

METHYL-CAFFURIC ACID *v.* CAFFEÏNE.

METHYL CARBAMATE $NH_2.CO_2Me$. *Methyl-urethane.* [52°] (G.); [56°] (F. a. K.). (177°). Formed from $NH_2.COCl$ and excess of methyl alcohol (Gattermann, *A.* 244, 39). Formed also from $C_2H_4(N(NO_2).CO_2Me)_2$ by the action of NH_3 (Franchimont a. Klobbie, *R. T. C.* 7, 343).

METHYL-CARBAMIC ACID $NHMe.CO_2H$. The methylammonium salt $NHMe.CO_2NH_3Me$ appears to be formed by pass-

ing CO_2 into dry methylamine (Wurtz, *A. Ch.* [3] 30, 450, 461).

Methyl ether $NHMe.CO_2Me$. (158°). S.G. $\frac{15}{}$ 1·065. Formed by treating methyl chloroformate $Cl.CO_2Me$ with an aqueous solution of methylamine (Franchimont a. Klobbie, *R. T. C.* 7, 353). Colourless liquid, with characteristic odour. With pure HNO_3 it yields a characteristic nitro- derivative.

Ethyl ether $NHMe.CO_2Et$. (170°). Formed from methylamine and chloro-formic ether (Schreiner, *J. pr.* [2] 21, 124). Oil, with pleasant odour. When boiled with potash or baryta it yields alcohol, methylamine, and K_2CO_3.

Chloride NHMe.COCl. [90°]. (94°). From $COCl_2$ and methylamine hydrochloride (Gattermann a. Schmidt, *B.* 20, 118). Decomposed on boiling.

Di-methyl-carbamic acid ×$NMe_2.CO_2H$.

Methyl ether $NMe_2.CO_2Me$. (131°). S.G. $\frac{15}{}$ 1·012. Formed by treating Cl.CO.OMe with an aqueous (33 p.c.) solution of dimethylamine (Franchimont a. Klobbie, *R. T. C.* 8, 299). Colourless liquid, smelling like menthol. Pure HNO_3 forms $NMe(NO_2).CO_2Me$.

Ethyl ether $NMe_2.CO_2Et$. (140°) (Schreiner, *J. pr.* [2] 21, 125); (147°) (Franchimont a. Klobbie, *R. T. C.* 3, 223). S.G. $\frac{15}{}$ ·973. From $Cl.CO_2Et$ and dimethylamine. With ammonia it does not form $NMe_2.CO.NH_2$.

Chloride $NMe_2.COCl$. (165°). From dimethylamine and a solution of $COCl_2$ in benzene (Michler a. Escherich, *B.* 12, 1162). Liquid, with peculiar odour, v. sol. ether and CS_2. Decomposed slowly by water into HCl, dimethylamine, and CO_2.

METHYL CARBAMINE C_2H_3N *i.e.* $CH_3.N:C$. *Methyl isocyanide. Methyl cyanide. Methyl carbylamine. Isoacetonitrile.* Mol. w. 41. [-45°]. (59·6°). V.D. 1·44 (calc. 1·42). S.G. $\frac{4}{}$ ·756. S. 10 at 15°. Formed by the action of MeI (1 mol.) on silver cyanide (2 mols.) the product being decomposed by KOH and dried over $CaCl_2$ (Gautier, *C. R.* 63, 924; 65, 468, 862; 66, 1214; *A.* 152, 222; *A. Ch.* [4] 17, 203). Formed also by the action of MeI on mercuric fulminate (Calmels, *J. pr.* [2] 30, 319; *C. R.* 99, 794).

Properties.—Liquid with powerful odour, producing nausea.

Reactions.—1. *Aqueous acids* decompose it into methylamine and formic acid.—2. HOAc forms $CH_3NH.CHO$ and Ac_2O.—3. Oxidised by HgO at 50° to methyl cyanate $CH_3N.CO$ and a compound $Me_3N_3C_3O_3(NH_2.CHO)$ [175°]. HgO in ethereal solution appears also to form di-formamide $NH(CHO)_2$ or, rather, a compound $Me_3N_3C_3O_3(NH(CHO)_2)$ [163°] (Gautier, *C. R.* 67, 804).—4. With AgCy it forms a compound MeNCAgCy [80°–90°] (Meyer, *J.* 1856, 523). Salt.—$(MeNC)_23HCl$. Formed by passing HCl into an ethereal solution of methyl carbamine. Crystalline. Decomposed by water, partially reproducing methyl carbamine.—5. MeI acts in a complicated manner (Lubavine, *Bl.* [2] 45, 246; Gautier, *A. Ch.* [4] 17, 148).

Tri-methyl-carbamine. A name used by Rudneff (*Bl.* [2] 33, 297) to denote *tert*-Butyl-amine.

METHYL-SEMI-CARBAZIDE $C_2H_7N_3O$ *i.e.* $NH_2.CO.NH.NH.Me$. [113°]. Formed from methyl-hydrazine acid sulphate KHO and KCNO (Brüning, *A.* 253, 10). Prismatic tables; v. sol. water and EtOH; m. sol. ether.

METHYL-CARBAZOLE $C_{13}H_{11}N$ *i.e.* $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!NMe$. [87°]. Formed by heating potassium carbazole with MeI at 180° (Graebe, *A.* 202, 23). Micaceous leaflets or needles, insol. water, sol. ether. Conc. H_2SO_4 containing a little HNO_3 gives a green colour.—Picrate $C_{13}H_{11}NC_6H_2(NO_2)_3OH$. [141°]. Dark-red needles.

METHYL-CARBIMIDO-ALLYL-THIO-UREA $SC\!<\!\begin{matrix} NC_3H_5 \\ NH \end{matrix}\!>\!C:NMe$ or $C_3H_5.NH.CS.N:C:NMe$. *Allyl-thio-carbamine-methyl-cyamide.* [110°]. Formed by the action of methyl iodide upon sodium carbimido-allyl-thio-urea. Crystalline. V. sol. water and alcohol. Indifferent body (Wunderlich, *B.* 19, 448).

METHYL-CARBIMIDO-ETHYL-THIO-UREA $SC\!<\!\begin{matrix} NEt \\ NH \end{matrix}\!>\!C:NMe$ or $EtNH.CS.N:C:NMe$. *Ethyl-thio-carbamine-methyl-cyamide.* [162°]. Formed by the action of methyl iodide upon sodium carbimido-ethyl-thio-urea (Wunderlich, *B.* 19, 448).

TRI-METHYL-CARBINOL *v.* *Tert*-Butyl alcohol.

METHYL CARBONATES.

Hydrogen methyl carbonate ×$MeHCO_3$. The Ba salt, $Ba(MeCO_3)_2$ appears to be the white pp. formed when CO_2 is passed into a solution of BaO in anhydrous methyl alcohol (Dumas a. Péligot, *A. Ch.* [2] 74, 6). It is insol. alcohol, but dissolves in water, the solution soon depositing $BaCO_3$.

Di-methyl carbonate $C_3H_6O_3$ *i. e.* $(CH_3)_2CO_3$. [0·5°] (Röse, *A.* 205, 231). (91°). S.G. $\frac{22}{}$ 1·069. H.F.p. 138,390. H.F.v. 136,360 (Thomsen, *Th.*). Formed by boiling methyl chloroformate $ClCO_2Me$ with lead oxide (Councler, *B.* 13, 1697). Formed also from $ClCO_2Me$ and NaOMe (Schreiner, *J. pr.* [2] 22, 354). Oil, insol. water, sol. alcohol and ether. Converted by dry chlorine into hexa-chloro-di-methyl carbonate (*q. v.*).

METHYL-CARBOPYRIDIC ACID *v.* Methyl-pyridine carboxylic acid.

METHYL-CARBOSTYRIL *v.* *Methyl ether* of Carbostyril and Oxy-methyl-quinoline.

METHYL CETYL KETONE $C_{18}H_{36}O$ *i.e.* $C_{16}H_{33}.CO.CH_3$. [52°]. (252° at 100 mm.). Formed by distilling a mixture of barium margarate and barium acetate (Krafft, *B.* 15, 1707). Yields palmitic and acetic acids on oxidation.

METHYL-CHELIDAMIC ACID *v.* Chelidonic acid.

METHYL-CHLORACETOL *v.* Di-chloro-propane.

METHYL CHLORIDE CH_3Cl. *Chloro-methane.* Mol. w. 50·5. (-23·7°) (Regnault). V.D. 1·73 (calc. 1·75). S.G. $\frac{-23.7}{}$ ·9915; $\frac{0}{}$ ·9523 (Vincent a. Delachanal, *A. Ch.* [5] 16, 429). S. 5·03 at 7°; 3·46 at 20° (Baeyer, *A.* 107, 181). S. (alcohol) 35. S. (HOAc) 40. H.F.p. 22,550. H.F.v. 21,970 (Thomsen). S.V. 50·8 (Lossen, *A.* 254, 68). *Latent heat of evaporation* 96,900 at 0° (Chappuis, *A. Ch.* [6] 15, 507).

Formation.—1. By heating a mixture of NaCl (2 pts.), wood spirit (1 pt.) and H_2SO_4 (3 pts.) and collecting the gas over water

(Dumas a. Péligot, *A. Ch.* 61, 193; *A.* 15, 17).—2. By exposing a mixture of equal volumes of methane and chlorine to daylight (Berthelot, *A. Ch.* [3] 52, 97).

Preparation.—1. HCl is passed into MeOH (2 pts.) containing $ZnCl_2$ (1 pt.). The gas is passed through KOH and H_2SO_4 (Groves, *C. J.* 27, 641; *A.* 174, 378).—2. By heating trimethylamine hydrochloride at 260°, the reaction being perhaps $3NMe_3HCl = 2NMe_3 + NH_3 + 3MeCl$ (Vincent, *J. Ph.* [4] 30, 132).

Properties.—Colourless gas, with ethereal odour. Burns with a bright flame, edged with green.

Reactions.—1. When passed through a *red-hot tube* it deposits charcoal and yields HCl, methane, ethylene, CO, and naphthalene (Perrot, *A.* 101, 375).—2. When passed over *heated potash-lime* it yields potassium formate, KCl, and hydrogen.—3. Not attacked by *chlorine* in diffused daylight, but when the mixture is exposed to direct sunlight, substitution occurs, the products being methylene chloride, chloroform, and CCl_4. The chlorination may also be effected by passing a mixture of chlorine and methyl-chloride over animal charcoal at 250°–350° (Damoiseau, *C. R.* 92, 42).—4. When equal volumes of methyl chloride and of an amine are submitted to a pressure of 25 atmospheres for 48 hours the following reactions occur.—(*a*) *Ammonia* forms $NMeH_3Cl$, NMe_3HCl, and $2NH_4Cl$.—(*b*) *Methylamine* forms $2NMeH_3Cl$ and NMe_4Cl.—(*c*) *Dimethylamine* reacts with formation of NMe_2H_2Cl and NMe_4Cl.—(*d*) *Trimethylamine* forms NMe_4Cl (Vincent a. Chappuis, *Bl.* [2] 45, 496).

Hydrate MeCl 9aq. Formed by cooling below 0° water into which MeCl is passed. Its vapour-tension has been studied by De Forcrand a. Villard, *C. R.* 106, 1357, 1404).

METHYL-CHLORO-ALLYL CARBINOL *v.* Chloro-pentenyl alcohol.

DI-METHYL-CHLORO-ANILINE *v.* Chloro-di-methyl-aniline.

TRI-METHYL CHLORO-AURO-PHOSPHITE $Me_3PAuClO_3$. [101°]. Formed by the action of pure methyl alcohol on aurous chloride and phosphorus (Lindet, *C. R.* 103, 1014). Slender colourless needles, insol. water, sol. MeOH.

METHYL CHLORO-BUTYL CARBINOL *v.* Chloro-hexyl alcohol.

METHYL - CHLORO - CARBOSTYRIL *v.* Chloro-oxy-methyl-quinoline.

METHYL CHLORO-ETHYL OXIDE C_3H_7ClO *i.e.* $CH_3.CHCl.OMe$. (72°–75°). S.G. $\frac{17}{}$ ·996. Formed from aldehyde (1 vol.), methyl alcohol ($1\frac{1}{2}$ vols.), and dry HCl at 0° (Geuther, *A.* 225, 270).

METHYL TETRA-CHLORO-ETHYL OXIDE $C_3H_4Cl_4O$ *i.e.* $CCl_3.CHCl.O.CH_3$. (178°). S.G. $\frac{0}{}$ 1·84. Formed by the action of PCl_5 on chloral methylate (Magnanini, *G.* 16, 330). Colourless liquid.

METHYL CHLORO-FORMAMIDE *v.* Chloro-formic acid.

METHYL CHLORO - PROPYL KETONE C_5H_9ClO *i.e.* $CH_3.CO.CHClEt$. (130°). Formed by heating $CH_3.CO.CClEt.CO_2Et$ with dilute HCl at 180° (Conrad, *A.* 186, 241).

Methyl tri-chloro-propyl ketone $C_5H_7Cl_3O$ *i.e.* $CH_3.CO.C_3H_4Cl_3$. (193°). Formed by oxidising $C_3H_4Cl_3.CHMe.OH$ with chromic acid mixture (Garzarolli-Thurnlackh, *A.* 223, 152). Heavy oil. Does not combine with $NaHSO_3$. Yields CO_2, acetic acid, and HCl on oxidation.

DI - METHYL - CHLORO - QUINALDINE *v.* Chloro-tri-methyl-quinoline.

METHYL-TRI-CHLORO-QUINOLINE *v.* Tri-chloro-methyl-quinoline.

METHYL DI - CHLORO - VINYL OXIDE $C_3H_4Cl_2O$ *i.e.* $CCl_2:CH.O.CH_3$. (110°). S.G. $\frac{0}{}$ 1·2934; $\frac{100}{}$ 1·1574. Prepared by heating tri-chloro-ethylene with KOMe, being ppd. on addition of water (Denaro, *G.* 14, 117). Colourless oil, with an odour resembling that of acetal. Decomposed on exposure to air, with evolution of HCl. When heated with dilute H_2SO_4 it yields di-chloro-acetic orthaldehyde.

Methyl tri-chloro-vinyl oxide $CCl_2:CCl.O.CH_3$. Readily absorbs dry oxygen, forming the compound $COCl.CCl(OMe)$, which, by the action of water, gives oxalic acid (Henry, *B.* 12, 1838).

METHYL-CHRYSOÏDINE *v.* *Benzene*-Azo-*methyl-phenylene-diamine.*

METHYL-CINCHENIC ACID *v.* Cinchene.

METHYL - CINCHONAMINE *v.* Cinchona bases.

DI-METHYL-CINCHONIC ACID *v.* Di-methyl-quinoline carboxylic acid.

METHYL-CINCHONIDINE *v.* Cinchonidine.

METHYL-CINCHONINE *v.* Cinchonine.

METHYL-CINNAMIC ACIDS *v.* Phenyl-methacrylic acid and Tolyl-acrylic acid.

METHYL - CINNAMIC ALDEHYDE *v.* Phenyl-methacrylic aldehyde.

METHYL CINNAMYL KETONE *v.* Benzyl-idene-acetone.

METHYL-CINNOLINE CARBOXYLIC ACID

$$C_{10}H_8N_2O_2 \text{ i.e. } C_6H_3(CO_2H)\Big\langle\begin{array}{l}CMe:CH\\ \quad\;\;|\\ N{=}N\end{array} . \;[c.\ 230°].$$

Small tables or fine needles. Sol. acetic acid, sl. sol. hot alcohol and hot water, insol. cold water. Dissolves both in aqueous acids and alkalis, forming easily soluble salts. Obtained, as a yellow pp., by adding $NaNO_2$ to a cold solution of the hydrochloride of amido-propenyl-benzoic acid $C_6H_3(CMe:CH_2)(NH_2)CO_2H$[1:2:4]; very probably di-azo-propenyl-benzoic acid $C_6H_3(CO_2H)\Big\langle\begin{array}{l}CMe:CH_2\\ N{=}N.OH\end{array}$ is first formed, which then splits off H_2O (Widman, *B.* 17, 722).

METHYL-CITRACONIC ACID $C_6H_8O_4$. [100°]. A product of the dry distillation of methyl-para-conic acid (Fränkel, *A.* 255, 25). Long needles (from $CHCl_3$). Reduced by sodium-amalgam to ethyl-succinic acid.—CaA″ aq.—BaA″ 4aq.—Ag_2A'.

METHYL-COCAÏNE $C_{18}H_{23}NO_4$. [47°]. Extracted from synthetical cocaïne (*cf.* vol. ii. p. 230), in which it occurs in very small quantity (Liebermann a. Giesel, *B.* 23, 508, 926). An oil, which crystallises after standing some hours. Ppd. by Na_2CO_3 from its salts. Very sol. ether, chloroform, benzene, and ligroïn. It can be separated from ordinary cocaïne by means of its nitrate. A 5·4 p.c. solution of the hydrochloride in a 2-dm. tube gave a rotation of +4·5°. By heating with water it is not so easily decomposed as ordinary cocaïne. By boiling with hydriodic acid MeI is split off. By hydrochloric acid it is split

up finally into methyl alcohol, benzoic acid, and methyl ecgonine hydrochloride. This reaction is also more difficultly brought about than with ordinary cocaïne. Methyl-cocaïne appears to be identical with 'dextro-cocaïne,' a body got by heating the methyl-ether of dextro-ecgonine with BzCl (Einhorn a. Marquardt, *B.* 23, 468).

Salts.—B'HCl. [210°]: needles or columns forming rosettes (from hot alcohol); much less soluble than the hydrochloride of ordinary cocaïne.—Sulphate: plates, v. sol. water, sl. sol. alcohol.—Nitrate: crystals, sl. sol. water.—Platino-chloride $(C_{18}H_{23}NO_4.HCl)_2PtCl_4$: glittering yellowish needles (from hot water).—Auro-chloride $C_{18}H_{23}NO_4HClAuCl_3$. [148°]: needles; melts under water to a yellow oil.

METHYL-CODEÏNE $C_{19}H_{23}NO_3$ *i.e.* $C_{18}H_{20}MeNO_3$ or $C_{17}H_{17}Me_2NO_3$. [118·5°]. $[\alpha]_D = -209°$ in a 4 p.c. solution (in 97 p.c. alcohol) at 15°. Formed by boiling codeïne methylo-iodide $C_{18}H_{21}NO_3MeI$ with potash, and extracting with benzene (Grimaux, *A. Ch.* [5] 27, 276; Hesse, *A.* 222, 218). Anhydrous prisms (from alcohol or ether), or hydrated crystals (containing aq) (from water). Insol. water, v. e. sol. hot alcohol, m. sol. ether. Its solution in conc. H_2SO_4 is violet, but becomes blue on heating. Boiling Ac_2O forms a compound $C_{17}H_{14}O_3$. [131°]. Its hydrochloride forms a brown solution in H_2SO_4, which becomes violet on warming, and finally blue on exposure to the air.—B'HCl 2aq: needles. S. 9 at 18°. V. e. sol. alcohol, sl. sol. NaClAq.—$B'_2H_2PtCl_6$ aq.

Acetyl derivative $C_{17}H_{16}AcMe_2NO_3$. [66°]. Formed by heating methyl-codeïne with Ac_2O at 85°, adding aqueous NH_3 and extracting with ether (Hesse, *A.* 222, 222). Glittering tables (from ether); v. sol. alcohol and ether, sl. sol. water, insol. KOHAq. Alcoholic potash forms potassium acetate and methyl-codeïne.—$(C_{17}H_{16}AcMe_2NO_3)HCl\,\frac{1}{2}aq$: satiny plates, sl. sol. cold water. — $(C_{17}H_{16}AcMe_2NO_3)_2H_2PtCl_6$ 4aq: yellow laminæ. — $(C_{17}H_{16}AcMe_2NO_3)HNO_3$ 3aq: satiny plates.—$(C_{17}H_{16}AcMe_2NO_3)_2H_2SO_4$ 8aq.

(α)-*Methylo-iodide* $C_{19}H_{23}NO_3MeI\,\frac{1}{2}aq$: prisms, formed at once on dissolving methyl-codeïne in a mixture of MeI and methyl alcohol (Hesse).

(β)-*Methylo-iodide* $C_{19}H_{23}NO_3MeI$. Slender crystals, formed by boiling the preceding with aqueous NaOH, and ppg. with KI. It is less soluble in water than its (α)-isomeride. Ag_2SO_4 forms $(C_{19}H_{23}NO_3Me)_2SO_4$, crystallising in plates.

(α)-*Methylo-chloride* $C_{19}H_{23}NO_3MeCl$. From the (α)-iodide and AgCl. Amorphous. With platinic chloride it yields a yellow flocculent pp. of $(C_{19}H_{23}NO_3MeCl)_2PtCl_4$ 8aq. With Ac_2O it yields $C_{19}H_{22}AcNO_3MeCl\,2\frac{1}{2}aq$, which crystallises in long satiny needles, v. e. sol. alcohol, sl. sol. cold water. Its platinochloride $(C_{19}H_{22}AcNO_3MeCl)_2PtCl_4$ 4aq is a yellow crystalline pp.

(β)-*Methylo-chloride* $C_{19}H_{23}NO_3MeCl\,\frac{1}{2}aq$. Radiating crystalline mass, v. sol. water and alcohol. With conc. H_2SO_4 it gives a purple colour. With platinic chloride it yields an orange pp. of small needles of the platinochloride $(C_{19}H_{23}NO_3MeCl)_2PtCl_4$ aq. With Ac_2O it yields amorphous $C_{19}H_{22}AcNO_3MeCl$, which forms $(C_{19}H_{22}AcNO_3MeCl)_2PtCl_4$ 3aq, a yellow powder.

Methylo-hydroxide $^{x}C_{19}H_{23}NO_3MeOH$. Formed from the (β)-methylo-sulphate and baryta. Colourless plates, insol. ether, v. sol. alcohol. Strongly alkaline in reaction. Conc. H_2SO_4 forms a blue solution. Gives off tri-methylamine when strongly heated.

METHYL-COLCHICINE $C_{23}H_{27}NO_6$ *i.e.* $C_{15}H_9(OMe)_3(NAcMe).CO_2Me$. Occurs in the mother-liquor from which the compound of colchicine with chloroform has separated (vol. ii. p. 234). Decomposed by boiling dilute HCl into methyl chloride and methyl-colchiceïn $C_{15}H_9(OMe)_3(NAcMe).CO_2H$ (Johanny a. Zeisel, *M.* 9, 871).

DI-METHYL-COLCHICINIC ACID *v. Di-methyl derivative* of COLCHICINIC ACID.

Tri-methyl-colchicinic acid $C_{19}H_{21}NO_5$ *i.e.* $C_{15}H_9(OMe)_3(NH_2).CO_2H$. [150°]. Formed by the action of HCl on colchiceïn (*q.v.*). Forms a platinochloride $B'_2H_2PtCl_6$ 2aq. On warming with acetic anhydride it yields colchiceïn $C_{15}H_9(OMe)_3(NHAc).CO_2H$. With MeOH it forms an addition-product $C_{19}H_{21}NO_5 2MeOH$. On warming with MeOH, methyl iodide, and sodium it yields 'tri-methyl-colchidimethinic acid' $C_{15}H_9(OMe)_3(NMe_2)CO_2H$ [125°]. The methyl ether of this body forms an iodomethylate $C_{23}H_{30}NO_5Iaq$ (Johanny a. Zeisel, *M.* 9, 877).

METHYL-CONIINE *v.* CONIINE.

METHYL-COUMARIC ACID *v. Methyl-derivative* of COUMARIC ACID.

Di-methyl-di-coumaric acid so-called *v.* DI-METHYL-DI-COUMARIN.

METHYL-COUMARILIC ACID $C_{10}H_8O_3$ *i.e.* $C_6H_4{<}{}^{CMe}_{O}{>}C.CO_2H$. [126°]. Formed by the action of dilute KOH upon the methyl-derivative of *exo*-bromo-coumaric acid (Perkin, *C. J.* 39, 423). Needles (from CS_2).

(β)-Methyl-coumarilic acid $C_{10}H_8O_3$ *i.e.* $C_6H_4{<}{}^{CMe}_{O}{>}C.CO_2H$. [189°]. Formed by saponifying its ethyl ether with alcoholic potash (Hantzsch, *B.* 19, 1290). Feathery needles (from dilute alcohol). Decomposed by heat into CO_2 and (β)-methyl-coumarone. — KA'aq: needles. — NH_4A'aq: needles (from water). — BaA'_2 3aq.—AgA': minute prisms.

Ethyl ether EtA'. [51°]. (290°). Formed by the action of sodium phenylate $NaOC_6H_5$ upon chloro-aceto-acetic ether, the resulting phenoxy-aceto-acetic ether being condensed by cold conc. H_2SO_4 (Hantzsch).

Amide $C_8H_4(CH_3)O.CO.NH_2$: [145°]; needles (Hantzsch, *B.* 19, 2401).

Di-methyl-coumarilic acid $C_{11}H_{10}O_3$ *i.e.* $C_6H_3(CH_3){<}{}^{C(CH_3):C.CO_2H}_{O}$. *Di-methyl-coumarone-α-carboxylic acid.* [225°].

Formation.—1. By the action of hot alcoholic KOH upon bromo-di-methyl-cumarin $C_6H_3(CH_3){<}{}^{C(CH_3):CBr}_{O\text{———}CO}$.—2. By saponification of the ethyl-ether obtained by the reaction of sodium *p*-cresol and chloro-aceto-acetic ether.

Properties.—Short prisms or tables. On heating the sodium salt with lime di-methyl-coumarone is obtained.

Ethyl ether A'Et: [55°]; (300° at 728 mm.) (Hantzsch a. Lang, *B.* 19, 1299).

Reference.—COUMARILIC ACID and OXY-METHYL-COUMARILIC ACID.

METHYL-COUMARIN *v. Anhydride* of OXY-PHENYL-CROTONIC ACID.

m-β-Di-methyl-coumarin $C_{11}H_{10}O_2$ *i.e.*

$$\left[5{:}\tfrac{1}{2}\right]C_6H_3(CH_3)\Big\langle\begin{matrix}CMe{:}CH\\ \quad\ \vert\\ O{-}{-}CO\end{matrix}$$ [148°]. Formed by the action of H_2SO_4 on a mixture of aceto-acetic ether and *p*-cresol (Pechmann a. Duisberg, *B.* 16, 2127; Pechmann a. Cohen, *B.* 17, 2187). Long colourless needles.

Reference.—BROMO-DI-METHYL-COUMARIN.

Di-methyl-di-coumarin $C_{14}H_{10}O_4$ *i.e.*

$$C_6H_2\left(\Big\langle\begin{matrix}CMe{:}CH\\ \quad\ \vert\\ O{-}{-}CO\end{matrix}\right)_2$$. Formed by dissolving resorcin (1 mol.) and acetoacetic ether (2 mols.) in conc. H_2SO_4; yield 10 p.c. Microcrystalline white powder. V. sl. sol. boiling alcohol, nearly insol. water, ether, chloroform, benzene, &c. Dissolves in aqueous alkalis to a yellow solution, from which acids ppt. di-methyl-di-coumaric acid $C_6H_2(OH)_2(CMe{:}CH.CO_2H)_2$. The latter forms a white powder, sol. alcohol; at 140° it is completely reconverted into the anhydride (Hantzsch a. Zürcher, *B.* 20, 1328).

Tri-methyl-tri-coumarin $C_{18}H_{12}O_6$ *i.e.*

$$C_6\left(\Big\langle\begin{matrix}CMe{:}CH\\ \quad\ \vert\\ O{-}{-}CO\end{matrix}\right)_3$$. Formed by dissolving phloroglucin (1 mol.) and acetoacetic ether (3 mols.) in conc. H_2SO_4; the yield is less than 10 p.c. Amorphous powder. Insol. all solvents. Dissolves in aqueous alkalis to a yellow solution, from which acids ppt. tri-methyl-tri-coumaric acid $C_6(OH)_3(CMe{:}CH.CO_2H)_3$, whose sodium salt is Na_3A''' 6aq (Hantzsch a. Zürcher, *B.* 20, 1330).

(β)-METHYL-COUMARONE C_9H_8O *i.e.*

$C_6H_4\Big\langle\begin{matrix}CMe\\ O\end{matrix}\Big\rangle CH$. [189°]. Formed, together with CO_2, by distilling (β)-methyl-coumarilic acid. Oil, volatile with steam. Does not react with hydroxylamine or phenyl-hydrazine.

Di-methyl-coumarone $C_{10}H_{10}O$ *i.e.*

$C_6H_3(CH_3)\Big\langle\begin{matrix}C(CH_3)\\ O\end{matrix}\Big\rangle CH$. (210° at 728 mm.). Indifferent oil. Formed by distilling the sodium salt of di-methyl-coumarilic acid (di-methyl-coumarone-α-carboxylic acid with lime (Hantzsch a. Lang, *B.* 19, 1300).

METHYL-CREOSOL *v. Methyl ether* of CREOSOL.

METHYL CROTONIC ACIDS *v.* ANGELIC ACID and TIOLIC ACID.

METHYL ISOCROTYL OXIDE *v. See*-ISO-BUTENYL ALCOHOL.

METHYL-CUMARIN *v.* METHYL-COUMARIN.

METHYL-CUMAZONIC ACID $C_{12}H_{13}NO_3$

i.e. $C_6H_3(CO_2H)\Big\langle\begin{matrix}CMe_2.O\\ \quad\ \vert\\ N{=}{=}CMe\end{matrix}$ (?). [218°].

Formation.—1. By boiling (3:4:1)-amido-oxypropyl-benzoic acid with acetic anhydride. 2. By boiling acetyl-amido-oxypropyl-benzoic acid with HCl.—3. By boiling acetyl-amido-propenyl-benzoic acid with HCl. Small colourless trimetric tables. V. sol. alcohol, insol. water. Its N is tertiary.

Reactions.—By reduction with sodium-amalgam it yields the acetyl derivative of amido-cuminic acid.

Salts.—$A'H,HCl^{x}$: very soluble white needles.—$(A'H,HCl)_2PtCl_4$: tables, cubes, or prisms.—$A'H,H_2SO_4$ aq: very soluble white silky needles (Widmann, *B.* 16, 2576).

METHYL-CUMENE *v.* CYMENE.

METHYL-ψ-CUMIDINE $C_{10}H_{15}N$ *i.e.* $C_6H_2(CH_3)_3NHMe$. [44°]. (237°). Formed by methylation of solid cumidine [63°].—$B'_2H_2Cl_2PtCl_4$: sparingly soluble needles (Hofmann, *B.* 15, 2896).

Di-methyl-ψ-cumidine $C_6H_2(CH_3)_3.NMe_2$. (222°). Oil. Formed by methylation of solid cumidine [63°].—$B'_2H_2Cl_2PtCl_4$ (Hofmann, *B.* 15, 2897).

Methylo-iodide $C_6H_2(CH_3)_3NMe_3I$. Prisms. Yields $(C_6H_2(CH_3)_3NMe_3Cl)_2PtCl_4$.

METHYL CUMYLETHYL KETONE $C_3H_7.C_6H_4.CH_2.CH_2.CO.CH_3$. *Cuminyl-acetone.* (260°–265°). Is one of the products of the action of NaOEt and cuminyl chloride on aceto-acetic ether (Widmann, *B.* 22, 2271). Colourless liquid, with fragrant odour. Is not acted upon by NaOBr. Oxidised by $KMnO_4$ to cuminic acid.

Oxim $C_3H_7.C_6H_4.CH_2.CH_2.C(NOH).CH_3$. [57°]. Long shining prisms (from ligroïn).

METHYL CUMYL KETONE $CH_3.CO.C_6H_4Pr$ [1:4]. (253°). S.G. $\frac{15}{}$ ·9755. Formed by the action of AcCl on cymene in presence of $AlCl_3$ (Widmann, *B.* 21, 2225).

Oxim $CH_3.C(NOH).C_6H_4Pr$. [71°]. Four-sided tables (from petroleum-ether).

Phenyl-hydrazide $CH_3.C(N_2HPh).C_6H_4Pr$. [82°]. Colourless thick six-sided tables (from petroleum-ether).

METHYL-CYANAMIDE *v. Cyanamide* in the article CYANIC ACIDS.

METHYL CYANATE *v.* CYANIC ACIDS.

METHYL-CYANETHINE *v.* CYANETHINE.

METHYL CARBIMIDE is *Methyl isocyanate v.* CYANIC ACIDS.

METHYL-CYANIC ACID *v.* CYANIC ACID.

METHYL CYANIDES *v.* ACETONITRILE and METHYL CARBAMINE.

Di-methyl di-cyanide $C_4H_6N_2$ *i.e.* $NH{:}CMe.CH_2.CN$ or $NH_2.CMe{:}CH.CN$. [53°]. V.D. 42·5. Formed by the action of dry sodium on acetonitrile dissolved in ether. Methane is evolved in the reaction, and the product is decomposed by water (Holtzwart, *J. pr.* [2] 38, 343; 39, 240). White needles, v. sol. ether, alcohol, chloroform, and benzene, m. sol. water, sl. sol. petroleum ether.

Reactions.—1. Boiling water liberates ammonia forming $C_8H_8N_2O$, a body which is converted by PCl_5 into crystalline $C_8H_8N_2Cl_2$ [175°], which, on recrystallisation from water, becomes $C_8H_6N_2$.—2. *Acetyl chloride* forms a compound $(C_4H_6N_2)_2CH_3COCl$, which on decomposition by water yields $C_8H_9N_3$, crystallising in beautiful white needles [223°].—3. Warm dilute (25 p.c.) HClAq forms NH_4Cl and an oil which has the composition of cyano-acetone. It solidifies to a glassy mass, carbonises above 230°, and forms with phenyl-hydrazine a condensation product [97°].

Tri-methyl tri-cyanide *v.* CYANMETHINE.

METHYL-CYANO-FORMAMIDE *v. Methyl-amide* of *Para*-CYANOFORMIC ACID.

METHYL-CYANO-SUCCINIC ETHER $C_{10}H_{15}NO_4$ *i.e.* $CO_2Et.CH_2.CMeCy.CO_2Et$. An oil formed by treating cyano-succinic ether with Na and MeI successively (Barthe, *C. R.* 108, 297).

s-**Di-methyl-cyano-succinic ether** $C_{11}H_{17}NO_4$ *i.e.* $CO_2Et.CHMe.CMeCy.CO_2Et$. (273°). S.G. $\frac{24\cdot5}{}$ 1·0577. A product of the action of alcoholic KCy on α-bromo-propionic ether (Zelinsky, *B.* 21, 3164). Formed also by adding α-bromo-propionic ether to cyano-propionic ether mixed with KCy (Z.).

METHYL-CYANURIC ACID *v. Cyanuric acid* in the article Cyanic acids.

METHYL CYMYL KETONE $C_{12}H_{16}O$ *i.e.* $CH_3.CO.C_6H_3Me.C_3H_7$ [2:1:4]. (247°). An oil, formed by the action of AcCl on cymene in presence of $AlCl_3$ (Claus, *B.* 19, 233).

METHYL-DAMBOSE *v.* Bornesite, vol. i. p. 524.

Di-methyl-dambose *v.* Dambonite.

METHYL-DAPHNETIN *v.* Daphnetin.

METHYL DECYL KETONE $C_{12}H_{24}O$ *i.e.* $CH_3.CO.C_{10}H_{21}$. [21°]. (247°). Formed by distilling a mixture of barium acetate and barium hendecoate (undecylate) (Krafft, *B.* 15, 1708). Yields acetic and decoic acids on oxidation.

METHYL - DESOXYBENZOÏN *v.* Tolyl benzyl ketone.

Dimethyldesoxybenzoïn *v.* Benzyl xylyl ketone.

METHYL DODECYL KETONE $C_{14}H_{28}O$ *i.e.* $CH_3.CO.C_{12}H_{25}$. [34°]. (206° at 100 mm.). Formed by distilling barium tridecoate $(C_{13}H_{25}O_2)_2Ba$ with barium acetate (Krafft, *B.* 15, 1708). Yields lauric and acetic acids on oxidation.

METHYL *c*-DURYL KETONE $C_{12}H_{16}O$ *i.e.* $CH_3.CO.C_6HMe_4$ [1:2:3:4:5]. (259°). From *c*-durene, AcCl, and $AlCl_3$ (Claus a. Föhlisch, *J. pr.* [2] 38, 230). Oil.

Phenyl hydrazide. [129°]. Laminæ.

Isomerides *v.* Duryl methyl ketones.

METHYL-ECGONINE $C_{10}H_{17}NO_3$. [264°]. A product of the action of HCl on methyl-cocaïne, the resulting methyl-ecgonine hydrochloride being decomposed by Ag_2O (Liebermann a. Giesel, *B.* 23, 510). May be crystallised from methyl alcohol containing a trace of water. Extremely sol. water, insol. absolute alcohol, v. sl. sol. absolute MeOH. Decomposed by fusion. A 9·6 p.c. solution of the hydrochloride exhibits $\alpha = +2°$.—B′HCl: [236°]; needles (from methyl alcohol-ether).—$B'HAuCl_4$: [220°]; lemon-yellow needles.

Benzoyl derivative. Hydrochloride $C_{17}H_{21}NO_4HCl$. The first product of the action of hydrochloric acid on methyl-cocaïne [47°], the base being just dissolved in HCl and then heated ½ hour at 90°. Glassy columns (from hot water). The base is not ppd. by carbonate of soda.—Aurochloride $C_{17}H_{21}NO_4.HCl.AuCl_3$. The nitrate is v. sl. sol. water.

METHYLENE. The radicle CH_2, which is not known to exist in the free state.

Dimethylene C_2H_4 *i.e.* $CH_2{:}CH_2$ is called Ethylene (*q. v.*).

Trimethylene C_3H_6 *i.e.* $CH_2\left<\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right.$. H.F.p. −3470. H.F.v. −4630. This gas is formed when trimethylene bromide $CH_2Br.CH_2.CH_2Br$ (140 g.) is boiled with sodium (5 g.). The contents of the flask become pasty, but still contain much of the bromide (120 g.), which can be mostly recovered by filtration (Freund, *J. pr.* [2] 26, 367). It is also formed by heating trimethylene bromide with zinc-dust and 75 p.c. alcohol (Gustavson, *J. pr.* [2] 36, 300). Trimethylene burns with a bright flame and smells like butylene.

Reactions.—1. Trimethylene is readily absorbed by fuming HI. The product is *n*-propyl iodide, whereas propylene gives *iso*-propyl iodide. 2. Trimethylene is very slowly absorbed by *bromine*; the product is trimethylene bromide (165°). Propylene is readily absorbed, forming propylene bromide.—3. Conc. H_2SO_4 forms liquid hydrocarbons, and on diluting and distilling *n*-propyl alcohol is got (G.).—4. $KMnO_4$ does not oxidise it (Wagner, *B.* 21, 1230).

References.—Trimethylene carboxylic acids, Trimethylenyl methyl ketone, and Phenyl trimethylenyl ketone.

Tri-methylene is a term also applied to the divalent radicle $CH_2.CH_2.CH_2$.

Tetra-methylene is a term applied to the ring $\begin{matrix}CH_2.CH_2\\|\quad\;\;|\\CH_2.CH_2\end{matrix}$, and it is also used to denote the group $CH_2.CH_2.CH_2.CH_2$.

Pentamethylene is a name used to denote $CH_2\left<\begin{matrix}CH_2.CH_2\\|\\CH_2.CH_2\end{matrix}\right.$, and also $CH_2.CH_2.CH_2.CH_2.CH_2$.

Hexamethylene is benzene hexahydride. According to Baeyer (*A.* 258, 156), it should be regarded as lying entirely in one plane.

METHYLENE ACETATE *v. Acetyl derivative* of Formic orthaldehyde, vol. ii. p. 570.

TRIMETHYLENE-ACETO-ACETIC ACID, so-called, *v.* vol. i. p. 24.

METHYLENE-DIAMINE *Di-benzoyl derivative* $CH_2(NHBz)_2$. [221°]. S. (alcohol) ·47 at 14·5°; ·63 at 22°; *Hipparaffin.*

Formation.—From hippuric acid, PbO_2 and HNO_3 or H_2SO_4 (H. Schwarz, *A.* 75, 201; *Sitz. W.* 77, ii. 762; J. Maier, *A.* 127, 162; Kraut a. Y. Schwarz, *A.* 223, 40).

Preparation.—From benzonitrile (15 g.), methylal (6 g.) and conc. H_2SO_4 (100 g.) (Hepp a. Spiess, *B.* 9, 1424).

Properties.—Long white felted needles (from alcohol), v. sol. CS_2, ether, and chloroform.

Reactions.—1. Dissolves unchanged in conc. H_2SO_4, and in fuming HNO_3.—2. On *distillation* some passes over unchanged along with benzoic acid.—3. Not affected by *bromine*.—4. Boiled for some time with dilute (32 p.c.) H_2SO_4 it gives formic aldehyde, NH_3 and benzoic acid.—5. Heated in sealed tubes with dilute HCl it yields benzamide and formic paraldehyde.

Trimethylene-diamine $C_3H_{10}N_2$ *i.e.* $NH_2.CH_2.CH_2.CH_2.NH_2$. (c. 140°). Formed by heating trimethylene bromide (1 mol.) and NH_3 (20 mols.) in alcohol for 10 hours at 100°. The liquid is decanted from NH_4Br and evaporated, treated with KOH and distilled (Fischer a. Koch, *B.* 17, 1799; Lellmann a. Würthner, *A.* 228, 227). Colourless mobile liquid, easily miscible with alcohol, ether, and benzene. Fumes in moist air, combining with water to form a

hydrate. Readily takes up CO_2 becoming solid. Condenses with benzoic aldehyde forming $C_3H_6(N{:}CHPh)_2$. Phenanthraquinone forms $C_{31}H_{17}NO_2$ a yellow powder, melting above 250°. Benzil forms $CH_2\left<\begin{matrix}CH_2.N{:}CPh\\CH_2.N{:}CPh\end{matrix}\right>$ a transparent vitreous mass [c. 76°].

Salts.—$B''H_2Cl_2$. Easily soluble prisms.—$B''H_2Cl_2PtCl_4$. Orange prisms. — $B''(HSCN)_2$. [102°]. At 140° it is partially decomposed into trimethylene thio-urea and NH_4SCN. — $B''H_2Br_2$.

Diacetyl derivative $C_3H_6(NHAc)_2$. [79°]. White needles, v. e. sol. water, v. sol. alcohol, chloroform, sl. sol. benzene, insol. ether, petroleum ether (Strache, *B.* 21, 2364).

Dibenzoyl derivative $C_3H_6(NHBz)_2$. [148°]. White crystalline powder, insol. water, m. sol. benzene, v. sol. alcohol and chloroform. On heating in a stream of HCl the product is $C_3H_6\left<\begin{matrix}N\\NH\end{matrix}\right>CPh$, an oily base which slowly becomes crystalline and forms crystalline salts (Hofmann, *B.* 21, 2337).

Oxalyl derivative $CH_2\left<\begin{matrix}CH_2.NH.CO\\CH_2.NH.CO\end{matrix}\right>$. A sparingly soluble white powder, formed on mixing trimethylene-diamine with an alcoholic solution of methyl oxalate. It does not melt at 250°.

Derivative.—*V.* Oxy-tri-methylene-diamine.

Trimethylene di-nitro-di-amine $C_3H_8N_4O_4$ *i.e.* $NO_2.NH.CH_2.CH_2.CH_2.NH.NO_2$. [67°]. Formed by heating $C_3H_6(N(NO_2).CO_2Me)_2$ (*v.* Tri-methylene dicarbamic acid) with aqueous ammonia (Franchimont a. Klobbie, *R. T. C.* 7, 343). Short thick prisms (from water or alcohol), v. sol. water and alcohol, less sol. ether and chloroform. Boiled with dilute (2 p.c.) H_2SO_4 it evolves N_2O. It has no acid reaction, and easily forms metallic derivatives.

Tetra-methylene-diamine $C_4H_{12}N_4$ *i.e.* $NH_2.CH_2.CH_2.CH_2.CH_2.NH_2$. [24°]. (159°). Obtained by reducing ethylene cyanide in alcoholic solution with sodium (Ladenburg, *B.* 19, 780). Identical with the ptomaïne 'putrescine' (*cf.* L. Brieger, 'Die Ptomaïne,' Berlin, 1885–1886, 1, 43; 3, 101) and also with a base obtained from a morbid urine (Udranszky a. Baumann, *B.* 21, 2938). Strong base, smelling like piperidine. Solutions of its salts give a crystalline pp. with iodine dissolved in KIAq but no pp. with $HgCl_2$ or $KCdI_3$. When shaken with aqueous NaOH and BzCl it gives a crystalline pp. of the dibenzoyl derivative. Methyl chloroformate $ClCO_2Me$ forms $(CH_2)_4(NH.CO_2Me)_2$ which crystallises in flattened needles [128°], sl. sol. cold water, and is nitrated by HNO_3, yielding $(CH_2)_4(N(NO_2)CO_2Me)_2$ which crystallises from ether and melts at 62° (Dekkers, *R. T. C.* 9, 97).

Salts.—$B''H_2Cl_2$. Plates (from alcohol).—$B''H_2PtCl_6$. Needles.—Picrate. Thin yellow needles. — Aurochloride. [210°]. Minute thread-like needles, v. sol. hot water (Ciamician a. Zanetti, *B.* 22, 1973).

Di-benzoyl derivative $C_4H_8(NHBz)_2$. [175°] (U. a. B.); [178°] (C. a. Z.). Plates, insol. water, almost insol. ether, v. sol. hot alcohol. May be sublimed.

Tetra-methylene-di-nitro-di-amine $C_4H_{10}N_4O_4$ *i.e.* $(CH_2)_4(NH.NO_2)_2$. [163°]. Got by heating $(CH_2)_4(N(NO_2)CO_2Me)_2$ with conc. NH_3Aq at 100° and ppg. by HOAc (D.). Small hard crystals (from water).

Penta-methylene diamine $C_5H_{14}N_2$ *i.e.* $NH_2.CH_2.CH_2.CH_2.CH_2.CH_2.NH_2$ (178·5°) (L.); (178°–180·5°) (Perkin, *C. J.* 55, 699). S.G. $\frac{0}{4}$ ·9174 (L.); $\frac{15}{15}$ ·8846; $\frac{25}{25}$ ·8784. M. M. 7·493 (P.). Formed from trimethylene cyanide by reduction in ethereal solution with zinc and HCl, or in alcoholic solution with sodium (Ladenburg, *B.* 16, 1151; 18, 2956; 19, 780, 2585). It is identical with 'cadaverine' a base discovered by Brieger in corpses, and among the products of putrefaction of flesh and fish (Brieger, *B.* 16, 1186; 18, 1922; 'Die Ptomaïne,' Berlin, 1885; Ladenburg, *B.* 19, 2585). Found also in the urine of a patient suffering from cystinuria, but not in normal urine (U. a. B.). Syrup, smelling like piperidine; v. sol. water and alcohol, m. sol. ether. Fumes in the air. Absorbs CO_2 from the air. The hydrochloride is converted by dry distillation into NH_3, HCl, and piperidine.

Salts.—$B''H_2Cl_2$.—$B''H_2PtCl_6$. Thick orange prisms (from water); m. sol. cold water.—Periodide. Almost black crystals (from alcohol).—$B''H_2Cl_2\,3HgCl_2$. Crystals (from hot water) (L.).—$B''H_2Cl_2\,4HgCl_2$. Crystals (from alcohol) (B.).

Di-acetyl derivative $CH_2(CH_2.CH_2.NHAc)_2$. Small needles (from alcohol). May be distilled.

Di-benzoyl derivative $CH_2(CH_2.CH_2.NHBz)_2$. [130°]. (above 360°). Ppd. by adding aqueous NaOH and BzCl to a solution of the base (Udranszky a. Baumann, *B.* 21, 2744). Long needles and plates; v. sol. alcohol, m. sol. ether, insol. water. Not affected by hot dilute acids or alkalis.

Penta-methylene-di-nitro-di-amine $CH_2(CH_2.CH_2.NH(NO_2))_2$. Formed by treating $CH_2(CH_2.CH_2.N(NO_2).CO_2Me)_2$ with aqueous ammonia (Franchimont a. Klobbie, *R. T. C.* 7, 343). Small oblong plates (from chloroform); v. sol. water and alcohol, sol. ether, sl. sol. $CHCl_3$. When boiled with dilute (2 p.c.) H_2SO_4 it evolves N_2O.

Di-nitroso-penta-methylene-tetramine (so-called) $C_5H_{10}N_6O_2$ *i.e.* $C_5H_{10}N_4(NO)_2$. [207°] (G.); [203°] (M.). Formed by the action of nitrous acid on 'hexamethylene tetramine' (Griess, *B.* 21, 2738; Mayer, *B.* 21, 2888). Needles (from alcohol), v. sol. hot alcohol, m. sol. chloroform, insol. ether. Not affected by boiling with zinc-dust. Dilute HCl decomposes it into nitrogen, ammonia, and formic aldehyde.

Hexa-methylene-tetramine (so-called) $C_6H_{12}N_4$. *Hexamethyleneamine.* [189°]. S. (alcohol) 7. Mol. w. 115 (by Raoult's method) (calc. 140) (Tollens a. Mayer, *B.* 21, 1566). Formed by passing dry NH_3 over heated tri-oxy-methylene (formic paraldehyde) (Butlerow, *A.* 115, 322; *Z.* [2] 5, 278). Prepared by dissolving methylal in dilute H_2SO_4, and distilling the product with steam into a receiver containing ammonia (Wohl, *B.* 19, 1842).

Properties.—Rhombohedra (from alcohol), v. sol. water, chloroform, and CS_2. May be sublimed. Scarcely attacked by sodium-amalgam. Acts nutritiously upon algæ (Loew a. Bokorny, *J. pr.* [2] 36, 272).

Reactions.—1. Split up by boiling dilute

acids into formic aldehyde and ammonia.—2. MeI at 190° forms NMe_4I (Tollens, *B.* 17, 656). 3. *Sodium nitrite* ($2\frac{1}{2}$ pts.) added to a solution of the base (1 pt.) in dilute HCl at 0° forms 'tri-methylene-tri-nitrosamine' $C_3H_6N_6O_3$, which crystallises from alcohol in needles or prisms [106°], and is split up by warming with dilute acids into nitrogen and formic aldehyde. It exhibits Liebermann's reaction. When acetic acid is added gradually to a solution containing hexamethylene-tetramine and sodium nitrite there is formed the so-called di-nitroso-penta-methylene-tetramine (*v. supra*), which is much less soluble in the usual menstrua than the tri-methylene-tri-nitrosoamine.

Salts.—$B''H_2Cl_2$ (dried at 100°). Long prismatic needles; v. e. sol. water, sl. sol. alcohol.—$B''_2H_2PtCl_6$ 4aq.—$B''_2 3AgNO_3$. White crystalline pp., formed on adding $AgNO_3$ to an aqueous solution of hexamethylene-tetramine (Pratesi, *G.* 13, 437). Sl. sol. cold, m. sol. hot, water, with partial reduction to silver.

Methylo-iodide B″MeI. [190°]. V. sol. water, sl. sol. alcohol, insol. ether, chloroform, and CS_2. Gives $(B''Me)_2PtCl_6$. [205°].

Ethylo-iodide B″EtI. [133°].

Methyleno-iodide $B''CH_2I_2$. [165°]. (Wohl).

Di-bromide $C_6H_{12}N_4Br_2$. Insol. ordinary solvents (Legler, *C. C.* 1888, 1604).

Tetrabromide $C_6H_{12}N_4Br_4$. Red crystals, obtained by the action of bromine-vapour on hexamethylene tetramine (Horton, *B.* 21, 1999). Decomposed by boiling water.

Di-iodide $C_6H_{12}N_4I_2$. Obtained by adding an alcoholic solution of iodine to an aqueous solution of the base. Crystalline, v. sl. sol. alcohol.

Tetra-iodide $C_6H_{12}N_4I_4$. Obtained when excess of iodine is used. Minute brown plates, v. sol. acetone, $CHCl_3$, and CS_2. Decomposed by boiling water.

METHYLENE DI-ISOAMYL DIOXIDE *v.* Formic aldehyde.

METHYLENE - ANILINE $(C_7H_7N)_x$ *i.e.* $(CH_2:NPh)_x$. *Anhydro-formaldehyde-aniline.* [138°]. Formed by mixing aniline and crude formic aldehyde in the cold (Tollens, *B.* 17, 657; 18, 3309; Kolotoff, *Bl.* [2] 43, 112). White silky crystals, v. sol. chloroform and benzene, sl. sol. alcohol, insol. water. Decomposed by boiling with water or alcohol.—$B'_2H_2PtCl_6$.

Methylene-aniline C_7H_7N. Formed, together with di-phenyl-methylene-diamine and the preceding body by the action of formic aldehyde on aniline (Pratesi, *G.* 14, 355). Minute crystals, decomposed by heat. V. sl. sol. alcohol.

Methylene-di-aniline *v.* Di-phenyl-methylene-diamine.

METHYLENE-DIBENZYLAMINE $C_{15}H_{18}N_2$ *i.e.* $CH_2(NH.CH_2Ph)_2$. [46°]. (c. 227°). Formed by the action of methylene chloride on benzylamine at 100° (Kempff, *A.* 256, 220). Rhombic prisms, insol. water, v. sol. absolute alcohol and ether.

Salts.—$C_{15}H_{18}N_2 2HCl$. [242°]. Colourless monoclinic plates.—B″2HBr: silky plates.—B″2HI: monoclinic plates (from benzene), sl. sol. water and alcohol.—$B''H_2SO_4$ 2aq: colourless prisms.—$B''2H_3PO_4$. [c. 230°]. Needles.—$B''H_2Cl_2PtCl_4$: monoclinic plates.—Aurochloride $B''H_2Cl_2 2AuCl_3$: golden-yellow needles.—Oxalate $B''(H_2C_2O_4)_2$. [c. 134°].—Picrate $B''(C_6H_2(NO_3)_2OH)_2$: not stable in a hot solution, sl. sol. alcohol, and water.

METHYLENE-BLUE *v.* Tetra-methyl-di-amido-imido-di-phenyl sulphide.

TRIMETHYLENE BROMHYDRIN *v.* Bromo-propyl alcohol.

METHYLENE BROMIDE CH_2Br_2. *Di-bromo-methane.* (97° cor.) (Perkin, *C. J.* 45, 520); (98·5° i. V.) (Henry). S.G. $\frac{0}{0}$ 2·493 (H.); $\frac{15}{15}$ 2·4985; $\frac{25}{25}$ 2·4775 (P.). M. M. 8·110 at 15·9°. Formed by adding bromine to methylene iodide under water (Butlerow, *A.* 111, 251; Henry, *A. Ch.* [5] 30, 266). Formed also by heating methyl bromide with bromine at 250° (Steiner, *B.* 7, 507). Found among the bromides obtained by passing into bromine the products got by passing ethylene through a red-hot tube (Norton a. Noyes, *Am.* 8, 362). Colourless mobile liquid, insol. water, sol. alcohol and ether. Converted by PCl_5 at 190° into CCl_4 and CBr_4 (Höland, *A.* 240, 230). When heated with 18 vols. water and excess of PbO at 145° it yields ethylene glycol, traces of ethylene oxide, and $PbBr_2$ (Jeltekoff, *B.* 6, 558). Slowly converted by $SbCl_5$ into methylene chloride. Potassium phenylate KOC_6H_5 yields $CH_2(OC_6H_5)_2$.

Trimethylene bromide *v.* Di-bromo-propane.

Tetra-methylene bromide $C_4H_8Br_2$. (189°). Formed from ethylene cyanide by successive conversion into tetra-methylene diamine and $CH_2(OH).CH_2.CH_2.CH_2(OH)$; the glycol being then treated with HBr (Gustavson a. Demjanoff, *J. pr.* [2] 39, 542). The yield is small.

Penta-methylene bromide $C_5H_{10}Br_2$ *i.e.* $CH_2(CH_2.CH_2Br)_2$. (205°). Formed by saturating the corresponding di-oxy-pentane (derived from tri-methylene-diamine) with HBr (G. a. D.).

METHYLENE BROMO-IODIDE *v.* Bromo-iodo-methane.

METHYLENE-TETRA-BUTYL-DIAMINE $CH_2(N(C_4H_9)_2)_2$. (250°). Obtained by distilling trimethylene oxide with di-isobutyl-amine (Ehrenberg, *J. pr.* [2] 36, 124).—$B''H_2PtCl_6$. [198°]. Pale-yellow powder.—Aurochloride [c. 195°].—$B''CS_2$. [54°].

METHYLENE DI-ISOBUTYL DIOXIDE *v.* *Di-isobutyl ether* of Formic orthaldehyde, vol. ii. p. 571.

METHYLENE CAFFEIC ACID *v.* vol. i. p. 659.

TRIMETHYLENE DICARBAMIC ACID $\times CH_2(CH_2.NH.CO_2H)_2$.

Methyl ether $CH_2(CH_2.NH.CO_2Me)_2$. [75°]. Formed by treating trimethylene-diamine with methyl carbonate (Franchimont a. Klobbie, *R. T. C.* 7, 343). Oblique rhombic plates. V. sol. water, alcohol, and $CHCl_3$; m. sol. ether, v. sl. sol. benzene and light petroleum. Pure HNO_3 yields a dinitro- derivative forming tufts of needles or prisms from alcohol [90°], and this when treated with solution of ammonia gives tri-methylene-dinitramine [67°].

Ethyl ether $CH_2(CH_2NH.CO_2Et)_2$. *Tri-methylene-diurethane.* [42°]. (210° at 30 mm.). When a solution of trimethylene-diamine in alcohol and ether is added to an ethereal solution of chloro-formic ether $ClCO_2Et$, a pp. of trimethylene-diamine hydrochloride is formed, and the filtrate leaves on evaporation oily

$C_3H_6(NH.CO_2Et)_2$ (Fischer a. Koch, *A.* 232, 225). It crystallises after some time, and separates from ether in colourless prisms. V. sol. ether, alcohol, and chloroform, sl. sol. ligroïn, insol. water. It dissolves in acids but is reppd. by alkalis.

Tetra-methylene dicarbamic acid. *Methyl ether* $C_4H_8(NH.CO_2Me)_2$. [128°]. Formed from tetra-methylene-diamine and $ClCO_2Me$ (Dekkers, *R. T. C.* 9, 97). Flattened needles, sol. warm water. Converted by HNO_3 into $C_4H_8(N(NO_2).CO_2Me)_2$ which separates from ether in small brilliant crystals [62°], v. sl. sol. cold water, sl. sol. ether, sol. warm alcohol, and is converted by NH_3Aq into $C_4H_8(NH.NO_2)_2$ [163°].

Pentamethylene dicarbamic acid. *Methyl ether* $CH_2(CH_2.CH_2.NH.CO_2Me)_2$. [114°]. Formed by treating penta-methylene-diamine with methyl carbonate. Fine needles (from boiling water). V. sol. hot alcohol (Franchimont a. Klobbie, *R. T. C.* 7, 343). Pure HNO_3 gives a di-nitro- derivative, forming small brilliant prisms [37°], and this treated with aqueous ammonia gives penta-methylene-dinitramine [60°] together with methyl carbamate.

TRIMETHYLENE CARBOXYLIC ACID

$C_4H_6O_2$ *i.e.* $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!CH.CO_2H$ or

$CH_2:CH.CH_2.CO_2H$. *Isomeride of crotonic acid.* [19°]. (183°). Formed by heating ethylene-malonic acid (trimethylene dicarboxylic acid) at 210° (Röder, *A.* 227, 24; Perkin, jun., *C. J.* 47, 817; *B.* 17, 57). White crystals, m. sol. water. Has a powerful odour and a burning taste.—CaA'_2 6aq. Needles, v. sol. water.—BaA'_2 2aq. Needles, v. sol. water.—AgA′. Small needles (from hot water). Gives off a low-boiling oil on distillation.

Ethyl ether EtA′. (134°). Formed by digesting the Ag salt with an ethereal solution of EtI. Volatile oil, with pleasant odour. Not affected by bromine in the cold, and only slowly attacked when boiled with bromine, HBr being given off.

Trimethylene (1:1)-di-carboxylic acid so called

$C_4H_6O_4$ *i.e.* $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!C(CO_2H)_2$ or

$CH_2:CH.CH(CO_2H)_2$. *Vinaconic acid. Ethylene-malonic acid.* [141°]. Obtained by saponification of its ether. Colourless triclinic crystals; $a:b:c = 0{\cdot}7712:1:{\cdot}8702$. Crystallises with aq (from water); v. e. sol. water, v. sol. ether. At 160° it begins to give off CO_2, leaving trimethylene carboxylic acid. It is not attacked by sodium-amalgam. When heated with bromine it gives off HBr slowly. It combines, however, with HBr, forming bromo-ethyl-malonic acid (Perkin, *C. J.* 47, 814), and it combines with bromine when this is dissolved in chloroform (Fittig). Boiling dilute H_2SO_4 forms γ-oxy-ethyl-malonic acid. Alkaline $KMnO_4$ does not attack it (Buchner, *B.* 23, 704).

Salts.—Ammonium salt. Four-sided plates.—CuA″ aq. Deep-blue octahedra, sl. sol. hot water. At 160° it becomes a light-green powder.—BaA″. Needles.—$BaH_2A''_2$ 4aq. Prismatic needles.—PbA″ (dried at 100°). Insol. cold, sl. sol. hot, water.—Ag_2A''. Needles, v. sl. sol. cold water, sl. sol. hot water.—AgHA″. Long colourless needles (from water).

Ethyl ether Et_2A''. (213°). V.D. 6·32 (calc. 6·43). S.G. $\frac{15}{15}$ 1·0646; $\frac{25}{25}$ 1·0566. Formed by the action of ethylene bromide on sodium-malonic ether (Perkin, jun., *C. J.* 47, 812; *B.* 17, 54; Fittig a. Röder, *A.* 227, 13). Oil. Not attacked when successively treated with benzyl chloride and NaOEt (Perkin, jun., *B.* 18, 1734).

Dibromide $C_3H_4Br_2(COOH)_2$. [110°]. From tri-methylene-di-carboxylic acid and Br in chloroform (Fittig a. Marburg, *B.* 18, 3413).

Trimethylene (1:2)-di-carboxylic acid

$CH_2\!<\!\begin{matrix} CH.CO_2H \\ | \\ CH.CO_2H \end{matrix}$ or $CH_2:C(CO_2H).CH_2.CO_2H$.

Allo-itaconic acid. [137°] (C. a. G.); [139°] (B.).

Formation.—1. By heating its anhydride with water at 140° (Conrad a. Guthzeit, *B.* 17, 1187).—2. From sodium propane tetracarboxylic ether $(CO_2Et)_2CNa.CH_2.CNa(CO_2Et)_2$ by treatment with bromine, the resulting trimethylene tetracarboxylic ether being saponified, and the free acid heated to 230°, and then distilled under 16 mm. pressure: the oil which passes over at 170° to 180° is heated with water at 140° (Perkin, jun., *B.* 19, 1056; Dressel, *A.* 256, 197).

Properties.—Prisms; v. sol. water, alcohol, and ether. Not attacked by alkaline $KMnO_4$, or by sodium-amalgam (Buchner, *B.* 23, 705).

Salts.—CaA″: silky crystals.—Ag_2A''.

Anhydride $C_5H_4O_3$ *i.e.* $CH_2\!<\!\begin{matrix} CH.CO \\ | \\ CH.CO \end{matrix}\!>\!O$ or

$CH_2:C\!<\!\begin{matrix} CO\,.\,O \\ | \\ CH_2.CO \end{matrix}$. [57°] (C. a. G.); [59°] (Buchner). Formed by heating trimethylene-

tricarboxylic acid $CH_2\!<\!\begin{matrix} CH.CO_2H \\ | \\ C(CO_2H)_2 \end{matrix}$ or possibly

$CH_2:C(CO_2H).CH(CO_2H)_2$ at 184° to 190° for a long time (C. a. G.). Needles, sl. sol. ether.

Trimethylene (1.2.)-di-carboxylic acid

$CH_2\!<\!\begin{matrix} CH.CO_2H \\ | \\ CH.CO_2H \end{matrix}$. [175°]. Γ-*cistrans-tri-methylene-1.2-di-carboxylic acid.* Formed by saponification of the di-methyl-ether (Eduard Buchner, *B.* 23, 705). Compact apparently rhombic crystals (from water), containing no water of crystallisation. Grouped needles (from ether). Less sol. water than the isomeric glutaconic acid, but more sol. ether. Distils without splitting off water. Acetyl chloride forms no anhydride. Not oxidised by permanganate in alkaline solution. Not reduced by sodium-amalgam. Chloride of iron gives a weak red-brown colour.

Salts.—The zinc salt is more sol. cold than hot water. It crystallises in nodular groups of needles. A solution of the ammonium salt gives no pp. with $CaCl_2$ and $BaCl_2$, but white crystalline pps. with silver and lead salts. By heating the silver salt a white body sublimes in needles, probably the anhydride.

Di-methyl-ether $C_3H_4(CO_2Me)_2$. (205°–215° at 718 mm.). Formed by heating acrylo-di-azo-acetic ether $C_3H_4N_2(CO_2Me)_2$ for 40 minutes to 160°–185°. Saponified by boiling with aqueous potash.

Isomerides of trimethylene dicarboxylic acid v. ITACONIC, CITRACONIC, MESACONIC, and GLUTACONIC ACIDS.

Trimethylene (1:1:2)-tricarboxylic acid $C_6H_6O_6$ *i.e.* $CH_2\left\langle\begin{array}{l}CH.CO_2H\\ |\\ C(CO_2H)_2\end{array}\right.$ or possibly $CH_2{:}C(CO_2H).CH(CO_2H)_2$. [184°]. Formed by saponification of its ether, which is prepared by the action of αβ-di-bromo-propionic ether on di-sodio-malonic ether (Conrad a. Guthzeit, *B.* 17, 1185). Its ether is also formed by the action of α-bromo-acrylic ether upon sodio-malonic ether $CHNa(CO_2Et)_2$ (Michael, *J. pr.* [2] 35, 132, 351; *Am.* 9, 121). Prisms (from water). At 184°–190° it is split up into CO_2 and the dicarboxylic acid or its anhydride.

Tri-ethyl ether Et_3A'''. (276°). S.G. $\frac{15}{}$ 1·127. Colourless liquid. Does not react with NaOEt and BzCl.

Trimethylene (1:2:3)-tri-carboxylic acid $(CO_2H)CH\left\langle\begin{array}{l}CH(CO_2H)\\ |\\ CH(CO_2H)\end{array}\right.$ or possibly $CO_2H.CH{:}C(CO_2H).CH_2.CO_2H$. [150°–153°]. Formed by heating the tetra-carboxylic acid (1:1:2:3) at 200° for a long time (Perkin, *B.* 17, 1654; *C. J.* 47, 826). Colourless crystalline solid. V. sol. water, alcohol, and acetone, sl. sol. benzene, chloroform, ligroïn, and CS_2. On heating it yields a sublimate, probably of an anhydride.

Salts.—$A'''Ag_3$: white granular pp. — A'''_2Ca_3: crystalline pp., soluble in cold water, nearly insoluble in hot. The cupric salt is a beautiful light-green pp., sl. sol. water. The Ba and Pb salts are white pps.

Trimethylene (1, 2, 3)-tri-carboxylic acid $CO_2H.CH\left\langle\begin{array}{l}CH.CO_2H\\ |\\ CH.CO_2H\end{array}\right.$. [220°]. Obtained by saponifying its methyl ether with alcoholic potash (Buchner, *B.* 21, 2641). Small aggregates of needles (from ether), v. sol. alcohol and water, sl. sol. ether. Not affected by bromine or by $KMnO_4$. Its ammonium salt crystallises in plates.

Methyl ether Me_3A'''. [61°]. (267°) at 732 mm.; (224° at 180 mm.). Obtained by distilling the compound of methyl fumarate with methyl diazo-acetate. Needles (from alcohol or water), v. sol. alcohol, ether, benzene, and petroleum-ether.

Anhydride $C_3H_3(CO_2H)\left\langle\begin{array}{l}CO\\ CO\end{array}\right\rangle O$. [189°]. (265° at 75 mm.). Obtained by distilling the acid under reduced pressure. Small prisms, v. sol. water and alcohol, m. sol. ether. Its Pb, Ba, and Ag salts are m. sol. water.

Trimethylene (1,1,2,3)-tetra-carboxylic acid $(CO_2H)_2C\left\langle\begin{array}{l}CH(CO_2H)\\ |\\ CH(CO_2H)\end{array}\right.$ or possibly $(CO_2H)_2C{:}C(CO_2H).CH_2.CO_2H$. [95°–100°]. The tetra-ethyl ether of this acid is obtained by the action of di-bromo-succinic ether on di-sodio-malonic ether (Perkin, *B.* 17, 1652; *C. J.* 47, 824). Crystalline colourless solid. V. sol. water, alcohol, ether, and acetone, sl. sol. ligroïn and benzene. Very strong acid. The acid loses CO_2 on heating to 200° giving the (1, 2, 3)-tri-carboxylic acid.

Salts.—$A^{iv}Ag_4$: white amorphous pp.—$A^{iv}Ca_2aq$: crystalline pp., more soluble in cold water than in hot.

Tetra-ethyl ether $A^{iv}Et_4$: (246° at 85 mm.); thick colourless oil.

Tri-methylene (1,1,2,2)-tetra-carboxylic acid $CH_2\left\langle\begin{array}{l}C(CO_2H)_2\\ |\\ C(CO_2H)_2\end{array}\right.$. [200°]. Formed by saponifying the ethyl ether with alcoholic KOHAq (Dressel, *A.* 256, 196). Large shining crystals (from water). When heated to 230° it gives off $2CO_2$ and H_2O and is converted into the anhydride of trimethylene dicarboxylic acid, and from this the dicarboxylic acid itself can be obtained by heating with water to 140°.

Ethyl ether $H_2C\left\langle\begin{array}{l}C(CO_2Et)_2\\ C(CO_2Et)_2\end{array}\right.$. [43°]. (187°). Formed by the action of bromine on the disodium compound of propane tetra-carboxylic ether (Dressel, *A.* 256, 194; *cf.* Perkin, *B.* 19, 1056). Long needles, v. sol. ether, alcohol, $CHCl_3$ and benzene (D.).

Tetra-methylene carboxylic acid $C_5H_8O_2$ *i.e.* $CH_2\left\langle\begin{array}{l}CH_2\\ CH_2\end{array}\right\rangle CH.CO_2H$. (191°) at 720 mm. S.G. $\frac{15}{15}$ 1·0548; $\frac{25}{25}$ 1·0476. M.M. 5·048 at 18°. μ_D 1·4403 at 26°. Formed by heating tetra-methylene dicarboxylic acid at 200°, CO_2 being given off (Perkin, *B.* 16, 1795; *C. J.* 51, 8). Colourless oil, smelling like butyric acid; sl. sol. water, miscible with alcohol and ether. Not attacked by bromine below 100°.

Reaction.—The calcium salt distilled with lime gives C_2H_4, H_2, CH_4, CO, di-tetramethylenyl ketone, and tetramethylenyl methyl ketone (Colman a. Perkin, jun., *C. J.* 51, 228; *B.* 19, 3112).

Salts.—AgA′: sparingly soluble white pp.—CaA'_2 5aq.

Ethyl ether EtA′. (151°) at 720 mm. (P.); (162°) (Freund, *B.* 21, 2694).

Chloride C_4H_7COCl. (143°) (F.). Obtained by heating the amide with PCl_3.

Amide $C_4H_7.CONH_2$. [138°]. (c. 240°). Formed by heating the ammonium salt of the acid to 250° (Freund, *B.* 21, 2694). Plates (from alcohol), v. sol. water, ether, chloroform, benzene. May be sublimed. Decomposed by treatment with bromine and KOH.

Nitrile $C_4H_7.CN$. (150°). Formed by distilling the amide of tetra-methylene carboxylic acid with phosphoric anhydride (Freund, *B.* 21, 2696). Colourless oil, with pleasant odour. Is converted into the amine by reducing with sodium and alcohol.

Anilide $C_4H_7.CONHPh$. [111°]. Formed by heating the amide with aniline until no more ammonia is given off (Freund). Long needles (from alcohol), sl. sol. hot water.

Anhydride $(C_4H_7.CO)_2O$. (160°). Formed by distilling the sodium salt with the chloride of the acid (F.).

Tetra-methylene (1,1)-dicarboxylic acid $C_6H_8O_4$ *i.e.* $CH_2\left\langle\begin{array}{l}CH_2\\ CH_2\end{array}\right\rangle C(CO_2H)_2$. [156°]. From the ether (Perkin, *C. J.* 51, 4). Monoclinic crystals (from ether); $a{:}b{:}c = 1{\cdot}0324{:}1{:}1{\cdot}1354$; $\beta = 88°\ 58'$. V. sol. ether and benzene, nearly

insol. chloroform and ligroïn, v. sol. water. A few degrees above its melting-point it splits off CO_2, becoming tetramethylene carboxylic acid.

Salts. — Ag_2A''. — CuA'' aq. — PbA'' aq. — BaA'' aq.

Ethyl ether Et_2A''. (221°) at 720 mm. S.G. $\frac{0}{0}$ 1·0533; $\frac{25}{25}$ 1·0405. M.M. 9·940 at 18·9°. μ_D 1·433. Formed from malonic ether, trimethylene bromide, and NaOEt (Perkin, *B.* 16, 1793; *C. J.* 51, 2). Oil, smelling like camphor.

Tetramethylene (1,2)-di-carboxylic acid $\begin{array}{l} CH_2.CH(CO_2H) \\ | \quad\ \ | \\ CH_2.CH(CO_2H) \end{array}$. [130°]. Formed by heating the tetra-carboxylic acid to 180°–200° (Perkin, *B.* 19, 2042; *C. J.* 51, 22). Colourless feathery crystals (from water). V. sol. water, alcohol, and ether, more sparingly sol. benzene and ligroïn. By alkaline $KMnO_4$ it is oxidised to oxalic acid.

Salts.—$A''Ag_2$: heavy white pp.—$A''Ba^x$: sparingly soluble six-sided transparent tables.

Di-ethyl ether $A''Et_2$. (238°–242°); colourless liquid.

Anhydride $\begin{array}{l} CH_2.CH.CO \\ | \quad\ \ | \\ CH_2.CH.CO \end{array}\!\!>O$. [78°]; colourless crystals; easily soluble in alcohol, sparingly in ether and benzene. Formed by heating the acid to 300°. Reconverted into the acid by boiling with water. Heated with resorcin it gives a beautifully fluorescent condensation-product.

Tetramethylene (1,3)-dicarboxylic acid $CO_2H.CH{<}^{CH_2}_{CH_2}{>}CH.CO_2H$. *Homoitaconic acid.* [171°]. Formed by boiling its ether with fuming HClAq (Markownikoff a. Krestownikoff, *A.* 208, 333). Prisms, v. sol. hot water and alcohol, sl. sol. ether. May be sublimed. Does not combine with bromine, but when heated with Br it gives off HBr and CO_2. It is not reduced by sodium-amalgam. Does not form an anhydride. Does not unite with HBr or HI.

Salts.—PbA'' ½aq. Crystalline crusts.—Ag_2A''. Amorphous pp., not decomposed by boiling water.

Methyl ether Me_2A''. (220°).

Ethyl ether Et_2A''. (230°). Formed in very small quantity when $CH_3.CH(OEt).CO_2Et$ is prepared by the action of dry NaOEt on α-chloro-propionic ether (M. a. K.).

Tetramethylene (1,1,2,2) - tetra - carboxylic acid $\begin{array}{l} CH_2.C(CO_2H)_2 \\ | \quad\ \ | \\ CH_2.C(CO_2H)_2 \end{array}$. [145°–150°]. Obtained by saponification of the tetra-ethyl ether, which is formed by the action of bromine upon the di-sodio- derivative of butane-tetra-carboxylic ether $\begin{array}{l} CH_2.CNa(CO_2Et)_2 \\ | \\ CH_2.CNa(CO_2Et)_2 \end{array}$ (Perkin, *B.* 19, 2041; *C. J.* 51, 21). Colourless crystals. Easily soluble in water, alcohol, and ether, more sparingly in benzene and ligroïn. It evolves CO_2 at its melting-point, and is converted into the di-carboxylic acid.

Tetramethylene (1,1,3,3) - tetracarboxylic acid. *Ethyl ether* $(CO_2Et)_2C{<}^{CH_2}_{CH_2}{>}C(CO_2Et)_2$. Formed by the action of methylene iodide on the di-sodium derivative of propane tetra-carboxylic ether in an alcoholic solution on the water-bath (Dressel, *A.* 256, 198). Colourless viscid oil, distilling with some decomposition between 220° and 250° at 15 mm.

Pentamethylene dicarboxylic acid

$$CH_2{<}\begin{array}{l} CH_2\text{—}CH.CO_2H \\ \quad\ \ | \\ CH_2\text{—}CH.CO_2H \end{array}. \ [160°].$$

Preparation.—Disodium pentane tetra-carboxylic ether, $(CO_2Et)_2CNa.CH_2.CH_2.CH_2.CNa(CO_2Et)_2$ is converted by Br into $CH_2{<}\begin{array}{l} CH_2\text{—}C(CO_2Et)_2 \\ \quad\ \ | \\ CH_2\text{—}C(CO_2Et)_2 \end{array}$, which yields pentamethylene tetracarboxylic acid on saponification, and this acid is decomposed by heat into CO_2 and pentamethylene dicarboxylic acid. This is purified by conversion into its ethyl salt (Perkin, jun., *C. J.* 51, 244; *B.* 18, 3250).

Properties.—Nodules (from water). V. sol. hot water, alcohol, and acetic ether; sl. sol. ether.

Salts.—Ag_2A''. Very stable white pp.

Ethyl ether Et_2A''. (c. 250°).

$$\textit{Anhydride}\ CH_2{<}\begin{array}{l} CH_2\text{—}CH.CO \\ \quad\ \ | \\ CH_2\text{—}CH.CO \end{array}\!\!>O.$$

[64°–67°]. Formed by heating the acid to 300°. M. sol. alcohol and ether, sl. sol. CS_2; insol. cold, but saponified by hot, Na_2CO_3Aq. With resorcin and H_2SO_4 it gives the fluoresceïn reaction.

Penta-methylene tetracarboxylic acid $CH_2{<}\begin{array}{l} CH_2\text{—}C(CO_2H)_2 \\ \quad\ \ | \\ CH_2\text{—}C(CO_2H)_2 \end{array}$. Formed as above. Sol. ether.

TETRAMETHYLENE-CARBOXYLIC ALDEHYDE $CH_2{<}^{CH_2}_{CH_2}{>}CH.CHO$. (115°–117°). From calcium tetramethylene carboxylate by distilling with calcium formate (Colman a. Perkin, *C. J.* 51, 238). Oil; smelling like isobutyric aldehyde. Gives a purple colour with rosaniline hydrochloride which has been bleached by SO_2; reduces ammoniacal $AgNO_3$Aq; combines with $NaHSO_3$; reacts with hydroxylamine and with phenyl-hydrazine.

TRIMETHYLENE CHLORHYDRIN *v.* CHLORO-PROPYL ALCOHOL.

METHYLENE CHLORIDE CH_2Cl_2. *Di-chloro-methane.* Mol. w. 85. (41·8°) (Thorpe, *C. J.* 37, 195). S.G. $\frac{0}{4}$ 1·3778 (T.); $\frac{15}{15}$ 1·3377; $\frac{25}{25}$ 1·3220. M.M. 4·313 at 11·9° (Perkin, *C. J.* 45, 527). C.E. (0°–10°) ·001335; (0°–40°) ·001416. S.V. 65·12. H.C.p. 106800 (Berthelot a. Ogier, *Bl.* [2] 36, 68).

Formation.—1. From chlorine and methyl chloride in sunlight (Regnault, *A.* 33, 328; *A. Ch.* [2] 70, 377).—2. By the action of zinc-dust and ammonia on chloroform, the yield being very small (Perkin, *C. N.* 18, 106).—3. By the action of chlorine on methylene iodide (Butlerow, *A.* 107, 110; 111, 251; *Z.* [2] 5, 276).—4. By the action of $AlCl_3$ on the compound of $Cl.CO_2CCl_3$ with $Cl.CO_2CH_3$ (Hentschel, *J. pr.* [2] 36, 474).

Preparation.—Aqueous HCl is cautiously added to a mixture of alcohol (5 vols.), chloroform (1 vol.), and zinc. Sufficient heat is pro-

duced in the reaction to distil over much of the methylene chloride. The product is fractionally distilled (Greene, *C. R.* 89, 1077; *A. Ph. S.* 18, 347; *C. N.* 50, 75; *A. C. J.* 1, 522).

Properties.—Oil. Like CCl_4 (but unlike CH_3Cl and $CHCl_3$) it exerts a poisonous action when inhaled (Regnault a. Villejean, *C. R.* 100, 1146).

Reactions.—1. Converted by ICl or ICl_3 into $CHCl_3$, and hexachloro-benzene. Converted by IBr into iodoform and di-chloro-di-iodo-methane (Höland, *A.* 240, 234). Converted by IBr_3 into CBr_4, $CHBr_3$, and C_2Br_4.—2. Heated with KI, iodine, and alcohol, it gives CH_2I_2, EtI, and alcohol (H.).—3. *Iodine* at 200° gives methylene iodide (H.).—4. *Bromine* at 170° forms $CHBrCl_2$ (91°), and a little CBr_2Cl_2 [38°] (150°) (Arnhold, *A.* 240, 204).—5. Alcoholic NaOAc forms $CH_2(OEt)_2$ and acetic acid (A.).—6. Converted by alcoholic NH_3 at 125° into so-called hexa-methylene-diamine (Höland, *A.* 240, 225). Aqueous ammonia at 140° forms NH_4Cl, methylamine hydrochloride and formic acid (André, *C. R.* 102, 1474).—7. Mixed with *benzene* it is converted by $AlCl_3$ into anthracene and other products (Friedel a. Crafts, *A. Ch.* [6] 11, 264). 8. *Water* at 200° forms HCl, formic acid, MeCl, and MeOH (André).—9. With H_2S it forms a crystalline compound $CH_2Cl_2(H_2S)_2 23aq$ (Forcrand, *A. Ch.* [5] 28, 17).

TRIMETHYLENE CHLORIDE *v.* $\omega\beta$-Di-chloro-propane.

METHYLENE CHLORO-BROMIDE *v.* Chloro-bromo-methane.

Tri-methylene chloro-bromide *v.* Chloro-bromo-propane.

METHYLENE CHLORO-IODIDE CH_2ClI. *Chloro-iodo-methane.* (109°). V.D. 88·14. S.G. $\frac{11}{11}$ 2·447; $\frac{14\cdot5}{14\cdot5}$ 2·444. Formed by the action of ICl on methylene iodide or of iodine on $IHg.CH_2Cl$ (Sakurai, *C. J.* 41, 361; 47, 198). Oil.

TRIMETHYLENE CYANHYDRIN *v. Nitrile* of γ-Oxy-butyric acid.

TRIMETHYLENE CYANIDE $C_5H_6N_2$ *i.e.* $CH_2(CH_2CN)_2$. *Glutaronitrile.* (274°) (H.); (286°) (Perkin, *C. J.* 55, 702); (203° at 100 mm.); (142° at 10 mm.) (Krafft a. Noerdlinger, *B.* 22, 817). S.G. $\frac{15}{15}$ ·9952; $\frac{25}{25}$ ·9894. M.M. 5·136 (P.). Formed from trimethylene bromide and alcoholic KCy (Henry, *Bl.* [2] 43, 618; *C. R.* 100, 742). Liquid, sol. water, alcohol, and chloroform, insol. ether and CS_2. Yields glutaric acid on saponification. Sodium reduces it in alcoholic solution to pentamethylene-diamine and piperidine.

TRIMETHYLENE-DI-ETHYL-ALKINE *v.* Ethyl-oxypropyl-amine.

METHYLENE-ETHYL-AMINE C_3H_7N *i.e.* $EtNCH_2$. (208° i. V.). V.D. 2. Formed by the action of ethylamine on formic aldehyde (trioxymethylene) (Kolotoff, *Bl.* [2] 43, 112; *J. R.* 17, 231). Liquid, with unpleasant odour, sol. cold water, but separates again on warming, v. sol. alcohol. HCl splits it up into ethylamine and trioxymethylene (formic paraldehyde).—$B'_2H_2PtCl_6$. Yellow crystalline pp. An isomeride $(CH_2)_4N_4Et_4$ of this base is described by Lermontoff (*B.* 7, 1252) as an oil formed by heating ethylamine with alcoholic methylene iodide at 100°.—$(CH_2)_4N_4Et_4H_2PtCl_6$. Amorphous.

Methylene tetra-ethyl-diamine $C_9H_{22}N_2$ *i.e.* $CH_2(NEt_2)_2$. *Tetra-ethyl-di-amido-methane* (169° i. V.). S. 10. Formed by heating trioxymethylene (formic paraldehyde) with diethylamine in sealed tubes at 100° (Kolotoff, *Bl.* [2] 43, 112; Ehrenberg, *J. pr.* [2] 36, 118). Liquid, with peppery odour, sl. sol. water, miscible with alcohol, ether, and $CHCl_3$. Split up by dilute acids, even by oxalic acid, into $NHEt_2$ and formic aldehyde. Combines with CS_2, forming $C_9H_{22}N_2CS_2$.

Tetra-methylene-tetra-ethyl-tetramine $C_{12}H_{28}N_4$ *i.e.* $CH_2<\begin{matrix}NEt.CH_2.NEt\\NEt.CH_2.NEt\end{matrix}>CH_2$. Formed by heating methylene iodide with alcoholic ethylamine at 100° (Lermontoff, *B.* 7, 1252). Liquid, yielding amorphous salts.—$B''H_2PtCl_6$: sl. sol. water.

METHYLENE-ETHYL-PHTHALIMIDINE $C_{11}H_{11}NO$ *i.e.* $C_6H_4<\begin{matrix}C(CH_2)\\CO\end{matrix}>NEt$. Obtained by heating $C_{23}H_{24}N_2O_5$ which is produced by adding aqueous ethylamine to phthalyl-acetic acid (Mertens, *B.* 19, 2369). Colourless oil, smelling of fresh carrots. Volatile with steam; v. sol. alcohol and ether.

METHYLENE DI-ETHYL DISULPHIDE $C_5H_{12}S_2$ *i.e.* $CH_2(SEt)_2$. *Formic aldehyde ethyl mercaptal. Ethyl derivative of di-thio-formic orthaldehyde.* (178°–181°). S.G. $\frac{20}{}$ ·987. Formed from methylene chloride and NaSEt in alcoholic solution (Niederist, *A.* 186, 391; Fromm, *A.* 253, 155).

METHYLENE DI-ETHYL DISULPHONE $C_5H_{12}S_2O_4$ *i.e.* $CH_2(SO_2Et)_2$. [104°]. Formed by the action of $KMnO_4$ and H_2SO_4 on $CH_2(SEt)_2$ (Fromm, *A.* 253, 156; *cf.* Baumann, *B.* 19, 2811). Needles, v. sol. water and alcohol, sl. sol. ether. Chlorine forms $CCl_2(SO_2Et)_2$ [99°] crystallising in needles; while bromine produces $CBr_2(SO_2Et)_2$ [132°].

Di-methylene di-ethyl trisulphone $(Et.SO_2.CH_2)_2SO_2$. [149°]. Formed by treating formic aldehyde with H_2S, dissolving the product in aqueous NaOH, shaking with EtBr, and oxidising the product with $KMnO_4$ (Baumann, *B.* 23, 1875). Sparingly soluble colourless plates.

METHYLENE-FURFURANE TRIHYDRIDE C_5H_8O *i.e.* $CH_2<\begin{matrix}CH_2.C(CH_2)\\|\\CH_2.O\end{matrix}$. (111°) at 718 mm. Formed by the action of solid KOH on methyl bromo-propyl ketone (Lipp, *B.* 22, 1207). Mobile liquid, m. sol. water. Yields a hydrazide. When heated with 5 p.c. HClAq at 100° it yields aceto-propyl alcohol (methyl oxypropyl ketone). Probably identical with trimethylenyl methyl ketone of Perkin, jun. (*B.* 17, 1440).

TRI-METHYLENE GLYCOL $C_3H_8O_2$ *i.e.* $CH_2(CH_2OH)_2$. (214°). S.G. $\frac{0}{0}$ 1·0625 (Z.); $\frac{18\cdot6}{4}$ 1·0536 (F.). C.E. (0°–10°) ·00060. S.V. 84 (Zander, *A.* 214, 178; Lossen, *A.* 254, 59). One of the products of the fermentation of glycerin by schizomycetes (Freund, *M.* 2, 636).

Formation.—1. By saponifying its diacetyl derivative with baryta-water (Reboul, *A. Ch.* [5] 14, 491).—2. By warming trimethylene bromide with moist Ag_2O (Beilstein a. Wiegand, *B.* 15,

1497).—3. By allowing $CH_2(CH_2Br)_2$ to stand for some time with a large excess of water (Niederist, *M.* 3, 839).—4. By boiling trimethylene bromide with dilute aqueous K_2CO_3 (Z.).

Properties.—Viscid liquid, with sweet taste, miscible with water.

Reactions.—1. Fuming HClAq at 100° converts it into $CH_2(CH_2Cl)_2$.—2. Trimethylene glycol (35 g.) heated with aldehyde (12 g.) at 100° yields the ethylidene derivative (*v. infra*).

Di-acetyl derivative $CH_2(CH_2OAc)_2$. (210° cor.). (c. 111°). S.G. $\frac{0}{}$ ·991; $\frac{18}{}$ 1·070. S. 11. Formed by boiling $CH_2(CH_2Br)_2$ with NaOAc (Reboul).

Ethylidene derivative $C_5H_{10}O_2$ *i.e.* $CH_2<\begin{matrix}CH_2.O\\CH_2.O\end{matrix}>CH.CH_3$. V.D. 3·62 (calc. 3·53). Obtained by heating the glycol with aldehyde at 100°, the yield being nearly the theoretical (Lochert, *A. Ch.* [6] 16, 49): Colourless liquid, with slight aldehydic odour. Dissolves in $1\frac{1}{2}$ volumes of water, v. sol. alcohol and ether. Separated from its aqueous solution by $CaCl_2$ and by KOH. Saponified by boiling water, alkalis, and dilute acids. With PCl_5 it yields aldehyde and $CH_2(CH_2Cl)_2$.

Amylidene derivative $C_8H_{14}O_2$ *i.e.* $CH_2<\begin{matrix}CH_2.O\\CH_2.O\end{matrix}>CH.C_4H_9$. (c. 165°). S.G. $\frac{0}{}$ ·995. V.D. 5·03 (calc. 4·98). Formed by heating trimethylene glycol (35 g.) with valeric aldehyde (20 g.) in a sealed tube at 125°. Colourless mobile liquid, v. sl. sol. water, v. sol. alcohol and ether. Saponified by boiling water.

Heptylidene derivative $C_{10}H_{20}O_2$ *i.e.* $CH_2<\begin{matrix}CH_2.O\\CH_2.O\end{matrix}>CH.C_6H_{13}$. (c. 216°). S.G. $\frac{0}{}$ ·933. From the glycol (30 g.) and heptoic aldehyde (œnanthol) at 160° (L.).

Bromhydrin *v.* BROMO-PROPYL ALCOHOL.

TRI-METHYLENE-IMINE C_3H_7N *i.e.* $CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>NH$. (65°–80°). Formed, together with a polymeride $C_6H_{14}N_2$ (160°–167°), from $CH_2Br.CH_2.CH_2.NH_2$ and NaOH in the cold (Gabriel a. Weiner, *B.* 21, 2669). Volatile liquid, smelling like NH_3 and fuming in the air. Eagerly combines with CS_2.—$B'HAuCl_4$.—$B'_2H_2PtCl_6$.—$B'C_6H_2(NO_2)_3OH$. [167°].

METHYLENE IODIDE CH_2I_2. *Di-iodo-methane.* [4°]. (152° at 330 mm.). S.G. $\frac{15}{15}$ 3·2853; $\frac{25}{25}$ 3·2656. M.M. 18·827 at 15° (Perkin, *C. J.* 45, 464).

Formation.—1. By heating iodoform (4 mols.) with NaOEt (9 mols.) dissolved in alcohol (Butlerow, *A.* 107, 110; 111, 242; *cf.* Brüning, *A.* 104, 187).—2. By heating chloroform with HIAq at 130° (Bljuducho, *Z.* [2] 7, 91).—3. By heating iodoform (50 g.) with conc. HIAq (200 g.) to boiling (127°) and adding phosphorus (Lieben, *Z.* 1868, 712; Baeyer, *B.* 5, 1095).—4. From methylene chloride and CaI_2 at 75° (Spindler, *A.* 231, 262).—5. By warming a mixture of iodoform (5 pts.), water (2 pts.) and reduced iron (5 pts.), and fractionally distilling *in vacuo* (Cazeneuve, *C. R.* 98, 369).—6. An alcoholic solution of iodoform is decomposed by light, yielding CH_2I_2 and iodine. Oxalic acid accelerates the reaction (Mulder, *R. T. C.* 7, 316).

Properties.—Yellowish liquid, boiling with partial decomposition at 180°.

Reactions.—1. *Potassium* has no action in the cold, but on heating it acts with explosive violence.—2. Heated with *copper* and water, the products are cuprous iodide and a mixture of CO_2, methane, CO, and ethylene (Butlerow, *A.* 120, 356).—3. *Silver acetate* forms the diacetyl derivative of formic orthaldehyde $CH_2(OAc)_2$.—4. *Silver oxalate* yields formic paraldehyde (tri-oxymethylene).—5. *Chlorine* yields CH_2Cl_2.—6. *Bromine* forms CH_2Br_2 (Arnhold, *A.* 240, 207).—7. Converted by PCl_5 at 70° into methylene chloride and a trace of chloroform (Höland, *A.* 240, 227).—8. Alcoholic Na_2S yields thioformic aldehyde.—9. NMe_3 combines with formation of $(CH_2I)NMe_3I$.—10. *Aniline* forms $CH_2(NHPh)_2$.—11. *Mercury* forms $IHg.CH_2I$ (Sakurai, *C. J.* 37, 658).

Trimethylene iodide *v.* DI-IODO-PROPANE.

DI-TETRAMETHYLENE KETONE *v.* DI-TETRAMETHYLENYL KETONE.

METHYLENE-MALONIC ETHER $C_8H_{12}O_4$ *i.e.* $CH_2{:}C(CO_2Et)_2$. [156°]. Formed by heating malonic ether with methylene iodide and NaOEt (Zelinsky, *B.* 22, 3294). Mobile liquid. Isomeric with fumaric and maleïc ethers. With bromine it yields $CH_2Br.CBr(CO_2Et)_2$ (185°–190° at 75–85 mm.).

Polymeride $\{CH_2{:}C(CO_2Et)_2\}_2$. [156°]. Accompanies the preceding (Z.). Minute amorphous granules; insol. water, m. sol. ether and alcohol. Its molecular weight determined by Raoult's method is 342 (calc. 344).

DI-METHYLENE-DI-METHYL-DIAMINE $C_4H_{10}N_2$ *i.e.* $(CH_2)_2N_2Me_2$. V.D. (H = 1) 41·5 (calc. 43). Formed by passing a mixture of trimethylamine and hydrogen through a red-hot tube (Romeny, *B.* 11, 835). Crystalline. Hot dilute HClAq splits it up into formic aldehyde and methylamine.—$B''H_2PtCl_6$.

A base, boiling at about 207°, formed by the action of methylamine upon trioxymethylene (formic paraldehyde) is perhaps identical with the preceding (Kolotoff, *Bl.* [2] 45, 253).

TRIMETHYLENE - HEXA - METHYL - DI - AMINE $(C_3H_6)N_2(CH_3)_6$. Formed by heating trimethylene bromide ($C_3H_6Br_2$) with trimethylamine.

Salts. — $B''H_2Br_2$ aq: soluble colourless needles.—$B''H_2Cl_2PtCl_4$: sparingly soluble (Roth, *B.* 14, 1351).

METHYLENE METHYL BUTENYL DI-KETONE $CH_3.CO.CH_2.CO.C_4H_7$. *Acetyl-mesityl oxide. Acetyl-angelicyl-methane.* (205°). Formed as a secondary product in the preparation of methylene dimethyl diketone by the action of acetone and NaOEt on acetic ether (Claisen a. Ehrhardt, *B.* 22, 1012; *Bl.* [3] 1, 498). Oil, soluble in aqueous alkalis. Its alcoholic solution gives a red colour with $FeCl_3$. Cupric acetate in concentrated solutions gives a dark-green pp.—CuA'_2. [123°]. Crystalline, v. sol. warm alcohol and ether.

METHYLENE DIMETHYL ETHER *v. Di-methyl ether of Ortho-*FORMIC ALDEHYDE.

METHYLENE METHYL ETHYL DIKETONE $C_6H_{10}O_2$ *i.e.* $C_2H_5.CO.CH_2.CO.CH_3$. *Acetyl-propionyl-methane.* (158°). S.G. $\frac{15}{}$ ·9538. Formed by the action of EtOAc and NaOAc upon methyl ethyl ketone (Claisen a. Ehrhardt, *B.* 22, 1014).—$Cu(C_6H_9O_2)_2$. [179°]. Slender blue needles (from hot alcohol).

METHYLENE METHYL HEXYL DIKETONE $C_{10}H_{18}O_2$ *i.e.* $CH_3.CO.CH_2.CO.C_6H_{13}$. (229°). Formed from methyl hexyl ketone, AcOEt, and AcONa (Claisen a. Ehrhardt, *B.* 22, 1015). Liquid.—$Cu(C_{10}H_{17}O_2)_2$. [122°]. Crystalline.

METHYLENE DI-METHYL DIKETONE $C_5H_8O_2$ *i.e.* $CH_2(CO.CH_3)_2$. *Di-acetyl-methane. Acetyl-acetone.* (136°). S.G. $\frac{15}{}$ ·987 (Combes).

Preparation.—1. By slowly adding acetone (1 mol.) to a mixture of acetic ether ($3\frac{1}{2}$ mols.) and dry NaOEt (1 mol.) heated on the water-bath. The product is poured into ice-cold water, and the aqueous liquid mixed with HOAc and cupric acetate, which ppts. $Cu(C_5H_7O_2)_2$. The yield is 35 p.c. of the weight of acetone employed (Claisen, *Bl.* [3] 1, 498).—2. Acetone (5·8 pts.) mixed with EtOAc (33 pts.) is treated in the cold with sodium-wire (2·3 pts.). When most of the sodium is dissolved, the mixture is heated on a water-bath. The product is ppd. as cupric salt, the yield of ketone being 55 p.c. of the acetone employed (Claisen a. Ehrhardt, *B.* 22, 1009). In either case the diketone is obtained from the copper compound by adding dilute H_2SO_4 and extracting with ether.—3. From the compound $C_{12}H_{14}O_6Al_2Cl_6$ (obtained from acetyl chloride and $AlCl_3$) by adding water and extracting with chloroform. The yield is 85 p.c. of the theoretical (Combes, *A. Ch.* [6] 12, 211).

Properties.—Colourless liquid with pleasant acetic odour, sol. water, v. sol. aqueous HCl, miscible with alcohol, ether, and chloroform. Not attacked by PCl_3.

Reactions.—1. *Phenyl-hydrazine* forms phenyl-dimethyl-pyrazole $CMe\Big\langle{CH \atop NPh.N}\Big\rangle CMe$ (270·5°) (Combes, *Bl.* [2] 50, 145).—2. *Potash* decomposes it into acetone and KOAc.—3. PCl_5 yields HCl and $C_5H_6Cl_2$ (145°), a di-chloro-amylene which readily combines with bromine.—4. *Sodium-amalgam* yields isopropyl alcohol and pinacone. But in acid solution the products of reduction by sodium-amalgam are di-oxy-pentane $CH_3.CH(OH).CH_2.CH(OH).CH_3$, and a tetra-hydric alcohol analogous to pinacone.—5. Conc. HIAq at 185° reduces it to pure *n*-pentane (38°). At lower temperatures it forms $CH_2(CHI.CH_3)_2$ and $CH_3.CHI.CH_2.CH_2.CH_3$.—6. Excess of *chlorine* in sunlight yields $(CCl_3.CO)_2CH_2$ as final product.—7. *Bromine* attacks the diketone vigorously, finally producing $(CBr_3.CO)_2CH_2$ [108°].—8. *Oxidation* by CrO_3 or by $KMnO_4$ yields acetic acid.—9. Warm dilute *nitric acid* produces $CH_2(NO_2)_2$ and HOAc.—10. Dry *ammonia* passed into its ethereal solution ppts. white pearly scales of the ammonium salt $CH(NH_4)(CO.CH_3)_2$.—11. *Ethylene-diamine* (2 mols.) forms $C_2H_4(N:CMe.CH_2Ac)_2$ [111°] which yields a violet cupric salt $C_{12}H_{18}N_2O_2Cu$ [137°] and a hydrochloride $C_{12}H_{20}N_2O_2H_2Cl_2$ melting above 280°. Other diamines act in like manner (Combes, *C. R.* 108, 1252).—12. Unites with *benzidine* (1 mol.) forming a base melting at 195° (Combes).—13. *Aldehyde-ammonia* ($\frac{1}{2}$ mol.) at 100° forms di-acetyl-tri-methyl-pyridine di-hydride $C_{12}H_{17}NO_2$ [153°] (Combes, *Bl.* [3] 1, 14). 14. Tolylene-*m*-diamine at 100°, followed by H_2SO_4, yields amido-trimethyl-quinoline $C_{12}H_{14}N_2$ [191°] (Combes, *C. R.* 108, 1254).—15. SO_2Cl_2 forms the chloro- derivative $C_5H_7ClO_2$ (156°) (Combes, *C. R.* 111, 272).

Salts.—$CH(NH_4)(CO.CH_3)_2$. Pearly scales, ppd. by passing NH_3 into the ethereal solution. Decomposes readily into acetone and acetamide. —Ac_2CHNa. Formed by dissolving sodium in the diketone (Combes, *C. R.* 104, 920). White six-sided prisms, insol. ether. Decomposed by water into acetone and NaOAc. With ethyl iodide at 140° it gives $CHEt(CO.CH_3)_2$, a liquid boiling at 171°. Amyl iodide, in like manner, yields $C_5H_{11}.CH(CO.CH_3)_2$. The second atom of hydrogen in the methylene group may, in such compounds, be displaced by Na, and by acting with an alkyl iodide R'I upon $RCNa(CO.CH_3)_2$ we may obtain compounds of the form $RCR'(CO.CH_3)_2$. These reactions take place with hardly any secondary decompositions. These homologues of methylene dimethyl diketone are decomposed by potash like the diketone itself (Combes, *A. Ch.* [6] 12, 211). $ClCO_2Et$ acting on the sodium derivative of methylene dimethyl diketone forms $C(COMe)_2(CO_2Et)_2$ (Claisen a. Zedel, *B.* 21, 3397).—$KCHAc_2$. White six-sided prisms, sl. sol. alcohol, insol. ether. Formed by adding KOEt to an alcoholic solution of the diketone. Decomposed by hot water into acetone and KOAc.—$Mg(CHAc_2)_2$ (dried at 125°). From the diketone and magnesium carbonate (Combes, *C. R.* 105, 868). Transparent six-sided prisms. —$Al(CHAc_2)_3$. A by-product in the rectification of the diketone, from which it may be obtained by treatment with $AlCl_3$. Small red crystals, insol. water, sl. sol. alcohol, v. sl. sol. ether. Can be partially volatilised. Acts on polarised light. Not decomposed by alcoholic NH_3.—$Cu(HCAc_2)_2$ (dried at 125°). Pale-blue needles, obtained by adding cupric acetate or chloride to an aqueous solution of the diketone. Insol. water, the ppn. being complete in dilute solutions. At 65° it forms with $COCl_2$ dissolved in benzene a crystalline compound melting at 121° (Thomas a. Lefèvre, *Bl.* [2] 50, 193).—$Fe(HCAc_2)_3$. Red crystals, deposited from the ethereal extract of the red solution obtained by adding $FeCl_3$ to the diketone dissolved in water.—$Pb(HCAc_2)_2$. From the diketone and lead carbonate. Transparent crystals, sol. water.

Oxim $CH_3.CO.CH_2.C(NOH).CH_3$. Anhydride $CH\Big\langle{CMe.O \atop CMe:N}\Big\rangle$. (142°). S.G. $\frac{15}{}$ ·985. Formed by the action of hydroxylamine on the diketone (Zedel, *B.* 21, 2178). Colourless oil, with peculiar alkaloidal odour.

Di-oxim $CH_2(C(NOH).CH_3)_2$. [150°]. Large transparent crystals (from ether).

Phenyl-methyl-hydrazide $CH_3.CO.CH_2.C(N_2PhMe).CH_3$ (Kohlrausch, *A.* 253, 22).

Di-methylene di-methyl triketone $(CH_3.CO.CH_2)_2CO$. *Di-acetyl-acetone.* [49°]. Formed from its anhydride (*v. infra*). Plates. Sl. sol. water, sol. alkalis, warm alcohol, and ether. $FeCl_3$ gives a deep-red colour. Converted by NH_3 into oxy-di-methyl-pyridine [225°].

Anhydride $CO\Big\langle{CH:CMe \atop CH:CMe}\Big\rangle O$. *Di-methyl-pyrone.* [132°]. (249°). Formed by the action of HIAq on dehydracetic acid at a high temperature (Feist, *B.* 22, 1570; *A.* 257, 253). The yield is 70 p.c. of the theoretical. Crystals, v. e. sol. water. Converted by baryta, followed by HCl, into di-methylene di-methyl tri-ketone. The carboxylic

acid of this anhydride is dehydracetic acid. The dicarboxylic ether $CO<\begin{matrix}C(CO_2Et):CMe\\C(CO_2Et):CMe\end{matrix}>O$ [80°]. S. ·8 at 20° is formed by the action of $COCl_2$ on copper acetoacetic ether, and is converted by P_2S_5 into $CS<\begin{matrix}C(CO_2Et):CMe\\C(CO_2Et):CMe\end{matrix}>O$ [110°] (Conrad, *B.* 19, 22; 20, 152; 2111).

Di-phenyl-hydrazide $(CH_3.C(N_2HPh).CH_2)_2CO$. [142°].

Trimethylene methyl ketone *v.* TRIMETHYLENYL METHYL KETONE.

Tetramethylene methyl ketone *v.* TETRAMETHYLENYL METHYL KETONE.

METHYLENE DIMETHYL ETHER *v. Methyl-ether* of FORMIC *orth*ALDEHYDE.

METHYLENE DIMETHYL DIOXIDE *v. Methyl ether* of FORMIC *orth*ALDEHYDE, vol. ii. p. 570.

METHYLENE METHYL PHENYL DIKETONE *v.* BENZOYL-ACETONE.

METHYLENE-METHYL-PHTHALIMIDINE $C_{10}H_9ON$ *i.e.* $C_6H_4<\begin{matrix}C=CH_2\\CO\end{matrix}>NMe$. Formed by heating phthal-methyl-imidyl-acetic acid $C_6H_4<\begin{matrix}CC=H.CO_2H\\CO\end{matrix}>NMe$ above 210°. Colourless crystals. Volatile with steam. V. sol. alcohol, ether, and chloroform, more sparingly sol. water. Very unstable body (Gabriel, *B.* 18, 2454).

METHYLENE METHYL PROPYL DIKETONE $C_7H_{12}O_2$ *i.e.* $CH_3.CO.CH_2.CO.C_3H_7$. (175°). S.G. $\frac{15}{}$ ·9411. Formed by the action of EtOAc and NaOAc upon methyl propyl ketone (Claisen a. Ehrhardt, *B.* 22, 1015). Formed also from butyric ether, acetone, and NaOEt. Colourless oil. Boiling alkalis yield acetic and butyric acids. Yields $C_6H_5N_2.CHAc.COPr$ [55°] crystallising in yellow prisms.—$Cu(C_7H_{11}O_2)_2$. [161°]. Blue needles.

TETRA-METHYL-TRIMETHYLENE-DI-PYRROLE $C_{15}H_{22}N_2$ *i.e.* $\left(\begin{matrix}CH:CMe\\|\\CH:CMe\end{matrix}>N.CH_2\right)_2CH_2$ [77°]. Formed by heating acetonyl-acetone with alcoholic tri-methylene-diamine at 120° (Paal a. Schneider, *B.* 19, 3157). Crystalline.

METHYLENE DI-METHYL DISULPHONE $(CH_3.SO_2)_2CH_2$. [141°]. Formed from methyl mercaptan and methylene chloride, and oxidation of the product (Baumann, *B.* 23, 1875). Plates. On treatment with bromine-water it gives $CBr_2(SO_2Me)_2$ [234°].

Di-methylene di-methyl trisulphone $(CH_3.SO_2.CH_2)_2SO_2$. [185°]. Formed by saturating a solution of formic aldehyde with H_2S, extracting with ether, evaporating, dissolving the residual oil in aqueous NaOH, adding MeI, and oxidising with $KMnO_4$ (Baumann, *B.* 23, 1872). Prisms, v. sl. sol. cold water, alcohol, and ether. Yields with bromine-water insoluble $C_4H_6Br_4S_3O_6$ [190°].

TRIMETHYLENE TRINITROSAMINE $C_3H_6N_6O_3$ *i.e.* $(CH_2N.NO)_3$. [106°]. Formed by the action of nitrous acid upon hexamethylene-amine (F. Mayer, *B.* 21, 2883). Yellow needles or prisms (from alcohol); v. sol. alcohol, insol. petroleum-ether. Decomposed by water with production of formic aldehyde.

METHYLENE DI-OCTYL OXIDE *v. Octyl ether* of FORMIC *orth*ALDEHYDE.

METHYLENE OXIDE is FORMIC ALDEHYDE (*q.v.*).

METHYLENE-DI-OXY compounds *v Methylene derivatives* of DI-OXY compounds.

METHYLENE-DI-PHENYL-DIAMINE *v* DI-PHENYL-METHYLENE-DIAMINE.

METHYLENE-DI-PHENYLENE *v.* DI-PHENYLENE-METHANE.

METHYLENE-DIPHENYLENE OXIDE *v.* DI-PHENYLENE-METHANE OXIDE.

METHYLENE DIPHENYL DIKETONE *v.* DI-PHENYL METHYLENE DIKETONE.

TRIMETHYLENE PHENYL KETONE *v.* PHENYL TRIMETHYLENE KETONE.

Tetramethylene phenyl ketone *v. Anhydride* of PHENYL OXYBUTYL KETONE.

METHYLENE-DIPHENYL OXIDE *v.* DI-PHENYLENE-METHANE OXIDE.

METHYLENE HEXAPHENYL PHOSPHONIUM IODIDE *v. Methyleno-di-iodide* of TRI-PHENYL-PHOSPHINE.

TRIMETHYLENE-DI-PHTHALAMIC ACID $C_{19}H_{18}N_2O_6$ *i.e.* $CH_2(CH_2.NH.CO.C_6H_4.CO_2H)_2$. [70°–123°]. Obtained by boiling trimethylene di-phthalimide with potash (Gabriel, *B.* 21, 2670). Crystalline. Decomposed by water. On boiling with aqueous HCl it is converted into phthalic acid and trimethylene-diamine.

METHYLENE-PHTHALIDE $C_9H_6O_2$ *i.e.* $C_6H_4<\begin{matrix}C=CH_2\\C=O\end{matrix}>O$. *Anhydride* of *o-Oxy-vinyl-benzoic acid.* [60°]. Formed by heating phthalyl-acetic acid *in vacuo* (Gabriel, *B.* 17, 2521). Small glistening crystals. Soluble in hot water, easily in alcohol, ether, benzene, &c. Volatile with steam. It readily polymerises. Combines with Br (1 mol.).

Dibromide $C_6H_4<\begin{matrix}CBr.CH_2Br\\C=O\end{matrix}>O$ [99°]. Thick glistening crystals. Formed by the combination of methylene-phthalide with bromine. On warming with aqueous KOH it yields acetophenone-o-carboxylic acid $C_6H_4(CO_2H).CO.CH_3$. Boiled with water it gives methylene-phthalide-oxide $C_9H_6O_3$ (Gabriel, *B.* 17, 2524).

Methylene-phthalide-oxide $C_9H_6O_3$. [146°]. Long needles. Formed by boiling the dibromide of methylene-phthalide with water. Formed also by the action of water on the product of the bromination of acetophenone-*o*-carboxylic acid (Gabriel, *B.* 17, 2524).

Di-chloro-methylene-phthalide $C_9H_4Cl_2O_2$ *i.e.* $C_6H_4<\begin{matrix}C=CCl_2\\C=O\end{matrix}>O$. [128°]. Formed by passing chlorine into a mixture of α-chloro-phenyl-acetic acid (1 pt.) and HOAc (10 pts.). Formed also by warming di-chloro-acetophenone carboxylic acid with conc. H_2SO_4 (Zincke a. Cooksey, *A.* 255, 383). Long slender needles, gradually becoming compact when left in the liquid. The needles are v. sol. hot alcohol, benzene, HOAc, and benzoline, the compact crystals are soluble with difficulty. Alcoholic potash

converts it into di-chloro-acetophenone-*o*-carboxylic acid. Forms a dichloride $C_6H_4\left\langle\begin{array}{l}CCl-CCl_3\\CO\end{array}\right\rangle O$ which crystallises in colourless prisms [94°], v. sol. alcohol and HOAc, and converted by alcoholic potash into phthalic acid.

Bromo-methylene-phthalide *v.* vol. i. p. 580.

Isomeride of methylene phthalide *v.* METHYLENE-PHTHALYL.

Polymeride of methylene-phthalide $C_{18}H_{12}O_4$. [216°]. Obtained by allowing a solution of acetophenone carboxylic acid (1 pt.) in H_2SO_4 (2 pts.) to stand in the cold, and then ppg. with water (Roser, *B.* 17, 2620; Gabriel, *B.* 17, 2666; *cf.* ACETOPHENONE *o*-CARBOXYLIC ACID, *reaction* 2). Plates. Insol. water and cold alkalis, sl. sol. alcohol, v. sol. HOAc.

Oxim $C_{18}H_{13}NO_4$. [180°]. Obtained by heating the substance with alcoholic hydroxylamine hydrochloride at 160°. Crystalline granules (from dilute HOAc).

METHYLENE-DI-PHTHALIMIDE $CH_2(N{<}^{CO}_{CO}{>}C_6H_4)_2$. [226°]. Formed by heating potassium phthalimide (2 mols.) with methylene iodide (1 mol.) at 175° (Neumann, *B.* 23, 1002). Light-brown crystals (from HOAc); insol. dilute alkalis. Yields phthalic acid on heating with HClAq.

TRIMETHYLENE-DI-PHTHALIMIDE $C_{19}H_{14}N_2O_4$ *i.e.* $C_8H_4O_2{:}N.CH_2.CH_2.CH_2.N{:}C_8H_4O_2$. [198°]. Formed by the action of tri-methylene bromide on potassium phthalimide (Gabriel, *B.* 21, 2669). White needles; m. sol. hot HOAc, sl. sol. ether, CS_2, chloroform, and cold alcohol, v. sl. sol. water and petroleum ether. Converted by heating with KOH into tri-methylene-di-phthalamic acid $C_3H_6(NHCOC_6H_4CO_2H)_2$. Decomposed by heating with HCl at 180° into phthalic acid and tri-methylene-diamine.

METHYLENE-PHTHALYL $C_9H_6O_2$ *i.e.* $C_6H_4{<}^{CO}_{CO}{>}CH_2$? [219°]. Fine yellow needles. Formed, together with *o*-tribenzoylene-benzene, by heating phthalic anhydride with malonic ether and sodium acetate (Gabriel, *B.* 14, 925).

METHYLENE-DI-PIPERIDINE $CH_2(NC_5H_{10})_2$. (230°). Formed by distilling piperidine with trimethylene oxide (formic paraldehyde) (Ehrenberg, *J. pr.* [2] 36, 126). Liquid, with pepper-like smell. Is decomposed by dilute acids into its constituents. CS_2 forms an addition product $B''CS_2$, [58°]; sol. alcohol and ether, insol. water.

METHYLENE-TETRA-PROPYL-DIAMINE $CH_2(NPr_2)_2$. (220°). Formed by distilling dipropylamine with trimethylene oxide (formic paraldehyde) (Ehrenberg, *J. pr.* [2] 36, 122). Liquid; sl. sol. water, v. sol. alcohol, ether, and chloroform.

METHYLENE DI-PROPYL OXIDE *v. Di-propyl ether* of FORMIC *orth*ALDEHYDE.

TRI-METHYLENE-SELENO-UREA *v.* SELENIUM COMPOUNDS, ORGANIC.

METHYLENE SULPHIDE *v.* THIOFORMIC ALDEHYDE.

Tri-methylene tetrasulphide $C_3H_6S_4$ *i.e.* $CH_2{<}^{S.CH_2.S}_{S.CH_2.S}{>}$. [84°]. Formed by the action of H_2S on formic aldehyde (Baumann, *B.* 23, 1869). Colourless needles, insol. water, m. sol. alcohol and ether, v. e. sol. $CHCl_3$ and benzene.

METHYLENE SULPHOCYANIDE $C_3H_2S_2N_2$ *i.e.* $CH_2(SCy)_2$. [102°]. Formed by digesting potassium sulphocyanide (2 mols.) with methylene iodide (1 mol.) in alcoholic solution for 2 or 3 hours on the water-bath, ppg. with water, and recrystallising from alcohol (Lermontoff, *B.* 7, 1282). Crystals; v. sol. alcohol and ether, m. sol. hot, nearly insol. cold, water. Oxidised by conc. HNO_3 to methane disulphonic acid.

TRI-METHYLENE-TRISULPHONE $C_3H_6S_3O_6$ *i.e.* $CH_2{<}^{SO_2.CH_2}_{SO_2.CH_2}{>}SO_2$. Formed by oxidising thioformic paraldehyde (trithio-formaldehyde) with $KMnO_4$ (E. Baumann a. R. Camps, *B.* 23, 69). Crystalline powder; insol. water, dilute acids, alcohol, ether, chloroform, and glacial acetic acid; v. sol. cold caustic soda, ammonia (by warming), and sodic carbonate. Expels CO_2 from Na_2CO_3 on warming. Conc. HNO_3 and H_2SO_4 have no action even on warming. Its solution in H_2SO_4 is ppd. by water unaltered. It partially sublimes. The six hydrogen atoms can be displaced by alkyl groups. The hexamethyl derivative

$$CMe_2{<}^{SO_2.CMe_2}_{SO_2.CMe_2}{>}SO_2$$

is identical with the product obtained by B. Jaffé, E. Baumann, and Fromm (*B.* 22, 2598, 2609) by oxidising trithio-acetone.

TRIMETHYLENE-DI-SULPHONIC ACID so-called *v.* PROPANE-DI-SULPHONIC ACID.

METHYLENE TRI-THIO-CARBONATE $CH_2{<}^{S}_{S}{>}CS$. Separates on gently heating $CS(SNa)_2$ with methylene iodide in alcoholic solution (Husemann, *A.* 126, 292). Amorphous yellowish-white powder; insol. water. Converted by fuming nitric acid into methane disulphonic acid.

TRIMETHYLENE-THIO-UREA $C_4H_8N_2S$ *i.e.* $CH_2{<}^{CH_2.NH}_{CH_2.NH}{>}CS$. [198°]. Formed, together with ammonium sulphocyanide, by heating the sulphocyanide of trimethylene-diamine $C_3H_6(NH_2)_2(HNCS)_2$ (Lellmann a. Würthner, *A.* 228, 232). White needles (from chloroform mixed with light petroleum). Sol. water, alcohol, $CHCl_3$, and benzene; m. sol. aqueous NaOH, insol. light petroleum. Forms a sparingly soluble compound with $HgCl_2$.

Trimethylene-ψ-thio-urea $CH_2{<}^{CH_2.\ S}_{CH_2.NH}{>}C{:}NH$. Formed by evaporating a solution of γ-bromo-propyl-amino hydrobromide and potassium sulphocyanide to dryness at 100° (Gabriel a. Lauer, *B.* 23, 94). Liquid, v. sol. water forming an alkaline solution, from which it can be extracted by benzene.—$B'HBr$. [136°]. —$B'C_6H_2(NO_2)_3OH$. [128°]. Long needles.

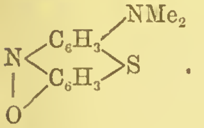
TRIMETHYLENE-UREA $C_4H_8N_2O$ *i.e.* $CH_2{<}^{CH_2.NH}_{CH_2.NH}{>}CO$. *Oxy-pyrimidine tetrahydride.* [260°]. Formed by heating trimethylene-diamine (1 mol.) with carbonic ether (1 mol.) for 6 hours at 180° (Fischer a. Koch, *A.* 232, 224).

White needles; v. sol. water, sl. sol. alcohol and ether. Its solution is neutral, and is not ppd. by HNO_3 or oxalic acid. By chromic acid mixture it is oxidised to a compound $C_4H_4N_2O_2$ crystallising in plates [275°].

Trimethylene-ψ-urea $CH_2{<}\substack{CH_2.O\\CH_2.NH}{>}C:NH$ or $CH_2{<}\substack{CH_2.O\\CH_2.N}{>}C.NH_2$. Formed by evaporating a solution of equivalent quantities of potassium cyanate and γ-bromo-propyl-amine hydrobromide (Gabriel a. Lauer, *B.* 23, 95). Thick liquid, v. sol. water.—$B'C_6H_2(NO_2)_3OH$. [200°]. Long yellow needles.

Trimethylene-di-urea $C_5H_{12}N_4O_2$ *i.e.* $CH_2(CH_2.NH.CO.NH_2)_2$. [182°]. Formed by warming a dilute aqueous solution of trimethylene-diamine hydrochloride with silver cyanate (F. a. K.). White needles; v. sol. water, sl. sol. alcohol, insol. ether.

METHYLENE VIOLET $C_{11}H_{12}N_2SO$ *i.e.*



. *Oxy-imido-di-methyl-amido-diphenylene sulphide. Oxy-dimethylamido-thio-diphenylimide.* Formed by boiling a solution of methylene blue (base). Formed also by oxidising a mixture of di-methyl-di-amido-phenyl, mercaptan, and phenol (Bernthsen, *A.* 230, 171; 251, 96). Needles; v. sl. sol. water, sl. sol. alcohol, ether, acetone, chloroform, benzene, ligroïn, and cumene, with a reddish-brown fluorescence; v. sol. aniline, without fluorescence.—B'HCl: v. sl. sol. cold dilute HClAq.

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DI-METHYL ENNYLENE DIKETONE $C_{13}H_{24}O_2$ *i.e.* $CH_2(CH_2.CHEt.CO.CH_3)_2$. *Di-acetyl-di-ethyl-n-pentane.* (208° at 110 mm.). Formed from its dicarboxylic ether by treatment with alcoholic potash (Kipping a. Perkin, jun., *C. J.* 57, 33). Colourless oil, with slight aromatic odour, v. sl. sol. water, miscible with alcohol and ether. It dissolves without change in conc. H_2SO_4, forming a yellowish-brown solution. It does not combine with $NaHSO_3$.

Oxim $CH_2(CH_2.CHEt.CMe:NOH)_2$. [111°]. Obtained by heating the ketone with an alcoholic solution of hydroxylamine, evaporating, adding water, and extracting with ether. Minute colourless crystals (from benzene-ligroïn), v. sol. alcohol, ether, HOAc, benzene, and aqueous alkalis.

DI-METHYL ENNYLENE DIKETONE DICARBOXYLIC ETHER $CH_2(CH_2.CEt(CO.CH_3).CO_2Et)_2$. *αε-Di-acetyl-αε-di-ethyl-pimelic ether.* [45°]. Obtained, together with compounds of low boiling-point, when sodium ethyl-acetoacetic ether is heated with an alcoholic solution of trimethylene bromide on a water-bath (Kipping a. Perkin, jun., *C. J.* 57, 31). Very slender needles (from ether-alcohol); v. sol. ether and alcohol, v. c. sol. benzene, light petroleum, xylene, and chloroform, insol. cold water. Gives no colour with $FeCl_3$. Readily decomposed by warm alcoholic potash.

METHYL ENNYL KETONE $CH_3.CO.C_9H_{19}$. [16°]. (224°). S.G. $^{17.5}$ ·8295. The chief constituent of oil of rue, obtained by distilling *Ruta graveolens* with steam (Greville Williams, *T.* 1858 [1] 99; Hallwachs, *A.* 113, 109; Harbordt, *A.* 123, 293; Giesecke, *Z.* [2] 6, 429; *cf.* Gerhardt, *C. R.* 26, 225, 361; Cahours, *C. R.* 26, 262). Occurs in the essential oil obtained from lime leaves (*citrus Limetta*) (F. Watts, *C. J.* 49, 316). Formed also by distilling a mixture of calcium acetate and calcium decoate (Gorup-Besanez a. Grimm, *A.* 157, 275; *B.* 3, 518); and by boiling octyl-acetoacetic ether with alcoholic potash (Guthzeit, *A.* 204, 4). It is oxidised by chromic acid mixture to acetic and ennoic acids. Sodium-amalgam reduces it, in alcoholic solution, to *sec*-hendecyl alcohol (229°), S.G. $\frac{19}{}$ ·826. It combines with NH_3. With alkaline bisulphites it forms compounds such as $C_9H_{19}CMe(OH)SO_3NH_4$ aq, which crystallises in pearly plates. PCl_5 converts the ketone into $C_{11}H_{22}Cl_2$, which is resolved by distillation into HCl and $C_{11}H_{21}Cl$ (222°).

Oxim $C_9H_{19}.CMe:NOH$. [42°]. Minute prisms (from alcohol), v. sol. ether (Spiegler, *M.* 5, 242; *B.* 17, 1575).

METHYL ENNYL KETONE CARBOXYLIC ACID $CH_3.CO.CHEt.CH_2.CH_2.CH_2.CHEt.CO_2H$. *ε-Acetyl-αε-di-ethyl-caproic acid.* (254° at 90 mm.). Formed, together with di-methyl ennylene diketone and acetic acid, by boiling di-ethyl ennylene diketone dicarboxylic acid with alcoholic potash (Kipping a. Perkin, *C. J.* 57, 36). Thick oil, miscible with alcohol, ether, and benzene.—AgA'. Amorphous pp., m. sol. hot water.

Oxim $CH_3.C(NOH).C_9H_{18}.CO_2H$. [103°]. Minute plates (from benzene-ligroïn), v. sol. alcohol and benzene, sl. sol. ligroïn, sol. alkalis and conc. HClAq.

TETRAMETHYLENYL-CARBINYL-AMINE $C_5H_{11}N$ *i.e.* $CH_2{<}\substack{CH_2\\CH_2}{>}CH.CH_2NH_2$. '*Tetramethylenylamine.*' (83°). Formed from the nitrile of tetramethylene carboxylic acid $CH_2{<}\substack{CH_2\\CH_2}{>}CH.CN$ by reduction in alcoholic solution with sodium (Freund a. Gudeman, *B.* 21, 2692). Oil, with alkaline reaction, which absorbs CO_2 from the air.—B'HCl. [236°]. Crystallises from alcohol-ether, v. sol. water and alcohol, insol. ether.—$B'_2H_2PtCl_6$. Crystalline.

TETRAMETHYLENYLCARBINYL-THIO-UREA $C_6H_{12}N_2S$ *i.e.* $CH_2{<}\substack{CH_2\\CH_2}{>}CH.CH_2.NH.CS.NH_2$. [68°]. Prepared by the action of ammonium sulphocyanide upon the hydrochloride of tetramethylenylcarbinyl-amine (Freund, *B.* 21, 2697). Slender needles (from water or alcohol).

TETRAMETHYLENYLCARBINYL-UREA $C_6H_{12}N_2O$ *i.e.* $CH_2{<}\substack{CH_2\\CH_2}{>}CH.CH_2.NH.CO.NH_2$. [116°]. Obtained by evaporating a solution of tetramethylenylcarbinylamine hydrochloride with potassium cyanate (Freund, *B.* 21, 2697). Needles, sol. alcohol, v. sol. hot, m. sol. cold water.

DI-TETRAMETHYLENYL KETONE $C_9H_{14}O$ *i.e.* $CH_2{<}\substack{CH_2\\CH_2}{>}CH.CO.CH{<}\substack{CH_2\\CH_2}{>}CH_2$. (205°). A product of the distillation of calcium tetramethylene carboxylate with lime (Colman a. Perkin, jun., *C. J.* 51, 235). Oil, smelling of

peppermint; combines with $NaHSO_3$. Bromine reacts, giving off HBr.

Oxim [51°].

TRIMETHYLENYL METHYL KETONE C_5H_8O *i.e.* $\left|\begin{matrix}CH_2\\CH_2\end{matrix}\right>CH.CO.CH_3$ or $CH_2:CH\left<\begin{matrix}CH_2.CH_2\\O-CH_2\end{matrix}\right>$. *Acetyl - trimethylene. Methylene furfurane tetrahydride.* (114°). S.G. $\frac{15}{15}$ ·9047; $\frac{25}{25}$ ·8971. M.M. 5·245 at 22·3°. Formed by distilling its carboxylic acid (Perkin, jun., *C. J.* 47, 836; 51, 832; *B.* 17, 1440). The same substance appears to be formed by treating methyl bromo-propyl ketone with solid potash (Lipp, *B.* 22, 1207). Oil. Sl. sol. aqueous $NaHSO_3$. Gives an oily phenyl-hydrazide. Does not combine with water when left in contact with it in the cold. According to Lipp the formula may be written $CH_2:C\left<\begin{matrix}CH_2.CH_2\\O-CH_2\end{matrix}\right>$ since it yields methyl oxy-propyl ketone (acetopropyl alcohol) on heating with dilute HClAq at 100°.

Tetramethylenyl methyl ketone $C_6H_{10}O$ *i.e.* $CH_2\left<\begin{matrix}CH_2\\CH_2\end{matrix}\right>CH.CO.CH_3$ or $CH_2\left<\begin{matrix}CH:CMe\\CH_2.CH_2\end{matrix}\right>O$ or $CH_2:C\left<\begin{matrix}CH_2.CH_2\\O-CH_2\end{matrix}\right>CH_2$. *Anhydride of methyl oxy-butyl ketone. Anhydride of acetobutyl alcohol. Acetyl-tetramethylene.* (137°). A product of the distillation of calcium tetramethylene carboxylate with lime (Colman a. Perkin, jun., *C. J.* 51, 237; *B.* 16, 1789; 19, 3112). Formed also by heating acetobutyl alcohol (Perkin, *B.* 19, 2558). Oil, smelling of peppermint; combines with $NaHSO_3$, forming a crystalline body, v. sol. water.

TRIMETHYLENYL METHYL KETONE CARBOXYLIC ACID $C_6H_8O_3$ *i.e.* $\left<\begin{matrix}CH_2\\CH_2\end{matrix}\right>C(CO_2H).CO.CH_3$ or $CH_2:C\left<\begin{matrix}CH(CO_2H)\\O-CH_2\end{matrix}\right>CH_2$. *Methylene-furfurane tetrahydride carboxylic acid.* Obtained by saponifying its ether which is formed by the action of ethylene bromide and NaOEt on aceto-acetic ether (Perkin, jun., *B.* 16, 2136; 19, 2561; *C. J.* 51, 823; Lipp, *B.* 22, 1210). Thick oil, converted by boiling with water into CO_2 and acetyl-propyl alcohol $CH_3.CO.CH_2.CH_2.CH_2OH$ (145° at 100 mm.).—AgA′. Easily soluble crystalline nodules.

Ethyl ether EtA′. (196°). S.G. $\frac{15}{15}$ 1·0517; $\frac{25}{25}$ 1·0439. M.M. 8·198 at 15°. According to Perkin, the physical constants of this ether indicate the presence of the trimethylene ring. Converted by HBr into bromo-ethyl-aceto-acetic ether $CH_3.CO.CH(CH_2.CH_2Br).CO_2Et$. Phosphorus pentachloride, followed by water, forms an oil $C_8H_{12}O_2Cl_2$ (173° at 150 mm.), which may possibly be chloro-ethyl chloro-crotonic ether $CH_3.CCl:C(CH_2Cl.CH_3).CO_2Et$, since it is reduced by sodium-amalgam to di-ethyl-acetic ether, and by zinc-dust and HCl to $CH_3.CCl:CEt.CO_2H$ [75°].

Phenyl hydrazide of the *ethyl ether* $C_{14}H_{18}N_2O_2$. Amorphous solid.

Trimethylenyl methyl ketone dicarboxylic acid $C_7H_8O_5$ *i.e.* $\left<\begin{matrix}CH_2\\CH_2\end{matrix}\right>C(CO_2H).CO.CH_2.CO_2H$, or $CO_2H.CH:C\left<\begin{matrix}CH(CO_2H)\\O-CH_2\end{matrix}\right>CH_2$. *Methylene-furfurane tetrahydride dicarboxylic acid.* [c. 175°]. Obtained from the ether which is got by acting on sodium acetone dicarboxylic ether with ethylene bromide (Perkin, *C. J.* 51, 847). White crystalline solid, sl. sol. water and chloroform, v. sol. other solvents. Boiling water splits it up into CO_2 and acetyl-propyl alcohol.—Ag_2A''.

Tetramethylenyl methyl ketone carboxylic acid $C_7H_{10}O_3$ *i.e.* $CH_2\left<\begin{matrix}CH_2\\CH_2\end{matrix}\right>C(CO_2H).CO.CH_3$. [115°]. The ether of the acid to which this constitution was at first assigned by Perkin, jun. (*B.* 16, 208, 1787), was subsequently shown by him (*B.* 19, 1244) to be indifferent towards phenyl hydrazine, and to possess a magnetic rotation at variance with this formula, and to behave rather as $CH_2\left<\begin{matrix}CH_2.CH_2\\O-CMe\end{matrix}\right>C.CO_2Et$. The acid is a crystalline solid, obtained by saponifying its ether, which is formed by the action of tri-methylene bromide and NaOEt on acetoacetic ether. On boiling with water it is converted into acetobutyl alcohol with evolution of CO_2 (Perkin, jun., *B.* 19, 2557). On distillation it is split up into CO_2 and $C_6H_{10}O$.

Salt.—AgA′.

Ethyl ether EtA′. (224°). V.D. 6·21 (obs.). M.M. 10·195. Does not react with phenyl hydrazine. Concentrated hydrobromic acid in the cold yields methyl ω-bromo-butyl-ketone $CH_3.CO.CH_2.CH_2.CH_2.CH_2Br$.

METHYL-ETHANE *v.* PROPANE.

Di-methyl-ethane *v.* BUTANE.

Tri-methyl-ethane *v.* PENTANE.

Tetra-methyl-ethane *v.* HEXANE.

Penta-methyl-ethane *v.* HEPTANE.

Hexa-methyl-ethane *v.* OCTANE.

METHYL - ETHENYL - TRICARBOXYLIC ACID *v.* PROPANE TRICARBOXYLIC ACID.

Di - methyl - ethenyl - tricarboxylic acid *v.* BUTANE TRICARBOXYLIC ACID.

METHYL ETHENYL ETHYL DIKETONE $C_7H_{12}O_2$ *i.e.* $CH_3.CO.CHMe.CO.Et$. (167°–170°). Formed by the action of NaOEt on a mixture of acetic ether and di-ethyl ketone (Claisen a. Ehrhardt, *B.* 22, 1016). Colourless oils.—CuA'_2. [192°]. Crystalline. Formed from the acid and an ammoniacal solution of cupric oxide.

METHYL-ETHENYL-TOLYLENE-DIAMINE $C_{10}H_{12}N_2$ *i.e.* $[4:\frac{1}{2}]CH_3.C_6H_3\left<\begin{matrix}NMe\\N\end{matrix}\right>CMe$. [192°]. Formed by reducing the acetyl derivative of nitro-methyl-*p*-toluidine with tin and HCl (Niementovsky, *B.* 20, 1878). Cubes (by sublimation at 110°), plates, or needles; v. e. sol. alcohol, ether, and boiling water. Its aqueous solution is coloured red by $FeCl_3$. The solution in alcoholic ammonia exhibits blue fluorescence.—B′HCl ½aq. Needles, v. sol. water.—$B'_2H_2PtCl_6$. [244°]. Tables, decomposed on fusion.—B′HI. Formed by heating ethenyl tolylene-diamine with MeI and MeOH at 130° (Niementovsky, *B.* 20, 1886). Grey plates.

Methylo-iodides B′MeI. [221°]. From $B'MeI_3$ and NaOH. Needles, v. sol. boiling alcohol and water, v. sl. sol. boiling chloroform, insol. ether.—$B'MeI_3$. Formed in small quantity in the preparation of B′HI as described above. Black crystals.

Methylo-hydroxide B′MeOH. [136°]. Formed by heating the methylo-iodide with

KOH on the water-bath. White plates, sol. boiling water, v. sl. sol. cold water, v. e. sol. alcohol and ether. Forms the salts :—×B'MeCl crystallising in rhombohedra, v. e. sol. water.—×$B'_2Me_2PtCl_6$.—Picrate [112°] crystallising in needles, m. sol. boiling water and alcohol.

METHYL ETHER *v.* DI-METHYL OXIDE.

PENTA-METHYL-ETHOL. A name sometimes employed to denote the alcohol $CMe_3.CMe_2OH$ *v.* HEPTYL ALCOHOL.

METHYL-ETHYL-ACETAL *v.* ALDEHYDE.

METHYL-ETHYL-ACETIC ACID *v.* VALERIC ACID.

Di-methyl-ethyl-acetic acid *v.* HEXOIC ACID.

METHYL-ETHYL-ACETOACETIC ETHER *v.* ACETOACETIC ACID.

METHYL-ETHYL-ACETOXIM *v. Oxim* of METHYL ETHYL KETONE.

METHYL-ETHYL-ACETOXIMIC ACID *v.* DI-ACETYL.

METHYL-ETHYL-ACETYLENE *v.* PENTINENE.

METHYL-ETHYL-ACROLEÏN *v.* HEXENOIC ALDEHYDE.

METHYL-ETHYL-ACRYLIC ACID *v.* HEXENOIC ACID.

PENTA-METHYL-ETHYL ALCOHOL *v. Tert*-HEPTYL ALCOHOL.

DI-METHYL-ETHYL-ALKINE *v.* DI-METHYL-OXY-ETHYL-AMINE.

METHYL-ETHYL-ALLYL ALCOHOL *v.* HEXENYL ALCOHOL.

METHYL-DI-ETHYL-AMINE $C_5H_{13}N$ *i.e.* $MeNEt_2$. Formed by distilling its methylochloride, or by distilling triethylamine methylohydroxide $NEt_3Me(OH)$ (V. Meyer a. Lecco, *A.* 180, 184; Lossen, *A.* 181, 379).—$B'_2H_2PtCl_6$. Monoclinic crystals (Hjortdahl, *J.* 1882, 476).

Methylo-chloride $C_6H_{16}NCl$ *i.e.* Me_2NEt_2Cl. *Di-methyl-di-ethyl-ammonium chloride.* Obtained from the crystalline iodide Me_2NEt_2I, which is formed by heating dimethylamine with EtI or diethylamine with MeI (Petersen, *A.* 91, 122; V. Meyer a. Lecco, *A.* 180, 177).—$(Me_2NEt_2Cl)_2PtCl_4$: yellowish dimetric prisms, m. sol. water, sl. sol. alcohol and ether. S. 1·025 at 15°.—$(Me_2NEt_2Cl)_2HgCl_2$: trimetric crystals (Topsoë, *J.* 1883, 620).—$Me_2NEt_2ClHgCl_2$.—$Me_2NEt_2Cl2HgCl_2$: trimetric crystals.—$Me_2NEt_2ClAuCl_3$: dimetric crystals.

Methylo-picrate [287°]. Needles (Lossen, *A.* 181, 374).

Ethylo-hydroxide *v. Tri*-ETHYLAMINE *methylo-hydroxide*, vol. ii. p. 476.

Di-methyl-ethyl-amine NMe_2Et. (41°). A product of the action of heat on trimethylamine ethylochloride (Collie a. Schryver, *C. J.* 57, 770). Formed also by distilling NMe_2Et_2OH.

METHYL-TRI-ETHYL-AMMONIUM COMPOUNDS *v. Methylo-hydroxide* of *Tri*-ETHYLAMINE.

Di-methyl-di-ethyl-ammonium compounds *v. Methylo-chloride* of METHYL-*di*-ETHYL-AMINE.

Tri-methyl-ethyl-ammonium compounds *v. Ethylo-chloride* of *Tri*-METHYL-AMINE.

METHYL-ETHYL-ISOAMYL-AMINE $C_8H_{19}N$ *i.e.* $MeNEtC_5H_{11}$. (135°). Formed, together with ethylene, by the dry distillation of methyl-di-ethyl-isoamyl-ammonium hydroxide $MeNEt_2(C_5H_{11})(OH)$, which is obtained by the action of moist Ag_2O on the product of the union of MeI with di-ethyl-isoamyl-amine (Hofmann, *C. J.* 4, 317). Fragrant liquid, sl. sol. water.—$B'_2H_2PtCl_6$: orange-yellow needles, v. sol. water.

METHYL-ETHYL-AMYL-PHENYL-AMMONIUM HYDROXIDE *v. Methylo-hydroxide* of ETHYL-ISOAMYL-ANILINE, vol. ii. p. 476.

METHYL-ETHYL-ANILINE $C_9H_{13}N$ *i.e.* $C_6H_5.NMeEt$. (201° uncor.).

Formation.—1. By methylation of ethyl-aniline (Hofmann, *A.* 74, 152).—2. By ethylation of methyl-aniline (Claus a. Howitz, *B.* 17, 1325).—3. From di-ethyl-aniline-methylo-iodide.

Properties.—Crystalline, forming extremely soluble salts. The hydrochloride melts at 114° (Claus a. Hirzel, *B.* 19, 2785).

Methylo-iodide B'MeI: [125°]; identical with di-methyl-aniline-ethylo-iodide (Claus a. Rautenberg, *B.* 14, 620; Hjortdahl, *J.* 1882, 510). Triclinic crystals, v. sol. water and alcohol. Decomposed by boiling with conc. KOHAq, yielding dimethylaniline.—B'HCl: [114°]; very hygroscopic crystals.—$(B'MeI)_2ZnI_2$: monoclinic crystals.—$(B'Me)_3H_5Fe_2Cy_{12}$ 2aq (Fischer, *A.* 190, 187).

Ethylo-iodide B'EtI: [102°]; identical with di-ethyl-aniline methyloiodide; by treatment with KOH it gives methyl-ethyl-aniline.

Propylo-iodide $C_6H_5.NMeEtPrI$. *Methyl-propyl-aniline-ethylo-iodide, ethyl-propyl-aniline-methylo-iodide.* Thick syrup, v. sol. water Formed by the combination of methyl-ethyl-aniline with propyl iodide, of ethyl-propyl-aniline with methyl iodide, or methyl-propyl-aniline with ethyl iodide. By boiling with aqueous KOH the propyl group is split off and methyl-ethyl-aniline regenerated (Claus a. Hirzel, *B.* 19, 2785).

Reference.—BROMO-METHYL-ETHYL-ANILINE.

METHYL-ETHYL-ARSINE *v.* ARSENIC COMPOUNDS, ORGANIC.

DIMETHYL-ETHYL-AZONIUM-CHLORIDE $C_4H_{13}N_2Cl$ *i.e.* $Me_2NEtCl.NH_2$. Crystalline compound. E. sol. water. Prepared by the combination of ethyl chloride with dimethyl-hydrazine. On reduction with zinc-dust and acetic acid it gives dimethyl-ethylamine, NH_3, and HCl (Renouf, *B.* 13, 2172).—$(C_4H_{13}N_2Cl)_2PtCl_4$: crystalline.

METHYL-ETHYL-BENZENE *v.* ETHYL-TOLUENE.

Di-methyl-ethyl-benzene *v.* ETHYL-XYLENE.

Laurene $C_{11}H_{16}$ (*Laurol*). (188°). S.G. $\frac{10}{}$ ·887. According to Armstrong a. Miller (*B.* 16, 2258) this liquid is di-methyl-ethyl-benzene $C_6H_3Me_2Et$ [1:2:4]. It is one of the products of the action of $ZnCl_2$ on camphor (Fittig, *A.* 145, 149). It yields di-methyl-benzoic acid on oxidation. Montgolfier (*A. Ch.* [5] 14, 91) described laurene as $C_{10}H_{14}$ (195°). Reuter (*B.* 16, 627) described two laurenes: (α)-laurene (190°) yielding $C_6H_3Me_2CO_2H$ [1:4:2] on oxidation by dilute HNO_3, and (β)-laurene (185°) yielding on oxidation $C_6H_3Me_2CO_2H$ [1:3:4] and forming a sulphonic acid whose Ba salt is more soluble than that of (α)-laurene. According to Uhlhorn (*B.* 23, 2346) laurene contains (1,2,4)- and (1,4,2)-di-methyl-ethyl-benzenes.

o-**METHYL-ETHYL-BENZENE HEXAHYDRIDE** C_9H_{20} *i.e.* $CH_2{<}^{CH_2.CHMe}_{CH_2.CH_2}{>}CHEt$.

o-Methyl-ethyl-hexamethylene. (151°). Formed by boiling $CH_2<\substack{CH_2.CHMe\\CH_2.CH_2}>CH.CH(OH).CH_3$ with fuming HIAq, diluting with water, extracting with ether, and heating the resulting oily $CH_2<\substack{CH_2.CHMe\\CH_2.CH_2}>CH.CHI.CH_3$ (179° at 110 mm.) with excess of HIAq (S.G. 1·96) and amorphous phosphorus for 8 hours at 235° (Kipping a. Perkin, jun., *C. J.* 57, 26). Mobile oil with odour of paraffin, miscible with alcohol and ether.

o-METHYL-ETHYL-BENZENE (β)-SULPHONIC ACID $C_6H_3MeEt.SO_3H$ [1:2:4?]. Formed by sulphonating o-ethyl-toluene (Claus a. Pieszcek, *B.* 19, 3087). Crystalline.—NaA'aq: plates, v. sol. water, insol. alcohol.—KA'aq: plates, v. sol. water. — CaA'_2 2aq: plates grouped in nodules, v. e. sol. water.—BaA'_2 3aq: plates, v. e. sol. water.—PbA'_2 3aq: plates, v. e. sol. water. —CuA'_2 aq: blue plates, v. e. sol. water.

Chloride $C_6H_3MeEt.SO_2Cl$. Oil.

Amide $C_6H_3MeEt.SO_2NH_2$. Yellowish-brown oil, v. sl. sol. cold water, sol. hot water.

m-**Methyl-ethyl-benzene-sulphonic acid** v. vol. ii. p. 524.

(1, 2, 4)-**Di-methyl-ethyl-benzene sulphonic acid** $C_6H_2Me_2Et.SO_3H$. Formed by sulphonating ethyl-o-xylene (O. Jacobsen, *B.* 19, 2516; Stahl, *B.* 23, 991). Large tables. — $BaA'_2$4aq. — $BaA'_2$3aq: white plates, m. sol. hot or cold water (S.).—NaA' $1\frac{1}{2}$aq. Small white plates, v. sol. water.

Amide $C_6H_2Me_2Et.SO_2NH_2$. [126°]. Long slender needles (from warm, very dilute, alcohol), or large prisms (from alcohol).

Di-methyl-ethyl-benzene sulphonic acid $C_6H_2Me_2Et.SO_3H$. *Laurene sulphonic acid.* Formed by sulphonating laurene. According to Reuter it is accompanied by an amorphous isomeride which forms a gummy Ba salt. Triclinic crystals (Reuter, *B.* 16, 627). When steam is passed into its solution in dilute H_2SO_4, hydrolysis begins when, through concentration, the temperature has reached 120° (Armstrong a. Miller, *C. J.* 45, 148).—BaA'_2 3aq. S. (of BaA'_2) 2·5 at 16°.

Amide $C_6H_2Me_2Et.SO_2NH_2$. [127°] (R.).

(1, 3, 4)-**Di-methyl-ethyl-benzene sulphonic acid** $C_6H_2Me_2Et.SO_3H$. Formed by sulphonating ethyl-*m*-xylene (J.).—BaA'_2 2aq: trimetric laminæ.—NaA' 2aq: prisms.

Amide $C_6H_2Me_2Et.SO_2NH_2$. [148°].

(1, 4, 3)-**Di-methyl-ethyl-benzene sulphonic acid** $C_6H_2Me_2Et.SO_3H$. Formed by sulphonating ethyl-*p*-xylene (Jacobsen, *B.* 19, 2516). Large plates (from dilute H_2SO_4).—NaA' aq: mass of large tables (from warm saturated solution).—KA' aq: flat needles, v. sol. water.—BaA'_2: long six-sided plates, sl. sol. cold, m. sol. hot, water. —$CuA'_2$8aq: light-blue needles (Stahl, *B.* 23, 990).

Amide $C_6H_2Me_2Et.SO_2NH_2$. [117°]. Pearly plates (from dilute alcohol), or large transparent crystals (from warm alcohol); v. sol. hot alcohol.

METHYL DI-ETHYL BORATE $MeEt_2BO_3$. (100°-105°). S.G. $\frac{0}{}$ ·904. Formed by heating $MeBO_2$ with absolute alcohol at 100°.

PENTA-METHYL-ETHYL BROMIDE v. *Tert*-HEPTYL BROMIDE.

METHYL-ETHYL-BROMANILINE v. BROMO-METHYL-ETHYL-ANILINE.

METHYL-ETHYL-CARBINOL v. *Sec*-BUTYL-ALCOHOL.

Methyl-di-ethyl-carbinol v. *Tert*-HEXYL ALCOHOL.

Di-methyl-ethyl-carbinol v. *Tert*-AMYL ALCOHOL.

METHYL ETHYL CARBONATE $MeEtCO_3$. [−14·5°]. (109° cor.) (Röse, *A.* 205, 230). S.G. $\frac{27}{}$ 1·002. Obtained by distilling a mixture of potassium methyl carbonate with potassium ethyl-sulphate (Chancel, *C. R.* 31, 521; *A.* 79, 90). Formed also by the action of NaOMe on $ClCO_2Et$, or of NaOEt on $ClCO_2Me$ (Schreiner, *J. pr.* [2] 22, 354).

PENTA-METHYL-ETHYL CHLORIDE v. HEPTYL CHLORIDE.

METHYL-ETHYLENE v. PROPYLENE.

Di-methyl-ethylene v. BUTYLENE.

Tri-methyl-ethylene v. AMYLENE.

Tetra-methyl-ethylene v. HEXYLENE.

METHYL-ETHYLENE-DIAMINE. *Nitro-derivative* $C_2H_4(NH.NO_2)(NMeNO_2)$. [122°]. Formed by the action of methyl iodide on ethylene dinitramine (Franchimont a. Klobbie, *R. T. C.* 7, 343).

Di-methyl-ethylene-diamine. *Nitro-derivative* $C_2H_4(NMe.NO_2)_2$ [137°]. Formed like the preceding.

Di-methyl-ethylene-diamine v. ETHYLENE-DIAMINE.

METHYL-ETHYLENE-TRI-ETHYL-PHOSPHAMMONIUM BROMIDE v. vol. ii. p. 509.

DI-METHYL-ETHYLENE GLYCOL v. DI-OXY-BUTANE.

TRI-METHYL-ETHYLENE GLYCOL v. DI-OXY-PENTANE.

DI-METHYL ETHYLENE DIKETONE v. ACETONYL-ACETONE.

DI-METHYL-ETHYLENE DIKETONE DI-CARBOXYLIC ACID v. *Di-aceto-succinic ether* described under ACETYL-SUCCINIC ETHER.

TETRA-METHYL-ETHYLENE-DI-PHENYL-DIPHOSPHONIUM BROMIDE v. *Ethylene bromide* of PHENYL-DI-METHYL-PHOSPHINE.

DI-METHYL-ETHYLENE-DI-PHENYL-DIPYRROLE DICARBOXYLIC ETHER $C_2H_4(C_4NHMePh.CO_2Et)_2$. [197°]. Formed from acetophenone-acetoacetic ether and ethylene-diamine (Paal a. Schneider, *B.* 19, 3156). Scales (containing 4aq). Yields on hydrolysis the corresponding acid [181°].

METHYL-ETHYLENE-PYRIDINE TETRA-HYDRIDE $C_8H_{13}N$ *i.e.* $C_5H_6NMe(C_2H_4)$. *Tropidine.* (162°). S.G. $\frac{0}{4}$ ·9665. Formed by heating atropine or tropine with fuming HClAq and HOAc at 180°; or by heating tropine with H_2SO_4 (Ladenburg, *A.* 217, 117). Liquid, smelling like coniine; v. e. sol. cold, sl. sol. hot, water, v. e. sol. alcohol and ether. Alkaline in reaction. Its hydrobromide is decomposed by bromine at 175° yielding di-bromo-methyl-pyridine and ethylene. — $B'_2H_2PtCl_6$. — $B'HAuCl_4$. — $B'HI_3$. [93°]. Brown prisms.—$B'C_6H_2(NO_2)_3OH$: yellow needles (from boiling water).

Methylo-iodide B'MeI. Cubes. Decomposed on distillation with KOH yielding tropilene $C_7H_{10}O$, an oil C_5H_8O (?) (202°-207°), dimethyl-amino and methyl-tropine. With moist Ag_2O it

gives a syrupy base which yields the salts: $(B'MeCl)_2PtCl_4$.—$B'MeBr$.—$B'MeC_6H_2(NO_2)_3O$.

TETRA-METHYL-ν-ETHYLENE-DI-PYRROL $C_{14}H_{20}N_2$ *i.e.*

CH:CMe⟩N.C$_2$H$_4$.N⟨MeC:CH
| | .
CH:CMe MeC:CH

[126°]. Obtained by adding ethylene-diamine (1 mol.) to a solution of acetonyl-acetone (2 mols.) in an equal weight of absolute alcohol. White pearly plates. Sublimable. Volatile with steam. V. sol. alcohol, ether, benzene, and petroleum-spirit, insol. water. Colours a chip of pine-wood carmine-red. Gives a purple-red colouration with phenanthraquinone and H_2SO_4 (Paal a. Schneider, *B.* 19, 3157).

DI-METHYL ETHYLENE DISULPHIDE $C_4H_{10}S_2$ *i.e.* $C_2H_4(SMe)_2$. *Di-methyl ether of di-thio-glycol.* (183°). Formed from ethylene bromide and NaSMe (Ewerlöf, *B.* 4, 716).

DI-METHYL ETHYLENE DISULPHONE *v.* *Di-methyl ether* of ETHANE DISULPHINIC ACID.

METHYL-ETHYLENE-ψ-THIO-UREA

CH$_2$.S⟩C:NMe or CH$_2$.S⟩C.NHMe.
| |
CH$_2$.NH CH$_2$.N

Methyl-imido-thiazole tetra-hydride. *Methyl-amido-thiazole dihydride.* [90°]. Formed, together with a crystalline compound $C_6H_{11}N_3O_2$ [70°], by the action of methyl-thiocarbimide on bromo-ethylamine (Gabriel, *B.* 22, 1148). Needles, v. e. sol. water, v. sol. ordinary solvents. Strongly alkaline. Oxidised by bromine-water to an acid (? $NHMe.CO.NH_2.CH_2.CH_2.SO_3H$), which is decomposed by fuming HClAq at 155° into CO_2, methylamine, and taurine.—Picrate [226°]: needles.—Aurochloride: needles.—Platinochloride: needles.

Methyl-ethylene-ψ-thiourea

CH$_2$—S⟩C:NH.
|
CH$_2$.NMe

Imido-methyl-thiazole. Formed by heating ethylene-ψ-thio-urea with methyl iodide (Gabriel). Oil. When it is oxidised by bromine-water it yields methyl-taurine $NHMe.CH_2.CH_2.SO_3H$. Salts.—B'HI. [160°]. Colourless crystals, sol. water and alcohol.—Picrate. [200°–203°].—The aurochloride and platinochloride form long needles, sol. boiling water.

METHYL ETHYL ETHER *v.* METHYL ETHYL OXIDE.

METHYL-ETHYL-ETHYLENE *v.* AMYLENE.

METHYL-ETHYL-GLYOXAL *v.* METHYL ETHYL DIKETONE.

METHYL-ETHYL-GLYOXALINE $C_6H_{10}N_2$ *i.e.* $C_3H_2(CH_3)(C_2H_5)N_2$ or

CH$_3$.C⟨NEt.CH
 ‖ .
 N . CH

Oxal-ethyl-ethyline. (213°). S.G. $\frac{15}{}$ ·98. Formed by the action of ethyl bromide on methyl-glyoxaline (glyoxal-ethyline) (Radziszewski, *B.* 16, 489). Formed also from di-ethyl-oxamide NHEt.CO.CO.NHEt by treatment with PCl_5 and heating the hydro-iodide (10 g.) of the resulting 'chloroxylethyline' $C_6H_9ClN_2$ with HIAq (7 g. of S.G. 1·9) and amorphous phosphorus (1 g.) for 6 hours at 140°. The product is dissolved in water, rendered alkaline, and extracted with chloroform (Wallach, *A.* 214, 298). Colourless liquid, with narcotic smell. Sol. water and alcohol. $AgNO_3$ gives a crystalline pp., $HgCl_2$ a white pp. The zinc double chloride forms crystals melting at [160°]. Burns with a blue flame. It is a strong base and ppts. metallic oxides from their salts. Its zinc double salt distilled with lime yields pyrrole, ammonia, HCy, ethylene, and methyl-glyoxaline (para-oxal-methyline) (Wallach, *A.* 214, 305). It acts physiologically like atropine (Schulz, *B.* 13, 2353). When heated in a sealed tube with dilute H_2SO_4 at 240° it yields ethylamine. $KMnO_4$ yields oxalic acid, NH_3, and acetic acid. When passed through a red-hot tube it yields HCy and methyl-glyoxaline (para-oxal-methyline). H_2O_2 oxidises it to ethyl-oxamide (Radziszewsky, *B.* 17, 1290).

Salts.—B'HCl: deliquescent crystals.—$B'_2H_2PtCl_6$.—$B'_2H_2ZnCl_4$. [160°].—B'_2AgNO_3.

Methylo-iodide $C_6H_{10}N_2MeI$. Crystals, v. e. sol. water and alcohol. Not decomposed by aqueous NaOH.—$C_6H_{10}N_2MeI_3$.

Benzylo-chloride $C_6H_{10}N_2C_6H_5CH_2Cl$.

Methyl-ethyl-glyoxaline $C_6H_{10}N_2$ *i.e.*

EtC⟨NMe.CH
 ‖ .
 N — CH

Oxalmethylpropyline. The methylo-iodide B'MeI of this body is formed by the action of MeI on para-ethyl-glyoxaline (Radziszewsky, *B.* 16, 490).

References. — DI-BROMO-, and CHLORO-, METHYL-ETHYL-GLYOXALINE.

METHYL-ETHYL-GLYOXIM *v.* *Oxim* of METHYL ETHYL DIKETONE.

METHYL-ETHYL-HYDROXYLAMINE *v.* HYDROXYLAMINE DERIVATIVES.

METHYL-ETHYLIDENE ETHYL DI-KETONE $C_7H_{12}O_2$ *i.e.* $CH_3.CO.CHMe.CO.C_2H_5$. *Acetyl-propionyl-ethane.* (167°–170°). Formed by the action of NaOEt on a mixture of di-ethyl ketone and acetic ether (Claisen a. Ehrhardt, *B.* 22, 1009). Colourless oil.—$Cu(C_7H_{11}O_2)_2$. [192°]. Blue crystals (from benzene-ligroïn).

METHYL-ETHYLIDENE DI-ETHYL SULPHONE *v.* DI-ETHYL PROPYLIDENE DI-SULPHONE.

DI-METHYL-ETHYLIDENE-DI-INDOLE $C_{20}H_{20}N_2$ *i.e.* $CH_3.CH(C_8H_5MeN)_2$ or $(NH\langle^{C_6H_4}_{CMe}\rangle C)_2.CHMe$. *Ethylidene-methyl-ketole.* [191°]. Formed by heating methyl-indole (methyl-ketole), paraldehyde, and $ZnCl_2$ on the water-bath (Fischer, *A.* 242, 376). Colourless prisms, v. sol. alcohol, ether, and acetone.

DIMETHYL ETHYLIDENE DIKETONE $(CH_3.CO)_2CHMe$. (1[illegible]5°). Formed from sodium methylene dimethyl diketone and MeI (Combes, *C. R.* 105, 868).

METHYL-ETHYL-INDAZINE $C_{10}H_{12}N_2$ *i.e.*

C$_6$H$_4$⟨CMe
 |\ .
 N.NEt

Formed by heating methyl-indazine with EtI at 100° (Fischer a. Tafel, *A.* 227, 303). Liquid, m. sol. water, v. e. sol. alcohol and ether, volatile with steam.—B'HCl: needles.

Methyl-ethyl-iso-indazine $C_6H_4\langle^{CMe}_{NEt}\rangle N$. *Ethyl-quinazole.* [30°]. (235°). Formed by heating its carboxylic acid at 160°–190° (Fischer a. Kuzel, *A.* 221, 285; *B.* 16, 655). Formed

also by reducing the nitrosamine of ethyl-amido-acetophenone, dissolved in dilute acetic acid, with zinc-dust, adding NaOH, and distilling with steam. The oily distillate is dissolved in dilute H_2SO_4, mixed with $NaNO_2$, and extracted with ether (Fischer a. Tafel, *A.* 227, 303). Plates, sl. sol. water, v. e. sol. alcohol and ether. Volatile with steam, giving off a pungent odour. Not affected by nitrous acid or by Ac_2O. Does not reduce Fehling's solution. Forms crystalline pps. with $AgNO_3$ and $HgCl_2$, which may be recrystallised from hot water in slender needles. Its salts are extremely soluble in water.—$B'H_2SO_4$: long needles.—$B'_2H_2PtCl_6$: sparingly soluble orange prisms.—Picrate: yellow needles.

Methylo-iodide B'MeI. [192°].

METHYL-ETHYL-ISO-INDAZINE CARBOXYLIC ACID $C_6H_4\left\langle\begin{matrix} C \!\!-\!\! CH_2.CO_2H \\ NEt \end{matrix}\right\rangle N$.

Formed by treating the nitrosamine of ethyl-*o*-amido-cinnamic acid with zinc-dust and acetic acid (Fischer a. Kuzel, *A.* 221, 285). Colourless plates [131°] (from water) or groups of smaller plates [126°] (from chloroform-ligroïn). Sl. sol. water, v. sol. alcohol, ether, and chloroform. Combines with alkalis and with acids. Does not reduce boiling alkaline solutions of silver or copper. With bromine in HOAc it forms a bromo- derivative [173°] and a di-bromo- derivative [196°].

METHYL-ETHYL-INDOLE $C_{11}H_{13}N$ *i.e.* $C_6H_4\left\langle\begin{matrix} CEt \\ NH \end{matrix}\right\rangle CMe$. (292° i.V.). Formed by heating the phenyl-hydrazide of methyl propyl ketone with $ZnCl_2$ at 180° (E. Fischer, *B.* 19, 1565; *A.* 236, 132). Yellowish oil, v. sl. sol. water, v. sol. alcohol and ether. Its picrate crystallises from hot benzene in dark-red needles. With $NaNO_2$ and HOAc it yields a nitrosamine.

Methyl - ethyl - indole $C_6H_4\left\langle\begin{matrix} CH \\ NEt \end{matrix}\right\rangle CMe$. *Ethyl-methyl-ketole.* (288° i.V.). Formed, together with a base boiling at 256°, by heating methyl-indole (methyl-ketole) with EtI and alcohol at 100° (E. Fischer a. Steche, *B.* 20, 2199). Oil, insol. dilute acids. Colours pine-wood red.—Picrate. [146°]. Slender dark-red needles (from benzene).

Methyl-ethyl-indole $C_6H_3Me\left\langle\begin{matrix} CH \\ NEt \end{matrix}\right\rangle CH$. *Ethyl-p-tolindole.* (254°). Formed by heating its carboxylic acid for some time at 205° (Hegel, *A.* 232, 218). Oil, volatile with steam. Resinified by conc. H_2SO_4. Colours pine-wood moistened with HCl red. Fuming HNO_3 gives a red colour and a pp.

Di-methyl-ethyl-indole $C_{12}H_{15}N$ *i.e.* $C_6H_4\left\langle\begin{matrix} CMe \\ NEt \end{matrix}\right\rangle CMe$. (281°). Formed by heating bromo-levulic (bromo-acetyl-propionic) acid with ethyl-aniline (Wolff, *B.* 21, 3363). Yellowish oil, v. sol. ether, alcohol, and benzene, sl. sol. water.—Picrate $B'C_6H_2(NO_2)_3OH$. [105°]. Red needles, m. sol. benzene.

METHYL-ETHYL-INDOLE CARBOXYLIC ACID $C_{12}H_{13}NO_2$ *i.e.* $CH_3.C_6H_3\left\langle\begin{matrix} CH \\ NEt \end{matrix}\right\rangle C.CO_2H$. [202°]. Formed from the *p*-tolyl-ethyl-hydrazide of pyruvic acid by warming with dilute (10 p.c.) HClAq, or with phosphoric acid (Hegel, *A.* 232, 218). V. sol. alkalis, ether, and benzene, insol. ligroïn. With NaOCl it yields a chloro- derivative, which is converted by boiling water into methyl-ethyl-ψ-isatin.

PENTA-METHYL-ETHYL IODIDE *v.* HEPTYL IODIDE.

METHYL-ETHYL-ISATIN *v.* ISATIN.

METHYL-ETHYL-KETOLE *v.* METHYL-ETHYL-INDOLE.

METHYL ETHYL KETONE C_4H_8O *i.e.* $CH_3.CO.CH_2.CH_3$. *Methyl-acetone.* Mol. w. 72. (81°) (F. a. D.); (78° at 740 mm.) (Schramm, *B.* 16, 1581). S.G. $\frac{13}{}$ ·8125 (F. a. D.); $\frac{20}{}$ ·8045 (S.).

Formation.—1. By the action of $ZnEt_2$ on acetyl chloride, or of $ZnMe_2$ on propionyl chloride (Freund, *A.* 118, 3; Popoff, *A.* 145, 289).—2. By boiling methyl-acetoacetic ether with potash (Frankland a. Duppa, *A.* 138, 336), or dilute H_2SO_4 (Böcking, *A.* 204, 17).—3. Among the products of the distillation of crude calcium acetate (Fittig, *A.* 110, 18).—4. By distilling a mixture of calcium acetate and calcium propionate (Schramm, *B.* 16, 1581).—5. By the oxidation of *sec*-butyl alcohol (Kanonnikoff a. Saytzeff, *A.* 175, 377).—6. By the action of H_2SO_4 on crotonylene (Lwoff a. Almédingen, *Bl.* [2] 37, 493).

Properties.—Colourless liquid, smelling like acetone, miscible with water and alcohol. With hydrogen sodium sulphite it forms the compound $MeCEt(OH).SO_3Na\,\frac{1}{2}aq$ (Fittig).

Reactions.—1. *Sodium* converts it into homologues of mesityl oxide, of phorone, and of pinacone (Lawrenovitch, *B.* 8, 767). Sodium, added to its solution in benzene, forms an oil $C_{12}H_{20}O$, smelling like camphor.—2. *Chromic acid* in HOAc oxidises it to acetic acid.—3. PCl_5 yields di-chloro-butane $CH_3.CH_2.CCl_2.CH_3$. On treating this body with alcoholic potash at 170° there is formed $CH_3.CH_2.C\vdots CH$, which ultimately changes into the isomeric $CH_3.C\vdots C.CH_3$, which yields hexa-methyl-benzene on condensation with H_2SO_4 (Favorsky, *Bl.* [2] 43, 112).—4. On warming with *pyrrol*, MeOH, and a little hydrochloric acid, there is formed a butylidene-pyrrole

$$\begin{matrix} Et \\ Me \end{matrix}\!\!>\!C\left\langle\begin{matrix} C = CH \\ | \qquad | \\ C{:}NH{:}CH \end{matrix}\right.$$

, or di-butylidene-di-pyrrole

$$\begin{matrix} Et \\ Me \end{matrix}\!\!>\!C\left\langle\begin{matrix} C = C - C = C \\ | \qquad | \qquad | \qquad | \\ C{:}NH{:}CH \quad CH{:}NH{:}C \end{matrix}\right\rangle C\!<\!\!\begin{matrix} Et \\ Me \end{matrix}.$$

This body, when crystallised as $C_{16}H_{22}N_2\,\frac{5}{3}aq$, melts at 80°, but when anhydrous it melts at 142°. With alcoholic $AgNO_3$ it yields slender needles of B'_2AgNO_3 (Dennstedt a. Zimmermann, *B.* 20, 2454).

Oxim $\begin{matrix} CH_3.CH_2 \\ CH_3 \end{matrix}\!\!>\!C{:}N.OH$. (153° cor.). S.G. $\frac{24}{24}$ ·9195. Formed by the action of an aqueous solution of hydroxylamine on methyl ethyl ketone (Janny, *B.* 15, 2779). Colourless liquid, soluble in ten volumes of water, miscible with alcohol and ether. Concentrated NaOHAq forms a crystalline Na salt.

Reference. — HEXA-BROMO-METHYL-ETHYL-KETONE.

Methyl ethyl diketone $CH_3.CO.CO.CH_2.CH_3$. *Diketopentane. Acetyl-propionyl.* (108°). S. 7 at 15°. Formed by the action of amyl nitrite on its mono-oxim (nitroso-di-ethyl ketone) (Manasso,

B. 21, 2177). Formed also from ethyl-aceto-acetic ether by saponifying with dilute (3 p.c.) alkali, treating the product with $NaNO_2$ and H_2SO_4, removing alcohol by distillation, adding dilute H_2SO_4 (15 p.c.) and distilling with steam (Von Pechmann, *B.* 21, 1411, 2140). Dark yellow liquid, smelling like quinone, v. sol. ordinary solvents. Forms an unstable compound with alcohol. Reacts with aniline, forming a compound crystallising in needles and melting at 137°. Aqueous NaOH converts it into a 'quinogen,' and finally into a quinone [112°], which may be reduced to a hydroquinone [220°], and yields a phenyl-hydrazide [225°].

(α)-*Oxim* $CH_3.C(NOH).CO.C_2H_5$. *Isonitroso-di-ethyl ketone.* [59°–62°]. Formed by the action of amyl nitrite and NaOEt upon di-ethyl ketone (Claisen a. Manasse, *B.* 22, 528). Colourless plates.

(β)-*Oxim* $CH_3.CO.C(NOH).C_2H_5$. *Isonitroso-methyl-propyl ketone.* [55°]. (183°–187° cor.). Formed by the action of KNO_2 and H_2SO_4 on ethyl-acetoacetic ether (V. Meyer a. Züblin, *B.* 11, 323, 695). Crystals, v. e. sol. alcohol and ether, m. sol. cold water. Dissolves readily in alkalis, forming a yellow solution.

Di-oxim $CH_3.C(NOH).C(NOH).C_2H_5$. [170°]. Formed by the action of hydroxylamine on the mono-oxim (Schramm, *B.* 16, 180, 2187). Small white needles. May be sublimed.—$C_5H_9N_2O_2Na$: white pp.

Di-acetyl derivative of the *di-oxim* $CH_3.C(NOAc).C(NOAc).C_2H_5$. Prisms, v. sol. alcohol and ether, sl. sol. hot water.

(α)-*Oxim*-(β)-*phenyl hydrazide* $CH_3.C(NOH).C(N_2HPh).C_2H_5$. [128°]. Formed from the (α)-oxim by treatment with phenyl-hydrazine (Otte a. Pechmann, *B.* 22, 2119). Crystallises from benzene and ligroïn.

(β)-*Oxim*-(α)-*phenyl hydrazide* $CH_3.C(N_2HPh).C(NOH).C_2H_5$. [131°]. Formed from the (β)-oxim and phenyl-hydrazine (Otte a. Pechmann, *B.* 22, 2118). Crystallises from benzene and ligroïn.

(α)-*Phenyl-hydrazide* $CH_3.C(N_2HPh).CO.C_2H_5$. [103°]. Formed by the action of phenyl-hydrazine on the diketone (Otte a. Pechmann, *B.* 22, 2115).

(β)-*Phenyl hydrazide* $CH_3.CO.C(N_2HPh).C_2H_5$. [117°]. Formed by saponifying ethyl-acetoacetic ether by allowing it to stand with aqueous KOH, then adding di-azobenzene chloride, and ppg. by sodium acetate solution (Japp a. Klingemann, *C. J.* 53, 519; *B.* 21, 550; *A.* 247, 220). Yellow radiating needles or prisms (from benzene).

Di-phenyl-hydrazide $CH_3.C(N_2HPh).C(N_2HPh).C_2H_5$. [162°] (J.); [166°–169°] (C. a. M.). Formed by the action of phenyl-hydrazine on the diketone, on the (β)-phenyl-hydrazide, or on the (α)-oxim (Von Pechmann, *B.* 21, 1414; Japp, *A.* 247, 221; Claisen a. Manasse, *B.* 22, 528). Yellow needles (from benzene), sol. cold conc. H_2SO_4, forming a brown solution.

METHYL-ETHYL-KETONE CARBOXYLIC ACID *v. Methyl*-ACETOACETIC ACID.

METHYL-ETHYL-MALONIC ACID $C_6H_{10}O_4$ *i.e.* $CH_3.CH_2.CMe(CO_2H)_2$. Mol. w. 146. [119°]. H.C.v. 67,200. H.C.p. 672,300. H.F. 236,700 (Stohmann, Kleber, a. Langbein, *J. pr.* [2] 40, 210).

Formation.—1. By saponifying its ether which is obtained by treating ethyl-malonic ether with MeI and NaOEt, or methyl-malonic ether with EtI and NaOEt (Conrad a. Bischoff, *B.* 13, 596; *A.* 204, 146).—2. Together with a larger quantity of the isomeric *s*-di-methyl-succinic acid [194°], by reducing the anhydride of di-methyl-maleïc acid (pyrocinchonic acid) with HI or sodium-amalgam (Otto a. Beckurts, *B.* 18, 841).

Properties.—Prisms, v. sol. water, alcohol, and ether. At 180° it splits off CO_2 giving valeric acid $CH_3.CH_2.CHMe.CO_2H$. A solution of its ammonium salt gives pps. with $FeCl_3$ and with salts of Hg and Pb.

Salt. — AgA′. Sparingly soluble white crystalline pp.

Ethyl ether Et_2A''. (208°). S.G. $\frac{15}{15}$ ·994. Oil, sol. alcohol and ether.

METHYL-ETHYL-METHANE *v.* BUTANE.

Methyl-di-ethyl-methane *v.* HEXANE.

Tri-methyl-ethyl-methane *v. Tert*-HEXANE.

METHYL - ETHYL - PENTAMETHENYLYL METHYL KETONE TRIHYDRIDE $C_{10}H_{16}O$ *i.e.*

$$CH_3.CO.C\left\langle\begin{array}{l}CMe.CHEt\\ \quad|\\ CH_2.CH_2\end{array}\right.$$

. *Ethyl-methyl-dihydro-pentene methyl ketone.* (210°–215°). Formed from di-methyl butylene diketone dicarboxylic ether (di-acetyl-adipic ether) by heating with EtI and alcoholic NaOEt. The product is freed from alcohol by distillation, mixed with water, and the oil, which can then be extracted by ether, hydrolysed by boiling alcoholic potash (Marshall a. Perkin, *C. J.* 57, 252).

Oxim $C_{10}H_{17}NO$. Oil.

METHYL-ETHYL-PENTAMETHYLENE

$$C_8H_{16} \text{ i.e. } CH_2\left\langle\begin{array}{l}CH_2.CHMe\\ \quad|\\ CH_2.CHEt\end{array}\right.$$

. (124°). Formed by heating methyl-iodo-ethyl-pentamethylene (obtained from methyl-pentamethylenyl-methyl carbinol and HI) with amorphous phosphorus and HI at 245° (Marshall a. Perkin, jun., *C. J.* 57, 250). Limpid oil, attacked by bromine with difficulty. Rapidly oxidised by boiling dilute HNO_3.

METHYL ETHYL OXIDE C_3H_8O *i.e.* $CH_3.O.C_2H_5$. Mol. w. 60. (11°). S.G. $\frac{0}{0}$ ·7252 (Dobriner, *A.* 243, 2). S.V. 84·0 (D.). V.D. 2·158. H.F.p. 58,450 (Thomsen, *Th.*). H.F.v. 56,420.

Formation.—1. By the action of MeI on NaOEt or of EtI on NaOMe (Williamson, *P. M.* [3] 37, 350; *C. J.* 4, 106, 229).—2. By distilling potassium methyl-sulphate with KOEt (Chancel, *C. R.* 31, 152).—3. By the action of Ag_2O on a mixture of MeI and EtI (Wurtz, *J.* 1856, 563).—4. Together with Me_2O and Et_2O by etherification of a mixture of methyl and ethyl alcohols by H_2SO_4 (Williamson; *cf.* Norton a. Prescott, *Am.* 6, 244).

Properties.—Colourless mobile liquid, with ethereal odour.

METHYL-ETHYL-OXY- *v.* OXY-METHYL-ETHYL.

METHYL-ETHYL-PHENOL $C_9H_{12}O$ *i.e.* $CH_3.C_6H_3Et.OH$. (215°). Prepared by fusing *p*-methyl-ethyl-benzene sulphonic acid with

potash, dissolving the product in water, acidifying, and extracting with ether (Mazzara, *G.* 10, 256). Oil, sl. sol. water. Gives an azure-blue colouration with $FeCl_3$.

Di-methyl-ethyl-phenol $C_6H_2Me_2Et(OH)$ [6:3:1:2]? [37°]. (245°). Obtained by potash-fusion from the corresponding di-methyl-ethyl benzene sulphonic acid (Stahl, *B.* 23, 990). $FeCl_3$ gives an intense green colour in alcoholic (not in aqueous) solution.

METHYL - ETHYL - PHENYL - AMINE *v.* AMIDO-TOLYL-ETHANE.

Tri-methyl-di-ethyl-phenyl-amine $C_{13}H_{21}N$ *i.e.* $C_6Me_3Et_2.NH_2$[1:2:5:3:6:4]. (286°–290°). S.G. ·971. Colourless oil. Obtained by heating a mixture of mono- and di-ethyl-pseudo-cumidine with an equal weight of ethyl iodide at 260°–280° for 8–10 hours (Ruttan, *C. J.* 49, 813; *B.* 19, 2383).

Salts.—B'HCl: needles; casily sol. alcohol, v. sl. sol. hot water, insol. cold water. The acetate and sulphate form easily soluble needles. The oxalate forms very sparingly soluble quadratic prisms.

Acetyl derivative $C_6Me_3Et_2.NHAc$: [182°]; needles.

DI-METHYL-DI-ETHYL-*p*-PHENYLENE-DIAMINE $C_{12}H_{20}N_2$ *i.e.* $C_6H_4(NMe_2)(NEt_2)$. (265°). Prepared by heating di-ethyl-*p*-phenylene-diamine with methyl alcohol and HCl (Lippmann a. Fleissner, *M.* 4, 788). Light-yellow oil.

Di-methylo-di-iodide $B''Me_2I_2$. [218°]. Formed by heating di-ethyl-amido-benzene-azo-di-ethyl-aniline with MeI. Transparent four-sided prisms.—$B''Me_2I_2CdI_2$: silky needles.—$B''Me_2PtCl_6$: orange-red needles.—$B''(MeAuCl_4)_2$: yellow leaflets.—$B''2MeOC_6H_2(NO_2)_3$. [235°]. Yellow needles.

DI-METHYL ETHYL PHOSPHATE $C_4H_{11}PO_4$ *i.e.* Me_2EtPO_4. (203° cor.). S.G. $\frac{0}{}$ 1·1752. S.V. 161·1 (Lossen, *A.* 254, 74). Formed from Me_2AgPO_4 and EtI (Weger, *A.* 221, 90).

METHYL-DI-ETHYL-PHOSPHINE $C_5H_{13}P$ *i.e.* Et_2PMe. (111°). Formed by heating tri-ethyl-phosphine methylo-chloride Et_3PMeCl at 300° (Collie, *C. J.* 53, 719). Combines with sulphur and with oxygen. Forms red crystals with CS_2.

Methylo-chloride v. Ethylo-chloride of *Di-methyl-ethyl-phosphine.*

Ethylo-iodide v. TRI-ETHYL-PHOSPHINE METHYL-IODIDE.

Di-methyl-ethyl-phosphine Me_2PEt. (84°). Formed by heating $Me_2PEtHCl$ (the product of the distillation of its ethylo-chloride) with aqueous NaOH (Collie, *C. J.* 53, 720).

Methylo-chloride v. Ethylo-chloride of TRI-METHYL-PHOSPHINE.

Ethylo-chloride Me_2PEt_2Cl. Formed from Me_2PEt_2I, the product of the union of Et_2PMe and MeI. Split up by heat into ethylene and $Me_2PEtHCl$ (Collie).

METHYL - TRI - ETHYL - PHOSPHONIUM CHLORIDE *v. Methylo-iodide* of TRI-ETHYL-PHOSPHINE.

Di-methyl-di-ethyl-phosphonium chloride *v. Ethylo-chloride* of *Di-methyl-ethyl-phosphine.*

Tri-methyl-ethyl-phosphonium chloride *v. Ethylo-chloride* of TRI-METHYL-PHOSPHINE.

METHYL-ETHYL-PINACONE *v.* DI-OXY-OCTANE.

METHYL-ETHYL-PIPERIDINE *v.* METHYL-ETHYL-PYRIDINE HEXAHYDRIDE.

METHYL-ETHYL-PROPIONIC ACID *v.* HEXOIC ACID.

METHYL-ETHYL-PROPYL ALCOHOL *v.* HEXYL ALCOHOL.

METHYL-ETHYL-PROPYL-AMINE $C_6H_{15}N$ *i.e.* C_3H_7NMeEt. A product of the destructive distillation of the methylo-hydroxide of ethyl-codeïne (Von Gerichten a. Schrötter, *B.* 15, 1484). Volatile base, smelling like trimethylamine.—$B'_2H_2PtCl_6$. Long orange needles, v. sol. water, sl. sol. alcohol.

METHYL-ETHYL-PROPYL-CARBINOL *v. Tert*-HEPTYL ALCOHOL.

METHYL-ETHYL-PROPYLENE *v.* HEXYLENE.

METHYL-ETHYL-PROPYL-METHANE *v.* HEPTANE.

DI-METHYL-DI-ETHYL-PYRAZINE

$C_{10}H_{16}N_2$ *i.e.* $N{<}^{CMe.CEt}_{CEt:CMe}{>}N$. *Di-ethyl-ketine.* (216° cor.). V.D. 5·63 (calc. 5·68). Prepared by reduction of the oxim of methyl ethyl diketone (methyl nitroso-propyl ketone) Me.CO.C(NOH).Et with tin and HCl, or with sodium-amalgam (Treadwell, *B.* 14, 1461). Colourless oil with narcotic smell and alkaline reaction. It is a weak poison. Combines with water forming a crystalline hydrate. Not affected by MeI, acetic anhydride, or HI. Bromine added to its solution in HOAc ppts. $C_{10}H_{16}N_2Br_2$ as an unstable yellow compound. Very dilute potassium permanganate oxidises it to di-methyl-pyrazine di-carboxylic acid $N{<}^{CMe.C(CO_2H)}_{C(CO_2H):CMe}{>}N$, which does not yield an anhydride (Oeconomides, *B.* 19, 2524).—B'HCl. Large colourless crystals.—$B'_2H_2PtCl_6$. Soluble red prisms.—$B'AgNO_3$. Crystals, almost insol. cold water, v. e. sol. dilute HNO_3 (Treadwell, *B.* 14, 2158).

Hydrate B'*x*aq. [43°]. Large prisms (by sublimation). Gives up its water in dry air, becoming liquid.

METHYL-ETHYL-PYRIDINE $C_8H_{11}N$ *i.e.* $N{<}^{CH.CH}_{CMe:CH}{>}CEt$. (*a*)-*Collidine.* Mol. w. 121. (179°). S.G. $\frac{0}{}$ ·929 (Richard, *Bl.* [2] 32, 488); $\frac{16.8}{}$ ·929 (Weidel a. Pick, *M.* 5, 659). S.V. 157·9 (Ramsay). A base found, together with many others, among the products of the dry distillation of bones (Anderson, *P. M.* [4] 9, 145, 214; *A.* 94, 360), of bituminous shale (Greville Williams, *C. J.* 7, 97) and of peat (Church a. Owen, *P. M.* [4] 20, 110). It occurs in coal tar. Colourless oil, with unpleasant odour. Fumes with HCl. V. sl. sol. water, separating again when warmed, v. sol. alcohol, ether, and oils. Ppts. ferric, aluminium, chromium, and mercurous oxides from their salts, but not manganese and nickel oxides. Its salts are deliquescent and gummy. $KMnO_4$ oxidises it to pyridine dicarboxylic (lutidinic) acid [219°], which is converted by heat into pyridine carboxylic acid [302°].—$B'_2H_2PtCl_6$. Orange-yellow flakes.

Ethylo-iodide B'EtI. Oil.—$(B'EtCl)_2PtCl_4$. Sparingly soluble crystalline pp. (Anderson, *P. M.* [4] 9, 221).

'*a*'-Collidine $C_8H_{11}N$. (179°–183°). This base, according to Oechsner de Coninck (*A. Ch.* [5] 27, 468), accompanies (*β*)-collidine in the

product of the distillation of cinchonine with KOH. It is perhaps identical with (α)-collidine.

When 'α'-collidine is heated with *ethylene chlorhydrin* and a little water for a few hours at 100° combination takes place. After removing uncombined collidine and chlorhydrin by shaking with ether, the residue is evaporated *in vacuo*. $PtCl_4$ forms with the product an orange-yellow pp. of $\{C_8H_{11}N(C_2H_4OH)Cl\}_2PtCl_4$. Boiling water removes HCl, forming oxethyl-α-collidine chloroplatinite $\{C_8H_{10}N(C_2H_4OH)Cl\}_2PtCl_2$. This forms brilliant scales (from alcohol). Oxethyl-α-collidine forms a gold salt, $B'AuCl_4$, crystallising in thin golden needles (Wurtz, *Pr.* 33, 450; *C. R.* 95, 263; *Bl.* [2] 39, 536).

Methyl-ethyl-pyridine $N{<}\genfrac{}{}{0pt}{}{CH.CEt}{CH:CH}{>}CMe$.

(β)-*Collidine*. (196°). S.G. $\frac{0}{}$ ·966. V.D. 4·25 (calc. 4·19). Obtained by distilling cinchonine or brucine with KOH (Oechsner de Coninck, *C. R.* 91, 296; *A. Ch.* [5] 27, 469; *Bl.* [2] 37, 457; 42, 100; *R. T. C.* 1, 132; *cf.* Greville Williams, *Tr. E.* 21, Part 2; *A. Ch.* [3] 45, 488). Colourless, mobile, highly refractive liquid, rapidly turning yellow on exposure to air. Sl. sol. water, sol. alcohol and ether. When left in contact with moist air it takes up water (1 mol.) but does not form a well-defined hydrate. Potassium permanganate oxidises it to homo-nicotinic acid $N{<}\genfrac{}{}{0pt}{}{CH:C(CO_2H)}{CH.CH}{>}CMe$, cinchomeronic acid $N{<}\genfrac{}{}{0pt}{}{CH:C(CO_2H)}{CH.CH}{>}C.CO_2H$, and formic acid. It is very poisonous, a sub-cutaneous injection of ·1 g. paralysing the nerve centres. HI reduces it to the hydride $C_8H_{13}N$, and, at 250°, forms a brown oil $C_8H_{12}NI_3$. Sodium in alcohol reduces it to the hexahydride $C_8H_{17}N$ (175°–180°).

S a l t s.—B'HCl. White deliquescent tables. —$B'_2H_2PtCl_6$. S. 2·1 at 60° (Richard, *Bl.* [2] 32, 488). Orange-red powder, converted by boiling water into B'_2PtCl_4, a yellow crystalline powder. — $B'HAuCl_4$. — $B'_2H_2Cl_23AuCl_3$. — $B'_2H_2HgCl_4$. Minute white needles, sl. sol. water, insol. alcohol.

Methyl-ethyl-pyridine $N{<}\genfrac{}{}{0pt}{}{CMe.CH}{CH:CEt}{>}CH$.

Aldehyde collidine. (176°). S.G. $\frac{0}{4}$ ·9389 (D.).

Occurrence.—As acetate in fusel oil (Krämer a. Pinner, *B.* 3, 77).

Formation.—1. By heating ethylidene chloride with alcoholic or aqueous ammonia for 12 hours at 160° (Krämer, *Z.* [2] 6, 568; *B.* 3, 202; Dürkopf, *B.* 18, 920). Ethylidene bromide may be used instead of the chloride, the temperature employed being then 125°–140° (Tavildaroff, *A.* 176, 12).—2. By heating an alcoholic solution of aldehyde-ammonia at 120° (Baeyer a. Ador, *A.* 155, 297). 'Para'-collidine, picoline, and lutidine are also formed in this reaction (Vohl, *J.* 1870, 807).—3. By distilling aldol-ammonia (aldehydine) (Wurtz, *Bl.* [2] 31, 433).—4. By heating glycol with ammonium chloride for 8 hours at 185°; the yield being from 15 to 20 p.c. of the theoretical quantity (Hofmann, *B.* 17, 1905).—5. By heating ethylene chloride with ethylamine at 190° (Hofmann, *B.* 17, 1907).—6. By heating paraldehyde with acetamide and P_2O_5 at 160° (Hesekiel, *B.* 18, 3091).—7. By heating aldehyde-ammonia with paraldehyde at 220° (Ladenburg a. Dürkopf, *A.* 247, 42).

Properties.—Oil, with aromatic odour, insol. water and dilute acids, v. sol. alcohol and ether. Fumes with HCl. Oxidised by $KMnO_4$ to methyl-pyridine carboxylic acid $N{<}\genfrac{}{}{0pt}{}{CMe.CH}{CH:C(CO_2H)}{>}CH$ and isocinchomeronic acid $N{<}\genfrac{}{}{0pt}{}{C(CO_2H).CH}{CH:C(CO_2H)}{>}CH$ (Dürkopf a. Schlaugk, *B.* 21, 294; *cf.* Wischnegradsky, *B.* 12, 1506). Bromine forms an oily compound. Fuming HIAq and amorphous phosphorus at 140° yield brownish-blue prisms of $C_8H_{14}NI_3$ or $C_8H_{12}NI_3$ (Ladenburg, *B.* 14, 232). Sodium, acting on its alcoholic solution, forms a hexahydride. Heated for some days at 100° with glycolic chlorhydrin and a little water it forms o x e t h y l - a l d e h y d i n e, of which the platino-chloride, $(C_8H_{11}N(C_2H_4OH)Cl)_2PtCl_4$, forms orange crystals (from dilute alcohol). It may be decomposed by H_2S; the hydrochloride produced would not crystallise, but it is converted by Ag_2O into a caustic base (Wurtz, *Pr.* 33, 448).

S a l t s.—$B'_2H_2PtCl_6$. [180°]. Very unstable trimetric crystals.—$B'HAuCl_4$. [72°]. Yellow needles, v. sol. water (Hesekiel, *cf.* Herzig, *M.* 2, 404).—$B'C_6H_2(NO_2)_3OH$. [157°]. Greenish-yellow four-sided tables.

E t h y l o - i o d i d e B'EtI. Trimetric tables, v. sol. water and alcohol. Yields $(B'EtCl)_2PtCl_4$ crystallising in needles or prisms.

Methyl-ethyl-pyridine $N{<}\genfrac{}{}{0pt}{}{CMe.CH}{CEt:CH}{>}CH$.

(161°). S.G. $\frac{0}{}$ ·9361. Formed by heating (α)-methyl-pyridine (α-picoline) with EtI at 280°–300° (Ladenburg a. Schultz, *A.* 247, 46; *B.* 20, 2720). Liquid, almost insol. water, but takes up water from the air. Very volatile with steam. Oxidised by $KMnO_4$ to pyridine dicarboxylic acid $N{<}\genfrac{}{}{0pt}{}{C(CO_2H).CH}{C(CO_2H):CH}{>}CH$ [226°]. Sodium reduces it, in alcoholic solution, to a hexahydride.

S a l t s.—$B'_2H_2PtCl_6$. [174°]. Triclinic tables, sl. sol. cold, v. sol. hot, water, insol. alcohol.—$B'HAuCl_4$. [110°]. Yellow needles, sl. sol. water, v. sol. ether-alcohol.

Methyl-ethyl-pyridine $N{<}\genfrac{}{}{0pt}{}{CMe.CH}{CH:CH}{>}CEt$.

(173°). S.G. $\frac{0}{}$ ·9353; $\frac{20}{}$ ·9218. Formed by heating (α)-methyl-pyridine with EtI at 280°–300°, and separated from the preceding by fractional distillation (Schultz, *B.* 20, 2720; Ladenburg, *A.* 247, 46). Colourless hygroscopic liquid, with unpleasant odour, sl. sol. water. Oxidised by $KMnO_4$ to pyridine dicarboxylic acid $N{<}\genfrac{}{}{0pt}{}{C(CO_2H).CH}{CH\text{———}CH}{>}C.CO_2H$. Sodium, added to its alcoholic solution, reduces it to the corresponding hexahydride.

S a l t s.—$B'_2H_2PtCl_6$. [190°]. Reddish-yellow plates, sl. sol. cold, v. sol. hot, water, insol. alcohol.—$B'HAuCl_4$. [90°]. Yellow needles, sl. sol. cold, m. sol. hot, water, v. e. sol. alcohol.—The p h o s p h o m o l y b d a t e and b i s m u t h - i o d i d e are amorphous, the c a d m i u m i o d i d e and p e r i o d i d e are oily.

Paracollidine $C_8H_{11}N$. (220°–230°). Formed, together with the collidine boiling at 176°, by heating aldehyde-ammonia (Baeyer a. Ador, *A.* 155, 307). Liquid, with pungent aromatic odour. Its salts crystallise with difficulty. Its ethylo-iodide is syrupy. The platinochloride is amorphous.

Isomeride of collidine.—Obtained by the putrefaction at 40° of pancreas (200 g.) mixed with gelatin (600 g.) and water (10,000 g.). After 5 days the liquid is distilled, first with H_2SO_4 and afterwards with baryta. The alkaline distillate is neutralised by HCl, evaporated to dryness, and extracted with alcohol. The hydrochloride of the base crystallises from alcohol in trimetric needles. The free base is got by adding NaOH to the hydrochloride and shaking with ether (Nencki, *J. pr.* [2] 26, 49).—$(B'HCl)_2PtCl_4$. Flat needles. Gives off an odour of xylene when distilled. The base is not identical with collidine (from NH_3 and ethylidene chloride), for it differs in odour, in the crystalline form of the platino-chloride, and in being more soluble in water.

Isomeride of collidine $C_8H_{11}N$. (202°). S.G. $\frac{0}{}$ ·987). Occurs in the flesh of putrid cuttle-fish (Oechsner de Coninck, *C. R.* 106, 858, 1604). Mobile liquid, v. sol. water, alcohol, and ether. Absorbs moisture from the air, becoming brown. —B'HCl. Deliquescent radiating masses. — $B'_2H_2PtCl_6$. Deep-yellow crystals, almost insol. cold water. Decomposed by hot water, with formation of B'_2PtCl_4, a pale-brown powder.— $B'_2H_2HgCl_4$. Small white needles.—$B'_2H_2Hg_3Cl_8$. Long yellowish needles.

Methylo-iodide B'MeI. Slender needles.

Isomeride of collidine *v.* TRI-METHYL-PYRIDINE.

Di-methyl-ethyl-pyridine $C_9H_{13}N$. *Parvoline.* (199° cor.) (D. a. G.). S.G. $\frac{0}{4}$ ·9419; $\frac{16}{4}$ ·9289 (D. a. S.).

Formation.—1. By heating propionic aldehyde-ammonia (Waage, *M.* 4, 718).—2. By heating methyl-ethyl-acroleïn-ammonia (Hoppe, *M.* 9, 643).—3. By heating propionic aldehyde with acetamide and P_2O_5 (Hesekiel, *B.* 18, 3097).— 4. By heating propionic aldehyde-ammonia with paraldehyde in sealed tubes for 10 hours at 210° (Dürkopf a. Schlaugk, *B.* 21, 832).—5. By heating propionic aldehyde-ammonia (4 g.) with propionic aldehyde (6·5 g.) for 6 hours at 210° (Dürkopf a. Göttsch, *B.* 23, 685).

Properties.—Colourless oil, not turned brown by light and air, with faint and not unpleasant smell. M. sol. cold water, sl. sol. hot water, v. sol. alcohol and ether. $KMnO_4$ oxidises it to methyl-pyridine dicarboxylic acid [225°] and pyridine tricarboxylic acid [318°].

Salts.—$B'_2H_2PtCl_6$. [189°]. Large monoclinic crystals, sl. sol. cold water.—$B'HAuCl_4$. [82°]. Glittering lemon-yellow spangles, sl. sol. cold water. Not hygroscopic. — $B'HHg_3Cl_7$. [119°]. Long pointed needles, almost insol. cold water.—$B'C_6H_2(NO_2)_3OH$. [152°]. Yellow plates.

Di-methyl-ethyl-pyridine $C_9H_{13}N$. (217°). Formed, together with the preceding, by heating propionic aldehyde-ammonia with propionic aldehyde at 200° (Dürkopf a. Göttsch, *B.* 23, 692). Colourless liquid, not affected by air and light. Has a faint odour of nicotine. V. sol. alcohol and ether, sl. sol. water. Yields a dimethyl-pyridine carboxylic acid on oxidation.

Salts.—$B'_2H_2PtCl_6$. [above 270°]. Yellowish-red needles, sl. sol. water.—$B'HAuCl_4$. [140°]. Slender lemon-yellow needles, sl. sol. water containing HCl.—$B'HHgCl_3$. [159°]. Long glittering spangles or well-formed monoclinic crystals, sl. sol. cold water.

Di-methyl-ethyl-pyridine $C_9H_{13}N$ *i.e.* $N\langle{}^{CMe.CH}_{CMe:CH}\rangle CEt$. (187°). S.G. $\frac{14}{}$ ·916. S. 1·3 at 0°. Obtained by the action of propionic aldehyde and ammonia on acetoacetic ether (Jaeckle, *A.* 246, 45). Formed also by heating to redness a mixture of potassium di-methyl-ethyl-pyridine dicarboxylate (1 mol.) with lime (2 mols.) (Engelmann, *A.* 231, 44). Liquid, more soluble in cold than in hot water. Its solution has a very bitter taste. $KMnO_4$ oxidises it to methyl-ethyl-pyridine carboxylic acid and uvitonic acid.

Salts.—$B'_2H_2PtCl_6$. [211°]. Crystalline pp., v. sol. hot water and alcohol.—$B'_2H_2Cr_2O_7$. Crystalline pp.—Picrate. [120°]. Needles.

METHYL-ETHYL-PYRIDINE DIHYDRIDE $C_8H_{13}N$. *(β)-Di-hydro-collidine.* (200°–205°). Formed by heating (β)-collidine with HIAq and red phosphorus at 140° (Oechsner de Coninck, *Bl.* [2] 42, 116).

Methyl-ethyl-pyridine hexahydride $C_8H_{17}N$. (c. 177°). Formed by adding sodium to an alcoholic solution of (β)-collidine (Oechsner de Coninck, *Bl.* [2] 42, 116).

Methyl-ethyl-pyridine hexahydride $C_8H_{17}N$ *i.e.* $NH\langle{}^{CHMe.CH_2}_{CH_2.CHEt}\rangle CH_2$. *Copellidine.* (164°). S.G. $\frac{0}{}$ ·8653; $\frac{15}{4}$ ·8546. Formed from the collidine derived from aldehyde, by reduction in alcoholic solution with sodium (Dürkopf, *B.* 18, 920; Ladenburg, *A.* 247, 90). Colourless alkaline liquid, sl. sol. water. Its physiological action resembles that of coniine, but is weaker.

Salts.—B'HCl. [171°]. Colourless needles, v. sol. water.—B'HBr. [165°]. Tufts of needles. —$B'HAuCl_4$. [104°]. Dimetric prisms, v. sol. hot water.—$B'_2H_2PtCl_6$. [147°]. Long yellow needles, v. e. sol. water.

Acetyl derivative $C_8H_{16}NAc$. (254°). S.G. $\frac{0}{4}$ ·9787; $\frac{21}{4}$ ·966.

Methyl-ethyl-pyridine hexahydride $NH\langle{}^{CHMe.CH_2}_{CHEt.CH_2}\rangle CH_2$. (147°–151°). S.G. $\frac{0}{}$ ·8550; $\frac{20}{}$ ·8410. Formed by reducing the corresponding methyl-ethyl-pyridine in alcoholic solution with sodium, the product being purified by means of its oily nitrosamine (Schultz, *B.* 20, 2723; Ladenburg, *A.* 247, 95). Colourless alkaline liquid, smelling strongly like ammonia and like piperidine, sl. sol. water.

Salts.—B'HCl. Needles, v. e. sol. water and alcohol.—B'HBr. Needles.

Methyl-ethyl-pyridine hexahydride $NH\langle{}^{CHMe.CH_2}_{CH_2\ .\ CH_2}\rangle CHEt$. *Copellidine.* (155°–160°). S.G. $\frac{0}{}$ ·8515; $\frac{20}{}$ ·8389. Obtained by reducing the corresponding methyl-ethyl-pyridine in alcoholic solution with sodium, the product being purified by means of the nitrosamine (Ladenburg a. Schultz, *B.* 20, 2723; *A.* 247, 96). Colourless, strongly alkaline liquid. —B'HCl. [c. 213°]. White needles, v. e. sol. water and alcohol.

ν-Methyl-ethyl-pyridine hexahydride $NMe\langle{}^{CHEt.CH_2}_{CH_2\ .\ CH_2}\rangle CH_2$. (c. 149°). S.G. $\frac{0}{}$ ·8495. Formed by the action of MeI on the corresponding ethyl-pyridine hexahydride dis-

solved in MeOH, the product being distilled with strong aqueous NaOH (Ladenburg, *A.* 247, 71). Liquid, smelling like *ν*-methyl-pyridine hexahydride; sl. sol. water. Its hydrochloride crystallises in small needles.

Di-methyl-ethyl-pyridine hexahydride $C_9H_{19}N$. *Parpevoline.* (177°). S.G. $\frac{0}{4}$ ·8628; $\frac{10}{4}$ ·8542; $\frac{20}{4}$ ·8474. Formed at the same time as di-methyl-ethyl-pyridine (199°), when propionic aldehyde-ammonia and propionic aldehyde are heated together at 200°. Formed also by reducing the same di-methyl-ethyl-pyridine by adding sodium to its alcoholic solution (Dürkopf a. Göttsch, *B.* 23, 690). Very mobile colourless liquid, with penetrating odour like rotten hay, v. sol. ether and alcohol, sl. sol. water. Strongly alkaline in reaction. — $B'_2H_2CdI_4$. [120°–130°]. White sparingly soluble needles (from hot water).—The hydrochloride and hydroiodide are hygroscopic. Chlorides of gold and of platinum give no pp. in dilute solntion, and oily pps. in concentrated solutions. Picric acid acts in like manner.

Di-methyl-ethyl-pyridine hexahydride $C_9H_{19}N$ *i.e.* $NMe{<}\begin{matrix}CHMe.CH_2\\CH_2.CHEt\end{matrix}{>}CH_2$. *ν-Methyl-copellidine.* (165°). V.D. (H=1) 139·5 (obs.). S.G. $\frac{0}{4}$ ·8519; $\frac{13}{4}$ ·844. Formed from methyl-ethyl-pyridine hexahydride (164°) and MeI in the cold (Ladenburg a. Dürkopf, *B.* 18, 925; *A.* 247, 90). Strongly alkaline colourless oil, sl. sol. water.—B'HBr [151°]. White needles.—Picrate [162°]. Yellow needles.

Methylo-iodide B'MeI. [268°]. Long white needles, m. sol. water; v. sol. alcohol, ppd. by ether from alcoholic solution. With moist Ag_2O it yields a methylo-hydroxide which is split up on distillation into water and tri-methyl-ethyl-pyridine.

Methylo-chloride B'MeCl. Formed from the iodide by shaking with AgCl.—$(B'MeCl)_2PtCl_4$. Yellow octahedra. — $(B'MeCl)_2HgCl_2$. [108°]. Long white needles.

Di-methyl-ethyl-pyridine hexahydride $C_9H_{19}N$ *i.e.* $NH{<}\begin{matrix}CHMe.CH_2\\CHMe.CH_2\end{matrix}{>}CHEt$. *Parpevoline. Ethyl-lupetidine.* (167°) at 725 mm. Formed by reducing di-methyl-ethyl-pyridine (187°) in alcoholic solution with sodium (Jaeckle, *A.* 246, 45). Liquid. Gives, in a dilute alcoholic solution, dark-brown pps. with silver or mercurous nitrate.—$B'_2H_2PtCl_6$. Orange prisms. —$B'_2H_2Cr_2O_7$. Long prisms.

Tri-methyl-ethyl-pyridine hexahydride $C_{10}H_{21}N$ *i.e.* $C_8H_{15}MeNMe$. *Di-methyl-collidine hexahydride. Di-methyl-copellidine.* (172°). S.G. $\frac{25}{4}$ ·7816. Formed by distillation of the methylo-hydroxide of *ν*-methyl-copellidine (di-methyl-ethyl-pyridine hexahydride) (165°) (Dürkopf, *B.* 18, 927; Ladenburg, *A.* 247, 94). Colourless alkaline liquid, sl. sol. water. Smells like trimethylamine.—$B'HAuCl_4$. Yellow needles or glistening plates.—$B'_2H_2PtCl_6$. [93°]. Silky yellow needles.

METHYL-ETHYL-PYRIDINE CARBOXYLIC ACID $C_9H_{11}NO_2$ *i.e.* $N{<}\begin{matrix}C(CO_2H).CH\\C(CH_3):CH\end{matrix}{>}CEt$. Formed by oxidising the corresponding di-methyl-ethyl-pyridine with $KMnO_4$ (Altar, *A.* 228, 189).—$(HA')_2H_2PtCl_6$. [195°]. Red prisms.

Di-methyl-ethyl-pyridine dicarboxylic acid $C_{11}H_{13}NO_4$ *i.e.* $N{<}\begin{matrix}CMe.C(CO_2H)\\CMe:C(CO_2H)\end{matrix}{>}CEt$. *Parvoline dicarboxylic acid.* [290°]. Obtained by saponifying its ether with alcoholic potash (Engelmann, *A.* 231, 40). Thick prisms, m. sol. cold water and alcohol; decomposed on fusion. On distillation with lime it yields di-methyl-ethyl-pyridine.—BaA″ 3aq. Plates, v. e. sol. water.—$(H_2A'')_2HCl$ aq. Prisms.

Ethyl ether Et_2A''. (305°–308°). Formed by passing nitrous acid gas into an alcoholic solution of the dihydride. Thick liquid.—$(Et_2A'')_2H_2PtCl_6$. [139°]. Long prisms (from alcohol).

DI-METHYL-ETHYL-PYRIDINE DIHYDRIDE DICARBOXYLIC ETHER $C_{15}H_{23}NO_4$ *i.e.* $NH{<}\begin{matrix}CMe:C(CO_2Et)\\CMe:C(CO_2Et)\end{matrix}{>}CHEt$. *Hydroparvoline dicarboxylic ether.* [110°]. Formed by boiling acetoacetic ether (45 g.) with propionic aldehyde (10 g.) and alcoholic ammonia (Engelmann, *A.* 231, 38). Prisms (from alcohol); v. e. sol. hot alcohol, ether, chloroform, and benzene.

METHYL-ETHYL-PYRIMIDINE $C_7H_{10}N_2$ *i.e.* $CEt{<}\begin{matrix}N.CMe\\N:CH\end{matrix}{>}CH$. (160°). Formed by reducing oxy-methyl-ethyl-pyrimidine with zinc-dust (Pinner, *B.* 22, 1619). Prisms.

(*Py.* 2:3)-**METHYL-ETHYL-QUINOLINE** $C_{12}H_{13}N$ *i.e.* $C_6H_4{<}\begin{matrix}CH:CMe\\|\\N:CEt\end{matrix}$ [56°]. (268° at 710 mm.). Formed by the action of propionic aldehyde and HCl upon aniline (Dœbner a. Miller, *B.* 17, 1714). Large monoclinic prisms. V. sol. alcohol, ether, and benzene, sl. sol. water. On oxidation with CrO_3 and H_2SO_4 it yields (*Py.* 2)-methyl-quinoline-(*Py.* 3)-carboxylic acid.

Salts.—$B'_2H_2Cl_2PtCl_4$: fine yellow needles. —Picrate $B'C_6H_2(NO_2)_3OH$: yellow crystals.— $B'_2H_2Cr_2O_7$: small yellowish-brown prisms.

Methylo-iodide B'MeI: [196°]; yellow needles, insol. ether.

(*B.* 2)-**Methyl-**(*Py.* 3)-**ethyl-qninoline** $C_6H_3(CH_3){<}\begin{matrix}CH:CH\\|\\N:C(C_2H_5)\end{matrix}$. *Ethyl-toluquinoline.* [60°]. (270° at 718 mm.). Formed by heating its (*Py.* 2)-carboxylic acid (Harz, *B.* 18, 3395). White needles. V. sol. ether or petroleum-ether. Yields on oxidation ethyl-quinoline carboxylic acid (Daniel, *B.* 23, 2267).

Salts.—B'HCl× : small white concentric crystals.—$B'HNO_3$× : fine white needles. — $B'_2H_2SO_4$× : colourless crystals.—$B'_2H_2Cl_2PtCl_4$: fine orange needles, sol. hot water, sparingly in cold.—$B'C_6H_2(NO_2)_3OH$: [244°]; very sparingly soluble yellow microscopic crystals.

(*B.* 4-*Py.* 2)-**Di-methyl-**(*Py.* 3)-**ethyl-quinoline** $C_6H_3(CH_3){<}\begin{matrix}CH:C(CH_3)\\|\\N:C(C_2H_5)\end{matrix}$. [44°]. (280° at 717 mm.). Formed by the action of propionic aldehyde and HCl upon o-toluidine (Harz, *B.* 18, 3400). Large colourless monoclinic crystals. It is reduced by tin and HCl to a tetra-hydride, which is a yellowish oil of boiling-point 275° at 724 mm. Yields methyl-ethyl-quinoline (*B.* 4)-carboxylic acid on oxidation.

Salts.—B'HCl× : easily soluble fine colour-

less needles.—$B'HI^{\times}$: very long colourless needles, v. sol. hot water, very sparingly in cold.—$B'_2H_2Cl_2PtCl_4$: large plates.—$B'C_6H_2(NO_2)_3OH$: [187°]; nearly insoluble yellow needles.

Methylo-iodide B'MeI 2aq: white needles. Gives $(B'MeCl)_2PtCl_4$: small glistening orange-red needles.

(*B.* 1or3 *Py.* 2)-**Di-methyl-**(*Py.* 3)-**ethyl-quinoline** $C_6H_3(CH_3)<\begin{matrix}CH:C(CH_3)\\ |\\ N:C(C_2H_5)\end{matrix}$. [41°]. (288°–292° at 720 mm.). Formed by the action of propionic aldehyde and HCl upon *m*-toluidine (Harz, *B.* 18, 3397). Colourless trimetric hexagonal plates. It is reduced by tin and HCl to a tetrahydride, which is a colourless oil of boiling-point 282°–285° at 720 mm.

Salts.—$B'HCl^{\times}$: easily soluble colourless prisms.—$B'HI^{\times}$: long colourless needles, soluble in hot water, very sparingly soluble in cold.—$B'_2H_2Cl_2PtCl_4$ 2aq: orange plates or fine needles, sl. sol. cold water.—$B'C_6H_2(NO_2)_3OH$: [220°]; yellow needles, sol. hot alcohol, nearly insol. water.

Methylo-iodide B'MeI aq: yellow needles, v. sol. hot water; gives $(B'MeCl)_2PtCl_4$: small glistening orange-red crystals.

(*B.* 2-*Py.* 2)-**Di-methyl-**(*Py.* 3)-**ethyl-quinoline** $C_6H_3(CH_3)<\begin{matrix}CH:C(CH_3)\\ |\\ N:C(C_2H_5)\end{matrix}$ [54°]. (288° at 720 mm.). Prepared by adding propionic aldehyde (60 g.) to a cooled mixture of *p*-toluidine (50 g.) and strong HCl (90 g.), finally heating for a short time on the water-bath. White trimetric crystals. Sparingly volatile with steam. V. sol. alcohol, ether, and benzene, insol. water. It is reduced by tin and HCl to a tetra-hydride (286°). It combines with bromine, forming a dibromide, which crystallises in yellow needles [91°]. By CrO_3 and dilute H_2SO_4 it is oxidised to (*B.* 2)-methyl-(*Py.* 3)-ethyl-quinoline (*Py.* 2)-carboxylic acid.

Salts.—B'HCl: syrup, which slowly crystallises.—B'HBr: easily soluble white silky needles.—B'HI: long colourless needles, v. sol. hot water, sparingly in cold.—$B'_2H_2Cr_2O_7$: sparingly soluble red needles.—$B'_2H_2Cl_2PtCl_4$ 2aq: orange-red needles. [208°] (Jungmann, *B.* 23, 2273).—$B'C_6H_2(NO_2)_3OH$: [177°]; small yellow needles.

Methylo-iodide B'MeI aq: [218°]; monoclinic yellow crystals.

Methylo-chloride B'MeCl, colourless soluble needles.—$(B'MeCl)_2PtCl_4$.

Ethylo-iodide B'EtI $\frac{1}{2}$aq: [114°]; small yellow crystals.—$(B'EtCl)_2PtCl_4$ aq: glistening crystals (Harz, *B.* 18, 3384).

References.—Amido-, Di-bromo-, Nitro-, and Oxy-methyl-ethyl-quinolines.

(*B.* 2,4 *Py.* 2)-**Tri-methyl-**(*Py.* 3)-**ethyl-quinoline** $C_6H_2(CH_3)_2<\begin{matrix}CH:CMe\\ N:CEt\end{matrix}$ [62°]. (291°). Formed from (1,3,4)-xylidine, propionic aldehyde and HCl (Waldbott, *B.* 23, 2270). Triclinic tables (from alcohol); gives on oxidation (*B.* 2, *Py.* 3)-di-methyl-(*Py.* 3)-ethyl-quinoline-(*B.* 4)-carboxylic acid [183°].—$B'_2H_2PtCl_6$.—B'HCl 3aq.—$B'H_2SO_4$. Monoclinic crystals.—$B'H_2Cr_2O_7$.—$B'HNO_3$. Monoclinic crystals (from alcohol-ether).—$B'C_6H_2(NO_2)_3OH$. [183°]. Yellow needles.

Methylo-iodide B'MeI. Needles.

(*Py.* 2,4)-**Methyl-ethyl-quinoline dihydride** $C_6H_4<\begin{matrix}CH:CMe\\ NEt.CH_2\end{matrix}$. (255°). Formed by heating methyl-ethyl-indole with MeOH and MeI for 15 hours at 120° (Fischer a. Steche, *A.* 242, 363). Oil, forming very soluble salts.

Py. (2,3)-**Methyl-ethyl-quinoline tetrahydride** $C_{12}H_{17}N$ *i.e.* $C_6H_4<\begin{matrix}CH_2.CHMe\\ |\\ NH.\ CHEt\end{matrix}$. (262° at 720 mm.). Formed by reduction of (*Py.* 2:3)-methyl-ethyl-quinoline with tin and HCl (Dœbner a. Miller, *B.* 17, 1716). Colourless liquid. Fe_2Cl_6 gives a red colouration.—B'HCl: sparingly soluble colourless concentric needles.

(*Py.* 3,4)-**Methyl-ethyl-quinoline tetrahydride** $C_{10}H_{12}NEt$ *i.e.* $C_6H_4<\begin{matrix}CH_2.CH_2\\ |\\ NEt.CHMe\end{matrix}$. (256°). Obtained by reducing (*Py.* 3)-methyl-quinoline ethylo-iodide with tin and hydrochloric acid (Möller, *A.* 242, 321). Colourless liquid.—$B'_2H_2PtCl_6$. Red granular crystals, decomposed by boiling water.

Methylo-iodide B'MeI. [187°]. Not acted on by KOHAq.

(*Py.* 2,3,4)-**Di-methyl-ethyl-quinoline dihydride** $C_{13}H_{17}N$ *i.e.* $C_6H_4<\begin{matrix}CH{=\!=}CMe\\ |\\ NEt-CHMe\end{matrix}$. (256° i.V.). Formed by heating methyl ketole (methyl-indole) with ethyl alcohol and ethyl iodide for 15 hours at 100° (E. Fischer a. Steche, *A.* 242, 360; *B.* 20, 2200). Oil. The salts are v. sol. water.

Methylo-iodide B'MeI. [189°]. Colourless crystals; sol. water and alcohol.

Di-methyl-ethyl-quinoline dihydride $C_{13}H_{17}N$. (255° i.V.) at 750 mm. Formed by heating methyl-ethyl-ketole (methyl-ethyl-indole) (1 pt.) with MeI (2 pts.) and MeOH (1 pt.) at 120° (F. a. S.).

(*B.* 4; *Py.* 2)-**Di-methyl-**(*Py.* 3)-**ethyl-quinoline tetrahydride** $C_6H_3Me<\begin{matrix}CH_2.CHMe\\ |\\ NH.CHEt\end{matrix}$. (275°) at 724 mm. Obtained by reducing the corresponding di-methyl-ethyl-quinoline with tin and HCl (Harz, *B.* 18, 3400). Yellowish oil; sparingly volatile with steam.

(*B.* 3? *Py.* 2)-**Di-methyl-**(*Py.* 3)-**ethyl-quinoline tetrahydride** $C_6H_3Me<\begin{matrix}CH_2.CHMe\\ |\\ NH.CHEt\end{matrix}$. (c. 284°) at 720 mm. Obtained by reducing the corresponding di-methyl-ethyl-quinoline with tin and HCl (Harz). Oil.

(*B.* 2; *Py.* 2)-**Di-methyl-**(*Py.* 3)-**ethylquinoline tetrahydride** $C_6H_3(CH_3)<\begin{matrix}CH_2.CH(CH_3)\\ |\\ NH.CH(C_2H_5)\end{matrix}$. (286° at 720 mm.). Formed by reduction of di-methyl-ethyl-quinoline with tin and HCl (Harz, *B.* 18, 3387). Colourless refractive fluid.

Salts.—B'HCl: colourless needles; sl. sol. cold water.—$B'_2H_2Cl_2PtCl_4$ 2aq: brown plates.

Nitrosamine $C_{13}H_{18}N(NO)$: crystalline solid; sparingly volatile with steam.

(*B.* 2-*Py.* 2:4)-Tri-methyl-(*Py.* 3)-ethyl-quinoline tetrahydride $C_6H_3(CH_3)\left\langle\begin{array}{l}CH_2 - CH(CH_3)\\ \quad\quad\;|\\ N(CH_3).CH(C_2H_5)\end{array}\right.$ (275°–280° at 720 mm.). Oil. Formed by heating (*B.* 2 - *Py.* 2) - di-methyl - (*Py.* 3) - ethyl - quinoline tetrahydride with methyl iodide.—$B'_2H_2Cl_2PtCl_4$ 2aq: needles (Harz, *B.* 18, 3388).

(*B.* 2,4; *Py.* 2)-Tri-methyl-(*Py.* 3)-ethyl-quinoline tetrahydride $C_{14}H_{21}N$. (288°). Formed by reducing the corresponding tri-methyl-ethyl-quinoline (Waldbott, *B.* 23, 2272). Oil. —$B'C_6H_2(NO_2)_3OH$ [146°].

(*B.* 2) - **METHYL** - (*Py.* 3) - **ETHYL - QUINOLINE CARBOXYLIC ACID** $C_6H_3(CH_3)\left\langle\begin{array}{l}CH:C(CO_2H)\\ \quad|\\ N:C(C_2H_5)\end{array}\right.$. [143°]. Formed by oxidation of (*B.* 2-*Py.* 2)-di-methyl-(*Py.* 3)-ethyl-quinoline with CrO_3 and dilute H_2SO_4 (Harz, *B.* 18, 3392; Daniel, *B.* 23, 2266). Triclinic needles, prisms, or plates (containing aq). Sol. water and alcohol. Yields on distillation methyl-ethyl-quinoline [60°].

Salts.—A'Na3aq: easily soluble glistening crystals.—A'Ag: granular powder.—$A'_2Ba\frac{1}{2}aq$: soluble needles.—A'_2Cu: microcrystalline blue pp.

Ethyl ether EtA'*x*aq. [170°–190°]. Decomposed on fusion (Harz, *B.* 18, 3394).

Methyl-ethyl-quinoline (*B.* 4) - **carboxylic acid** $CO_2H.C_6H_3\left\langle\begin{array}{l}CH:CMe\\ \quad|\\ N:CEt\end{array}\right.$. [216°]. Formed by oxidation of (*B.* 4, *Py.* 2)-Di-methyl-(*Py.* 3)-ethyl-quinoline (Miller a. Daniel, *B.* 23, 2266). Insol. water, sl. sol. cold alcohol. Gives on distillation methyl-ethyl-quinoline [56°].—$BaA'_2\frac{1}{2}aq$.

(*B.* 2; *Py.* 2)-**Di-methyl**-(*Py.* 3)-**ethyl-quinoline** (*B.* 4)-**carboxylic acid** $C_{14}H_{15}NO_2$ *i.e.* $\begin{array}{l}CMe:CH\text{——}C.CH:CMe\\ CH.C(CO_2H).C.\;N:CEt\end{array}$. [183°]. Formed by oxidising (*B.* 2,4; *Py.* 2)-tri-methyl-(*Py.* 3)-ethyl-quinoline by CrO_3 and H_2SO_4 (Jungmann, *B.* 23, 2273). Needles (from alcohol), v. e. sol. alcohol and water, sl. sol. benzene. On dry distillation it gives CO_2 and (*B.* 2; *Py.* 2)-di-methyl-(*Py.* 3)-ethyl-quinoline (254°).

(*B.* 2)-**METHYL**-(*Py.* 3)-**ETHYL-QUINOLINE CARBOXYLIC ALDEHYDE** $C_{13}H_{13}NO$ *i.e.* $C_6H_3Me\left\langle\begin{array}{l}CH:C.CHO\\ \quad|\\ N:CEt\end{array}\right.$. [57°]. (above 300°). Formed, in small quantity, in the preparation of the preceding acid (Harz, *B.* 18, 3397). Large trimetric prisms (from ether), not very volatile with steam. Reduces ammoniacal $AgNO_3$. Ag_2O oxidises it to the corresponding acid (Daniel, *B.* 23, 2267).

(*B.* 2 - *Py.* 2) - **DI - METHYL** - (*Py.* 3) - **ETHYL-QUINOLINE SULPHONIC ACID** $C_{13}H_{14}N(SO_3H)$. [above 290°]. Formed by heating di-methyl-ethyl-quinoline with fuming sulphuric acid (20 p.c. SO_3) (Harz, *B.* 18, 3389). White silky scales or thick trimetric crystals. Easily soluble in hot water, sparingly in cold; insol. strong alcohol.

Salts.—A'_2Ba aq: easily soluble white needles.—A'_4H_2Pb 6aq: easily soluble needles.

METHYL-TRI-ETHYL-RESORCIN $C_6MeEt_3(OH)_2$. [144°]. Obtained by heating with HCl its mono-ethyl derivative $C_6MeEt_3(OH)(OEt)$ which is formed, together with the di-ethyl ether of orcin, by treating orcin with EtI and KOH (Herzig a. Zeisel, *M.* 11, 318). Needles, insol. water, v. sol. ether. Neutralises only 1 mol. NaOH.

Acetyl derivative $C_6MeEt_3(OAc)(OH)$. [c. 73°]. Monoclinic needles.

METHYL TRI-ETHYL SILICATE $C_7H_{18}SiO_4$ *i.e.* $MeEt_3SiO_4$. (156°). S.G. $\frac{0}{}$ ·989. Formed from $MeO.SiCl_3$ by the action of EtOH (Friedel a. Crafts, *A. Ch.* [4] 9, 32).

Di-methyl di-ethyl silicate $Me_2Et_2SiO_4$. (143°–146°). V.D. 6·18 (calc. 6·23). S.G. $\frac{0}{}$ 1·004. Formed from MeOH and Et_4SiO_4. Formed also by the action of EtOH on $(MeO)_2SiCl_2$. Liquid.

Tri-methyl ethyl silicate Me_3EtSiO_4. (134°). S.G. $\frac{0}{}$ 1·023. Formed from $(MeO)_3SiCl$ and EtOH.

METHYL-ETHYL-STIBONIUM SALTS *v.* ANTIMONY, vol. i. p. 294.

METHYL-ETHYL-SUCCINIC ACID $C_7H_{12}O_4$ *i.e.* $CO_2H.CHEt.CHMe.CO_2H$. [168·5°]. Formed by the action of H_2SO_4 on pentane tricarboxylic ether (Bischoff a. Walden, *B.* 22, 1817). It is accompanied by the isomeric 'meso' acid [88°] (Bischoff a. Mintz, *B.* 23, 647). The same acid [160°] appears to be formed in small quantities in the saponification of $CH_3.CO.CMe(CO_2Et).CHEt.CO_2Et$ with HCl (Young, *C. J.* 43, 180). White crystals.

Di-methyl-ethyl-succinic acid $C_8H_{14}O_4$ *i.e.* $CO_2H.CHEt.CMe_2.CO_2H$. Formed by the action of H_2SO_4 on the product of the action of α-bromo-isobutyric ether on sodium ethyl-malonic ether (Bischoff a. Mintz, *B.* 23, 651). It occurs in two varieties, one melting at 63° the other at 105°.

DI-METHYL-DI-ETHYL-SULPHAMIDE $C_6H_{16}N_2SO_2$ *i.e.* $O_2S\left\langle\begin{array}{l}NMe_2\\ NEt_2\end{array}\right.$. (229°). Formed by the action of di-ethyl-amine on di-methyl-amido-sulphonic chloride, or of di-methyl-amine on di-ethyl-amido-sulphonic chloride (Behrend, *B.* 15, 1610; *A.* 222, 125, 136). Volatile with steam. Heavy oil. Insol. water, sol. alcohol, ether, and benzene.

METHYL ETHYL SULPHIDE C_3H_8S *i.e.* Me.S.Et. (67° i.V.). S.G. $\frac{20}{}$ ·837. V.D. 2·61 (calc. 2·63). Formed by distilling an alcoholic solution of NaSEt with MeI (Krüger, *J. pr.* [2] 14, 193; Claesson, *J. pr.* [2] 15, 174; *B.* 20, 3413). Occurs also among the products obtained by heating di-thio-phosphoric ether $Et_3PO_2S_2$ with MeOH at 150° (Carius, *A.* 119, 313; 120, 61). Liquid, with unpleasant odour. Yields ethane sulphonic acid on oxidation with HNO_3. —$EtSMeHgCl_2$: laminæ (C.).—$(EtSMe)_2HgI_2$. Yellow crystalline powder.

Methylo-iodide $EtSMe_2I$ *v.* DI-METHYL-SULPHIDE *ethylo-iodide.*

Ethylo-iodide Et_2SMeI *v. Methylo-compounds* of DI-ETHYL-SULPHIDE, vol. ii. p. 516.

METHYL - ETHYL - SULPHONAMIDE *v.* METHYL-ETHYL-SULPHAMIDE.

METHYL ETHYL SULPHONE $C_3H_8SO_2$ *i.e.* $MeEtSO_2$. [36°]. Formed by oxidising MeSEt with $KMnO_4$ (Beckmann, *J. pr.* [2] 17, 455). Formed also by heating $C_2H_5.SO_2.CH_2.CO_2H$ to 190° (Otto, *B.* 21, 993). White needles (from ether). V. sol. water, alcohol, benzene, chloroform, and strong acids. Sl. sol. CS_2 and ether. Not affected by reducing agents.

METHYL ETHYL SULPHONE CARBOXYLIC ACID $C_4H_8SO_4$ *i.e.* $Et.SO_2.CH_2.CO_2H$. *Ethyl-sulphono-acetic acid.* Obtained by saponifying its ether with cold conc. KOHAq. Formed also by oxidising the barium salt of the ethyl derivative of thioglycollic acid with $KMnO_4$ (Claesson, *Bl.* [2] 23, 447). Thick colourless syrup. At 190° it splits up into CO_2 and methyl ethyl sulphone [36°]. Bromine added to its aqueous solution gives a di-bromo-methyl-ethyl-sulphone. Zinc and HCl reduce it to ethyl mercaptan.

Salts.—NaA′. Pearly plates, v. sl. sol. hot alcohol, v. sol. water.—KA′. Small tables (from alcohol).—BaA'_2. Nodules.—CuA'_2 2aq. Broad tables.

Ethyl ether EtA′. Formed by the action of chloro-acetic ether on sodium ethane-sulphinate (Claesson, *J. pr.* [2] 15, 223; Otto, *B.* 21, 993). Oil.

METHYL-ETHYL-THIAZOLE
$<\begin{matrix}S\ .CEt\\CH:CMe\end{matrix}>N$. (161° cor.). Formed by the action of thiopropionamide on chloro-acetone in alcoholic solution (Hubacher, *A.* 259, 230). Liquid, smelling like pyridine, miscible with alcohol, insol. hot water, sl. sol. cold water.—$B'_2H_2PtCl_6$. [177°].

METHYL ETHYL DITHIOCARBONATE *v.* ETHYL THIOCARBONATES, vol. ii. p. 521.

METHYL-ETHYL-THIO-UREA $C_4H_{10}N_2S$ *i.e.* NHMe.CS.NHEt. [54°]. Formed by addition of methylamine to ethyl thio-carbimide (Hofmann, *B.* 1, 27; *Z.* 1868, 655). Fine crystals, sol. water, alcohol, and HClAq.

Methyl-di-ethyl-thio-ψ-urea $C_6H_{14}N_2S$ *i.e.* NHEt.C(SMe):NEt. Formed from di-ethyl-thio-urea and MeI (Noah, *B.* 23, 2196). Oil. With alcoholic NH_3 at 100° it yields di-ethyl-guanidine and MeSH.—B′HI.—$B'C_6H_2(NO_2)_3OH$. [116°].—$B'_2H_2PtCl_6$: laminæ.

METHYL-ETHYL-TOLUQUINOLINE *v.* DI-METHYL-ETHYL-QUINOLINE.

METHYL-ETHYL-UREA $C_4H_{10}N_2O$ *i.e.* NHMe.CO.NHEt. [53°]. (267°) (Wurtz, *Rép. chim. pure*, 4, 199). [92°–112°] (Schreiner). Formed from methylamine and cyanic ether (Wurtz). When methylamine acts on ethyl-carbamic ether there is formed a methyl-ethyl-urea which melts at 105° and solidifies again at 101°. When, on the other hand, ethylamine acts on methyl-carbamic ether the methyl-ethyl-urea which is produced melts at 75° and solidifies again at 72° (Schreiner, *J. pr.* [2] 22, 360). After frequent meltings and solidifyings, both these forms begin to melt at 92° and end at 112°.

METHYL-EUGETIC ACID *v. Methyl derivative* of EUGETIC ACID.

METHYL-ISO-FERULIC ACID *v. Iso*-FERULIC ACID and the *dimethyl derivative* of CAFFEÏC ACID, vol. i. p. 659.

METHYL-FLAVOLINIUM HYDRATE *v. methylo-hydrate* of (*Py.* 3:1)-PHENYL-METHYL-QUINOLINE (*flavoline*).

METHYL-FLUORESCEÏN *v.* so-called '*homo-fluoresceïn*,' vol. ii. p. 558.

METHYL FLUORIDE CH_3F. V.D. 1·22 (calc. 1·19). S. 1·66 at 15° (D. a. P.). Formed, together with Me_2O, by the action of KF on $KMeSO_4$ (Dumas a. Péligot, *A.* 15, 59). Formed also, in small quantity, together with NMe_3, by heating NMe_4F at 180° *in vacuo* (Lawson a. Collie, *C. J.* 53, 628; 55, 110). Prepared by the action of MeI upon silver fluoride (Moissan a. Meslans, *C. R.* 107, 1155). Gas, sl. sol. water, v. sol. alcohol and MeI. Liquefied by a pressure of 30 atmospheres. It burns with a blue flame, yielding HF. Saponified with difficulty by heating in sealed tubes with water or dilute aqueous KOH at 120°. In the presence of a little water it forms a crystalline hydrate, decomposing at 18·8° (Villard, *C. R.* 111, 184). Chlorine, acting upon it in sunlight, forms CH_2ClF, a gas which is decomposed by water, and is hardly inflammable.

METHYL-FORMAMIDE *v. Formamide* in the article on FORMIC ACID.

Di-methyl-formamidine $C_3H_8N_2$ *i.e.* NMe_2.CH:NH. *Form-imid-di-methyl-amide.* Formed by the action of an alcoholic solution of di-methyl-amine on the hydrochloride of form-imido-ether (Pinner, *B.* 16, 1650).—B′HCl: thick prisms, [169°], v. sol. water and alcohol.

s-**Di-methyl-formamidine** NHMe.CH:NMe. *Form-methyl-imid-methyl-amide.* Formed by the action of an alcoholic solution of methyl-amine on the hydrochloride of formimido-ether NH:CH.OEt.—$B'_2H_2Cl_2PtCl_4$: short red prisms, [172°] (Pinner, *B.* 16, 358, 1648).

METHYL-FORMANILIDE *v.* FORMIC ACID.

DI-METHYL-FUMARIC ACID *v.* DI-METHYL-MALEÏC ACID.

METHYL-FURFURALDEHYDE $C_6H_6O_2$ *i.e.* C_4H_2MeO.CHO. *Methyl-furfurol.* (187° i.V.). S. 3·3. Appears to accompany furfuraldehyde in the product of the dry distillation of wood (Hill, *B.* 22, 607). Formed also by distilling isodulcite with dilute H_2SO_4 (Maquenne, *C. R.* 109, 604). According to Bieler a. Tollens (*A.* 258, 110; *B.* 22, 3062) fucusol or fucus aldehyde (*q.v.*) is a mixture of furfuraldehyde and methyl-furfuraldehyde. Combines with $NaHSO_3$. Aqueous ammonia converts it into crystalline methyl-furfuramide $N_2(C_6H_6O)_3$ [87°]. Yields, on oxidation, methyl-pyromucic acid $C_6H_6O_3$ [109°]. Reduces Ag_2O. Gives Schiff's reaction with rosaniline and SO_2. Its phenyl-hydrazide is liquid. With resorcin and HCl it yields an orange-yellow condensation-product. Pyrogallol and HCl form a crimson compound. Paper moistened with aniline acetate is coloured yellow, and finally deep orange-red by an aqueous solution of methyl-furfuraldehyde.

(*αα*)-**DI-METHYL-FURFURANE** C_6H_8O *i.e.*
$O<\begin{matrix}CMe:CH\\ \vert\\ CMe:CH\end{matrix}$. (94°).

Formation.—1. By dry distillation of pyrotritaric or carbopyrotritaric acid; the yield being 5–7 p.c. — 2. By distilling acetonyl-acetone $CH_3.CO.CH_2.CH_2.CO.CH_3$ with $ZnCl_2$; the yield being 25 p.c. (Dietrich, *B.* 20, 1085).—3. Occurs also in the product obtained by distilling sugar (1 pt.) with lime (3 pts.) (E. Fischer a. Laycock, *B.* 22, 101).

Properties.—Colourless mobile very volatile liquid of characteristic odour. Insol. water; miscible with other solvents. Does not react with phenyl-hydrazine. By PCl_5 or $POCl_3$ it is resinified. By heating with acidified water it is converted back into acetonyl-acetone.

METHYL-FURFURANE CARBOXYLIC ACID *v.* METHYL-PYROMUCIC ACID.

Di-methyl-furfurane carboxylic acid *v.* PYROTRITARIC ACID

Di-methyl-furfurane dicarboxylic acid

$C_8H_8O_5$ *i.e.*

```
C(CO2H).C(CO2H)
||           ||
CMe.   O.  CMe
```

(Knorr; *cf.* Fittig, *B.* 18, 3410). *Carbopyrotritaric acid.* [230°]. Formed by boiling diacetyl-succinic ether for a long time with dilute H_2SO_4 (Harrow, *C. J.* 33, 425; *A.* 201, 152). Formed also by the action of fuming HCl on acetonyl-aceto-acetic ether $CH_3.CO.CH_2.CH(CO_2Et).CO.CH_3$ (Paal, *B.* 17, 2765).

Properties.—Needles (by sublimation), m. sol. hot water, v. sol. alcohol and ether, volatile with steam. On heating above its melting-point it is decomposed into CO_2 and di-methyl-furfurane carboxylic acid (pyrotritaric acid). Potash-fusion yields acetic and succinic acids.

Salts. — K_2A'': silky needles.—BaA''. — Ag_2A'': white pp. — $HAgA''$: slender white needles.

Mono-methyl ether $MeHA''$. [129°]. Formed by leaving a mixture of the di-methyl ether (1 pt.) and fuming HClAq (10 pts.) to stand in the summer-time (K. a. C.). Slender needles.—$AgMeA''$. Ppd. by adding ammoniacal $AgNO_3$ to a solution of $MeHA''$.

Di-methyl ether Me_2A''. [64°]. (258°). From Ag_2A'' and MeI at 100° under pressure (Knorr a. Cavallo, *B.* 22, 155). Snow-white crystals, v. sol. alcohol, ether, chloroform, and benzene, v. sl. sol. water, dilute acids, and alkalis.

Methyl ethyl ether $MeEtA''$. (268°). From $AgMeA''$ and EtI, or from $AgEtA''$ and MeI (K. a. C.). The identity of the ethers prepared in these two ways shows that the carboxyls are similarly situated in the molecule of di-methyl-furfurane di-carboxylic acid. $MeEtA''$ exhibits blue fluorescence. With HCl it yields H_2A'', and the ethers Me_2A'' and Et_2A''.

Mono-ethyl ether $EtHA''$. [83°]. Formed by heating di-acetyl-succinic ether at 200°, or by allowing it to stand with conc. HClAq for some hours in the cold (Knorr, *B.* 17, 2863). Formed also from $AgHA''$ and EtI (Harrow). Flat glistening needles, v. sol. alcohol and ether, sl. sol. water. May be distilled. $AgEtA''$. Bulky white pp. (Knorr a. Cavallo, *B.* 22, 154).

Di-ethyl ether Et_2A''. (275°) at 735 mm. Formed by dissolving di-acetyl-succinic ether in cold H_2SO_4, or by heating it with conc. phosphoric acid (Knorr). Formed also, together with pyrotritaric and iso-carbo-pyrotritaric ethers, by heating diacetyl-succinic ether at 175° (Knorr, *B.* 22, 158). Oil. Does not react with hydroxylamine or with phenyl hydrazine. Easily saponified by alcoholic potash.

Di-methyl-furfurane dicarboxylic acid *v.* METHRONIC ACID.

METHYL - FURFURINE $C_{18}H_{18}N_2O_3$. Formed by heating (5g. of) methyl-furfuramide (*v.* METHYL-FURFURALDEHYDE) with NaOH (2·5 g.) dissolved in water (25 c.c.) at 100° (Bieler a. Tollens, *A.* 258, 123). Oil, which solidifies as an amorphous resin.—$^{\times}B'HNO_3$: lustrous crystals.—$B'H_2SO_4$: minute needles.—$B'_2H_2PtCl_6$ yellow crystalline pp.

METHYL-FURFUROL *v.* METHYL-FURFURALDEHYDE.

METHYL-FURFURYL-ACETIC ACID (?)

$C_7H_8O_3$ *i.e.*

```
CH:CMe
|     >O
CH:C.CH2.CO2H
```

or

```
CMe:CH
|     >CO
CH2.CH.CO2H
```

. *Sylvane-acetic acid.* [138°]. Formed by heating its carboxylic acid (Polonowsky, *A.* 246, 14). Prisms (from water), v. e. sol. alcohol, m. sol. ether, almost insol. cold water. Somewhat volatile with steam. It gives no colouration with $FeCl_3$, and is dissolved without alteration by conc. H_2SO_4. Nitric acid oxidises it, yielding acetic and oxalic acids.—$AgA'\ \frac{1}{2}aq$: bulky white pp.—$BaA'_2\ 4\frac{1}{2}aq$: transparent plates or spherical aggregates.

Methyl-carboxy-furfuryl-acetic acid (?)

$C_8H_8O_5$ *i.e.*

```
CO2H.C : CMe
      |     >O
      CH:C.CH2.CO2H
```

. *Sylvane carboxyacetic acid.* [207°]. Formed, together with methyl-furfuryl-carbinyl methyl ketone carboxylic ether and a neutral substance $C_{14}H_{18}O_6$ [139°], by adding a conc. solution of $ZnCl_2$ to a mixture of glyoxal and aceto-acetic ether in the cold (Polonowsky, *A.* 246, 1). Needles (from hot water), v. sol. alcohol.—$(NH_4)_2A''\ \frac{1}{2}aq$: minute needles.—$BaA''\ 2aq$: transparent needles.—$Ag_2A''aq$.

Mono-methyl ether $MeHA''$. [98°]: needles.—$AgMeA''$.

Di-methyl ether Me_2A''. Oil.

Mono-ethyl ether $EtHA''$. [76°].

METHYL-FURFURYL-CARBINYL METHYL KETONE DI-CARBOXYLIC ACID. *Ethyl ether*

```
CO2Et.C : CMe
       |     >O
       CH:C.CH(CO2Et).CO.CH3
```

. (c. 295°). One of the products formed by the condensation of aceto-acetic ether (2 mol.) with glyoxal (1 mol.) in presence of aqueous $ZnCl_2$ (Polonowsky, *A.* 246, 18). Light-yellow oil, miscible with alcohol, ether, benzene, and chloroform. Insol. water and alkalis, resinified by warming with conc. H_2SO_4.

DI - METHYL - FURFURYL METHYL KETONE CARBOXYLIC ACID $C_9H_{10}O_4$ *i.e.*

```
  /CMe:C.CO.CH3
O<      |
  \CMe:C.CO2H
```

. *Acetyl-di-methyl-furfurane carboxylic acid.* [152°]. Formed by heating at 225° in a sealed tube a mixture of β-acetyl-propionic acid (3 g.) with Ac_2O (15 g.), the product being freed from Ac_2O by distillation *in vacuo* and the residue extracted with water (Magnanini, *B.* 21, 1523). Small needles (from hot water).—AgA': crystalline pp., sl. sol. water.—BaA'_2 aq: crystalline pp.

DI - METHYL - GENTISIC ALDEHYDE *v.* *Di-methyl derivative* of DI-OXY-BENZOIC ALDEHYDE.

METHYL-GLUTACONIC ACID $C_6H_8O_4$ *i.e.* $CH_3.CH(CO_2H).CH:CH.CO_2H$. [137°]. Formed by boiling methyl-dicarboxy-glutaconic ether (vol. i. p. 706) with conc. alcoholic potash (Conrad a. Guthzeit, *A.* 222, 259). Nodules (from water), v. sol. water, alcohol, and ether.

α-METHYL-GLUTARIC ACID $C_6H_{10}O_4$ *i.e.* $CO_2H.CHMe.CH_2.CH_2CO_2H$. *Butane dicarboxylic acid.* Mol. w. 146. [77°]. H.F. 238,200. H.C.v. 670,500. H.C.p. 670,800 (Stohmann, Kleber a. Langbein, *J. pr.* [2] 40, 214). Formed by saponifying with conc. alcoholic KOH the product of the action of β-iodo-propionic ether on sodium methyl acetacetic ether (Wislicenus a. Limpach, *A.* 192, 133). Formed also by the action of HI and P on γ-oxy-α-methyl-glutaric acid (Krekeler, *B.* 19, 3270), and on saccharonic acid $CO_2H.CMe(OH).CH(OH).CH(OH).CO_2H$ a product of the decomposition of glucose (Kiliani, *A.* 218, 369). Obtained by boiling γ-cyano-valeric acid (*q. v.*) with aqueous NaOH (Wislicenus, *A.* 233, 101). Prisms, v. sol. water, alcohol, and ether. The zinc-salt is a viscid mass.—Ag_2A''.

β-Methyl-glutaric acid $C_6H_{10}O_4$ *i.e.* $CH_3.CH(CH_2.CO_2H)_2$. *Ethylidene-di-acetic acid* [85°–86°]. Formed from malonic acid, paraldehyde, and Ac_2O, by heating at 100° for several days. On rectification the anhydride (282°–284°) is obtained (15 p.c. of weight of malonic acid). Boiling water changes it into the acid (Komnenos, *A.* 218, 150). Colourless glass-like prisms or tables (from CS_2 mixed with $CHCl_3$). V. sol. water, alcohol, or ether, m. sol. cold benzene or CS_2, v. sl. sol. CS_2 or benzoline. On distillation it splits up into H_2O and its anhydride. On distilling its sodium salt with P_2S_5 there is formed, as an oil, the homologue of thiophene $CH_2<\begin{matrix}CMe:CH\\CH:CH\end{matrix}>S$, boiling at 134° (Krekeler, *B.* 19, 3270).

Salts.—Ag_2A''.—CaA''.—$PbA''\frac{1}{2}aq$. Trimetric needles $a:b:c = \cdot6331:1:\cdot6072$.

Anhydride $C_6H_8O_3$ [46°]. (282°–284°). V.D. 4·61 (calc. 4·43). Mass of slender prisms (from CS_2). V. sl. sol. cold water, neutral to litmus, on boiling it dissolves, becoming strongly acid, changing to the hydrated acid. V. sol. alcohol, ether, benzene, chloroform, or glacial acetic acid, v. sl. sol. petroleum.

s-Di-methyl-glutaric acid $C_7H_{12}O_4$ *i.e.* $CO_2H.CHMe.CH_2.CHMe.CO_2H$. [114°] (Z.); [c. 90°] (D.); [101°] (B.); [106°] (A. a. J.). Formed by treating α-cyano-propionic ether with methylene iodide and alcoholic NaOEt, heating the mixture on the water-bath, and saponifying the product with HCl (Zelinsky, *B.* 22, 2823). Formed also by heating pentane tetracarboxylic acid either by itself, or in aqueous solution, or by heating its ether with H_2SO_4 (Dressel, *A.* 256, 184). Obtained from sodium methyl-malonic ether and methylene iodide (Bischoff, *B.* 23, 1464, 1951). Crystals resembling those of di-methyl-succinic acid; v. sol. water, alcohol, and ether. Not volatile with steam. According to Zelinsky the product obtained by his method really consisted of two isomeric modifications, melting at 102°–104° and 128° respectively. A solution of the ammonium salt gives white pps. with $AgNO_3$ and $HgCl_2$, and a brown pp. with $FeCl_3$.—Ag_2A''.

Anhydride $CH_2<\begin{matrix}CHMe.CO\\CHMe.CO\end{matrix}>O$. [93°]. Formed by boiling the acid for five minutes or by warming it with AcCl (Auwers a. Jackson, *B.* 23, 1611). Rectangular prisms (from hot ligroïn).

Tri-methyl-glutaric acid $C_8H_{14}O_4$ *i.e.* $CO_2H.CMe_2.CH_2.CHMe.CO_2H$. [97°]. S. 2·2 at 11°. Formed, together with the isomeric tetramethyl-succinic acid, by the action of finely divided silver on α-bromo-isobutyric acid (Hell a. Wittekind, *B.* 7, 320; Auwers a. V. Meyer, *B.* 23, 300). Flat plates (from hot water), sol. cold water, m. sol. CS_2 and ligroïn, v. sol. other solvents. Can be distilled in small quantities. Not volatile with steam. When the acid (6 g.) is mixed in the cold with dry red phosphorus (·8 g.) and bromine (16 g.) the product is bromo-trimethyl-glutaric anhydride [114°].

Anhydride $CH_2<\begin{matrix}CMe_2.CO\\CHMe.CO\end{matrix}>O$. [96°]. (262°). Formed by boiling the acid for some time, or by heating it with excess of Ac_2O. Coarse flat satiny needles (from hot ligroïn).

Ethyl ether Et_2A''. (230°). S.G. $\frac{0}{}$ 1·012.

METHYL-GLYCERAMINE $C_4H_{11}NO_2$ *i.e.* $CH_2(OH).CH(OH).CH_2NMeH$. Formed, together with the following body, by heating the (α)-chlorhydrin of glycerin with aqueous NMe_3 in sealed tubes at 100° (Hanriot, *A. Ch.* [5] 17, 62; *cf.* vol. ii. p. 623).

Tri-methyl-glyceramine chloride $CH_2(OH).CH(OH).CH_2NMe_3Cl$. Formed by heating glycerin chlorhydrin with trimethylamine on the water-bath for 12 hours (Hanriot, *C. R.* 86, 1335).—$C_3H_7O_2NMe_3Cl$: syrup.—$(C_3H_7O_2NMe_3Cl)_2PtCl_4$: orange tables, sol. water, insol. alcohol; not decomposed by boiling the aqueous solution.

DI-METHYL-GLYCERIC ACID *v.* DI-OXY-VALERIC ACID.

α-METHYL-GLYCIDIC ACID $C_4H_6O_3$ *i.e.* $O<\begin{matrix}CH_2\\ |\\ CMe.CO_2H\end{matrix}$. *Propylene oxide carboxylic acid.* Formed by decomposing chloro-oxy-isobutyric acid (the product of the union of HOCl with methacrylic acid) with alcoholic potash (Mélikoff, *Bl.* [2] 41, 311; 43, 115). Thick liquid, v. sol. water and ether.

Reactions.—1. When heated with *water* for half an hour it forms di-oxy-butyric acid $CH_3.CH(OH).CH(OH).CO_2H$ [100°].—2. Heated with *ammonia* it forms oxy-amido-isobutyric acid.—3. Conc. HCl combines, forming chloro-oxy-isobutyric acid [107°].—4. HBr forms bromo-oxy-iso-butyric acid [101°].

Salts.—$KA'\frac{1}{2}aq$: glittering plates, sl. sol. cold alcohol.—AgA': thin needles (from hot water).

Ethyl ether EtA'. (164°). S.G. $\frac{15}{4}$ 1·0546. From AgA' and EtI (Mélikoff, *B.* 21, 2053). Oil.

β-Methyl-glycidic acid $O<\begin{matrix}CHMe\\ |\\ CH.CO_2H\end{matrix}$. [84°]. Formed by the action of alcoholic potash on chloro-oxy-butyric acid [63°] (the product of the union of HOCl with crotonic acid) (Mélikoff, *Bl.* [2] 43, 115). Trimetric crystals (from ether), v. e. sol. water, m. sol. ether. Volatile with steam.

Reactions.—1. Combines with HCl forming chloro-oxy-butyric acid [86°].—2. HBr yields bromo-oxy-butyric acid [90°].—3. *Ammonia* forms oxy-amido-butyric acid.—4. When heated with *water* it slowly combines, forming di-oxy-butyric acid [80°].

Salts.—$KA'\frac{1}{2}aq$: powder, v. sol. water, sl. sol. cold alcohol.—AgA': crystalline powder.

Ethyl ether EtA'. (174°). S.G. $\frac{15}{15}$ 1·0534 (Mélikoff a. Zelinsky, *B.* 21, 2052).

$\alpha\beta$-**Di-methyl-glycidic acid** $C_5H_8O_3$ *i.e.*

$$O\left\langle\begin{array}{l}CHMe\\ |\\ CMe.CO_2H\end{array}\right. \text{ or } O\left\langle\begin{array}{l}CH_2\\ |\\ CH.CHMe.CO_2H\end{array}\right. . \quad [62°].$$

Formed by the action of alcoholic potash on chloro-oxy-valeric acid (the product of the union of HOCl on angelic acid) [45°] (Mélikoff, *Bl.* [2] 47, 166; *A.* 257, 118). Minute prisms, v. sol. water, alcohol, and ether. Unites with HCl, forming chloro-oxy-valeric acid [75°]. Water at 99° converts it into di-oxy-valeric acid [107°].

Salts.—KA' $\frac{1}{2}$aq: prisms.—AgA': thin scales.

Ethyl ether EtA'. (178°). S.G. $\frac{15}{15}$ 1·0250. From AgA' and EtI. Oil.

METHYL-GLYCOLLIC ACID *v. Methyl derivative* of GLYCOLLIC ACID.

DI-METHYL-GLYCOLURILE *v.* DI-METHYL DIKETONE.

Tetra-methyl-glycolurile *v.* GLYOXAL, *Reaction* 13.

METHYL-GLYOXAL *v.* PYRUVIC ALDEHYDE.

DI-METHYL-GLYOXAL *v.* DI-METHYL DIKETONE.

METHYL-GLYOXALINE $C_4H_6N_2$ *i.e.*

$$CH\left\langle\begin{array}{l}NMe.CH\\ \quad\ \ \|\\ N - CH\end{array}\right.$$

(Japp, *C. J.* 43, 17). *Oxalmethyline. Methyl-imidazole.* [−6°]. (198°). S.G. $\frac{10}{}$ 1·0363.

Formation.—1. By the action of sodium-amalgam on tri-bromo-methyl-glyoxaline (*q. v.*) in alcoholic solution (Wyss, *B.* 10, 1372).—2. By methylation of glyoxaline (Wallach, *B.* 15, 644; *A.* 214, 319).—3. From sulphydro-methyl-glyoxaline $HS.C\left\langle\begin{array}{l}NMe.CH\\ \quad\ \ \|\\ N - CH\end{array}\right.$ by treatment with dilute nitric acid (Wohl a. Marckwald, *B.* 22, 1359).—4. By reducing chloro-methyl-glyoxaline with HIAq and P at 140° (Wallach, *A.* 214, 310).

Properties.—Liquid, sol. water. With aqueous $HgCy_2$ it gives a pp. composed of slender needles [119°]. Combines readily with MeI, forming a methylo-iodide, whence $B'Me_2PtCl_6$ [206°] may be obtained.

Salts.—$B'_2H_2PtCl_6$. [191°]. S. 4·4 at 13° (W.): 7·55 at 13° (W. a. M.). Orange-red prisms.—$B'_2H_2ZnCl_4$. [128°–131°]. Soluble crystals.—$B'HNO_3$. Prisms.—$B'C_6H_2(NO_2)_3OH$. [158°]. Needles, sl. sol. alcohol and ether.—$B'HAuCl_4$. [120°].

Methyl-glyoxaline $CMe\left\langle\begin{array}{l}NH.CH\\ \quad\ \ \|\\ N - CH\end{array}\right.$. *Glyoxalethyline. Para-oxalmethyline.* [137°]. (267°).

Formation.—1. By saturating an aqueous solution of glyoxal (1 mol.) and acetic aldehyde (1 mol.) with ammonia (Radziszewsky, *B.* 15, 2706; 16, 487).—2. By passing the preceding methyl-glyoxaline [−6°] through a red-hot tube (Wallach, *B.* 16, 541).—3. By distilling the zinc salt of the preceding methyl-glyoxaline or of chloro-methyl-ethyl-glyoxaline with lime (Wallach, *A.* 214, 296).

Properties.—Long thin needles, v. sol. water, alcohol, and hot benzene, m. sol. cold benzene. Decolourises bromine, forming $C_4H_3Br_3N_2$ [258°]. Yields oxamide on oxidation with H_2O_2 (Radziszewsky, *B.* 17, 1290). Its solutions are ppd by tannin and by picric acid.

Salt.—$B'H_2PtCl_6$. Trimetric needles.

Di-methyl-glyoxaline $C_5H_8N_2$ *i.e.*

$$CMe\left\langle\begin{array}{l}NMe.CH\\ \quad\ \ \|\\ N - CH\end{array}\right.$$

. *Oxalmethylethyline.* (206°). S.G. $\frac{11}{}$ 1·0051. Formed by the action of MeI on methyl-glyoxaline (Radziszewsky, *B.* 16, 488). Liquid with narcotic odour, sol. water, alcohol, and ether. Its solution gives with $CuSO_4$ a blue pp., with $AgNO_3$ a crystalline pp., with $HgCl_2$, with tannin, and with phosphomolybdic acid white pps., and with picric acid a yellow pp. All these pps. are soluble in hot water.—$^{x}B'_2H_2PtCl_6$. [138°].

Methylo-iodide B'MeI. Crystalline.

Chloro-di-methyl-glyoxaline $C_5H_7ClN_2$. (213°). Formed by the action of PCl_5 on methyl-ethyl-oxamide (Wallach, *A.* 184, 71).—B'HCl. Prisms.—$B'_2H_2PtCl_6$.—B'_2AgNO_3.—B'MeI.

Tri-methyl-glyoxaline $C_6H_{10}N_2$ *i.e.*

$$CHMe\left\langle\begin{array}{l}N:CMe\\ \quad\ \ |\\ N:CMe\end{array}\right. \text{ or } CMe\left\langle\begin{array}{l}NH.CMe\\ \quad\ \ \|\\ N - CMe\end{array}\right. . \quad [132°].$$

(271°). Formed by adding di-methyl diketone $CH_3.CO.CO.CH_3$ to an ammoniacal solution of $AgNO_3$, and decomposing the resulting pp. with dilute HCl (Fittig, *A.* 249, 206). Formed also, with other bases, by heating di-methyl diketone with conc. NH_3Aq at 100° for an hour (Von Pechmann, *B.* 21, 1411). Small white needles (from ether or ligroïn). Not affected by nitrous acid.—B'HCl: tufts of snow-white needles.

METHYL-GLYOXIM *v. Oxim* of PYRUVIC ALDEHYDE.

Di-methyl-glyoxim *v.* DI-ACETYL and DI-METHYL DIKETONE.

DI-METHYL-GLYOXYL-UREA $C_5H_8N_2O_3$ *i.e.*

$$CO\left\langle\begin{array}{l}NMe.CH(OH)\\ \qquad\ \ |\\ NMe.CO\end{array}\right.$$

. Formed by reducing cholestrophane $CO\left\langle\begin{array}{l}NMe.CO\\ \qquad\ \ |\\ NMe.CO\end{array}\right.$ in aqueous solution with zinc and H_2SO_4 (Andreasch, *M.* 3, 436). Small needles, melting below 100°. May be sublimed. V. e. sol. water and alcohol, insol. ether. Decomposed by boiling baryta-water into CO_2, methylamine, and glyoxylic acid. Readily re-oxidised to cholestrophane.

METHYL-GUANACIL *v.* GUANIDINE, *Reaction* 11.

METHYL-GUANAMINE. The name originally given by Nencki to *Acetoguanamine*, vol. ii. p. 655.

METHYL-DIGUANIDE $C_3H_9N_5$. Obtained, in combination with $CuSO_4$, by adding a 20 p.c. solution of methylamine to a mixture of di-cyan-di-amide $C_2N_2(NH_2)_2$ and copper sulphate; the crystalline $(C_3H_9N_5)_2CuSO_4$ $2\frac{1}{2}$aq which separates is then decomposed by baryta (Reibenschuh, *M.* 4, 388). Thick alkaline syrup, which absorbs CO_2 from the air.

Salts.—Colourless leaflets or prisms; v. sol. water.—$B'_2H_2SO_4$. Prisms, obtained by decomposing B'_2CuSO_4 by H_2S.—$B'H_2SO_4$. From $B'_2H_2SO_4$ and H_2SO_4. Crystalline powder. V. sl. sol. alcohol.—$Cu(C_3H_8N_5)_2$ $3\frac{1}{2}$aq. Formed by shaking di-cyan-diamide with cupric oxide and methylamine. Rose-red crystalline powder.—

$B'_2CuSO_4 2\frac{1}{2}aq$. Pink needles.—The chromate and picrate form yellow prisms.

METHYL-GUANIDINE $C_2H_7N_3$ *i.e.* $NH:C(NH_2)(NHMe)$. *Methyl-uramine.*

Formation.—1. By boiling an aqueous solution of creatine with HgO or with PbO_2 and dilute H_2SO_4 (Dessaignes, *C. R.* 38, 839; 41, 1258; *A.* 92, 407; 97, 340).—2. By oxidising creatinin with $KMnO_4$ (Neubauer, *A.* 119, 46).—3. By heating cyanamide with methylamine hydrochloride in alcoholic solution at 100° (Erlenmeyer, *B.* 3, 896).—4. By the action of methyl-cyanamide on NH_4Cl (Tavildaroff, *B.* 5, 477).

Properties.—Strongly alkaline, deliquescent, crystalline mass. Decomposed by KOH, giving off NH_3 and methylamine. When boiled with chloro-acetic acid it yields glycolyl-methyl-guanidine $C_4H_{11}N_3O_3$, which crystallises in tablets, v. e. sol. water, and neutral in reaction, and forms the salts $C_4H_{11}NO_{33}HCl$, and $C_4H_{11}N_3O_3H_2PtCl_6$.

Salts.—$B'_2H_2PtCl_6$. Monoclinic crystals (Haushofer, *J.* 1878, 351). S. 14·3 at 19°.—$B'HAuCl_4$. Trimetric crystals; v. sol. ether, m. sol. water.—$B'_2H_2C_2O_4 2aq$. Crystals; v. sol. water.

Di-methyl-guanidine $C_3H_9N_3$ *i.e.* $NH:C(NH_2)(NMe_2)$. Formed by heating equimolecular quantities of cyanamide and dimethylamine hydrochloride at 110° (Tartarinoff, *C. R.* 89, 608).

Salts.—B'HCl. Trimetric crystals, $a:b:c = ·862:1:x$ (Haushofer, *Z. K.* 6, 130).—$B'_2H_2PtCl_6$. Triclinic crystals, $a:b:c = ·941:1:·678$; $\alpha = 90° 55'$; $\beta = 90° 20'$; $\gamma = 90° 4'$.—$B'HAuCl_4$. Trimetric crystals (Haushofer, *J.* 1882, 364).

s-Di-methyl-guanidine $NH:C(NHMe)_2$. Formed by the action of methylamine on cyanogen iodide (Erlenmeyer, *B.* 14, 1868).

Platinochloride $B'_2H_2PtCl_6$. Triclinic crystals, $a:b:c = 1·212 : 1 : 1·761$; $\alpha = 90° 22'$; $\beta = 110° 20'$; $\gamma = 90° 5'$.

METHYL-GUANIDO-ACETIC ACID *v.* CREATINE.

(α)-METHYL-GUANIDO-BENZOIC ACID $C_9H_{11}N_3O_2$ *i.e.* $NH:C(NH_2).NMe.C_6H_4.CO_2H$. (α)-*Benzcreatin.* Formed by methylation of benzglycocyamine (Griess, *B.* 8, 324). Small acicular plates (containing $1\frac{1}{2}$ aq), sl. sol. hot water and alcohol. Decomposed by boiling baryta-water into methyl-amido-benzoic acid and urea.—HA'HClaq: plates; m. sol. water.—$(HA')_2H_2PtCl_6 2aq$.

Anhydride v. BENZCREATININE.

(β)-Methyl-guanido-benzoic acid $C_9H_{11}N_2O_2$ *i.e.* $NH:C(NHMe).NH.C_6H_4.CO_2H$. Formed by the action of a cold concentrated solution of methylamine on the so-called ethoxy-carbimidamido-benzoic acid (Griess, *B.* 8, 325; vol. i. p. 157). Plates; sl. sol. cold water and alcohol. Decomposed by baryta-water into *m*-amido-benzoic acid, CO_2, and methylamine.—HA'HCl.—$(HA')_2H_2PtCl_6 2aq$.

Anhydride v. (β)-BENZCREATININE.

METHYL-GUANIDO-ETHANE SULPHONIC ACID $CN_3H_3Me(CH_2.CH_2.SO_3H)$ or probably $NH:C(NHMe)NH.CH_2.CH_2.SO_3H$. Formed by heating methyl-amido-ethane sulphonic acid (2 grms.) and cyanamide (·7 grms.) with enough water to dissolve them, for 5 hours at 120°. Crystals of the new body are found in the tube (E. Dittrich, *J. pr.* [2] 18, 72). Transparent monoclinic prisms. Crystallises with a molecule of water that goes off at 110°. V. sol. hot, m. sol. cold, water; insol. alcohol and ether. Turns brown at 285°, giving off methylamine. Does not form salts.

METHYL-GUANIDO-VALERIC ACID. *Anhydride* $C_7H_{13}N_3O$ *i.e.* $(CH_3)_2CH.CH{<}^{NMe}_{CO.NH}{>}C:NH$. *Isovalercreatinin.* Formed by heating methyl-amido-isovaleric acid with cyanamide and ammonia (Duvillier, *Bl.* [2] 39, 539). Sol. alcohol.

METHYL-HEMIPIC ACID *v. Methyl ether* of HEMIPIC ACID.

METHYL HENDECYL KETONE $C_{13}H_{26}O$ *i.e.* $CH_3.CO.C_{11}H_{23}$. *Methyl undecyl ketone.* [28°]. (263°). S.G. (liquid) $\frac{28}{}$ ·823. Formed by distilling a mixture of barium laurate and barium acetate (Krafft, *B.* 12, 1667; 15, 1724). Yields acetic and hendecoic acids on oxidation.

Isomeride $C_{13}H_{26}O$. (265°–275°). S.G. $\frac{15}{}$ ·887. One of the products of the action of CO on a mixture of NaOAc and $NaOC_5H_{11}$ at 180° (Poetsch, *A.* 218, 62). Liquid.

METHYL HEPTADECYL KETONE $C_{19}H_{38}O$ *i.e.* $CH_3.CO.C_{17}H_{35}$. [56°]. (267° at 110 mm.). S.G. (liquid) $\frac{58}{}$ ·811. Prepared by distilling a mixture of barium stearate and barium acetate. On oxidation it gives margaric acid (Krafft, *B.* 12, 1672; 15, 1724).

Methyl heptadecyl ketone $C_{19}H_{38}O$ *i.e.* $CH_3.CO.CH(C_8H_{17})_2$. *Di-octyl-acetone.* (325°–330°). Formed by boiling di-octyl-acetoacetic ether with alcoholic potash (Guthzeit, *A.* 204, 10). Liquid.

METHYL HEPTINYL KETONE $C_9H_{14}O$ *i.e.* $CH_3.CO.CH(C_3H_5)_2$. *Di-allyl-acetone.* (175°). Formed by boiling di-allyl-acetoacetic ether with conc. KOHAq (Wolff, *A.* 201, 48). V. sol. alcohol and ether.

METHYL HEPTINYL OXIDE $C_8H_{14}O$ *i.e.* $CH_3.O.CH(C_3H_5)_2$. (136°). S.G. $\frac{0}{0}$ ·8258. Formed from $NaOCH(C_3H_5)_2$ and MeI (Riabinin, *J. pr.* [2] 23, 270). Yields, on oxidation by cold $KMnO_4$, $CH_3O.CH(CH_2.CO_2H)_2$.

METHYL HEPTYL KETONE $C_9H_{18}O$ *i.e.* $CH_3.CO.CHPr_2$. *Di-propyl-acetone.* (174°). Formed by heating di-propyl-acetoacetic ether with alcoholic potash (Burton, *Am.* 3, 390). Liquid. Appears not to combine with $NaHSO_3$

Methyl heptyl ketone $CH_3.CO.C_7H_{15}$ (177°). Formed by the decomposition of *sec*-hexyl-acetoacetic ether by KOH (Lundahl, *B.* 16, 789).

METHYL HEPTYL OXIDE $C_8H_{18}O$ *i.e.* $CH_3.O.C_7H_{15}$. (161°). S.G. $\frac{16·5}{}$ ·830. V.D. 4·2 (calc. 4·5). S.V. 194·6 (Lossen, *A.* 254, 57). Formed by the action of MeI on $NaOC_7H_{15}$ derived from œnanthol (Wills, *C. J.* 6, 314). Mobile liquid, with strong odour; insol. water, v. sol. alcohol and ether.

METHYL-HESPERETIC ACID *v. Dimethyl derivative* of CAFFEÏC ACID.

METHYL-HEXADECYL-BENZENE *v.* HEXADECYL-TOLUENE.

Di-methyl-hexadecyl-benzene *v.* HEXADECYL-XYLENE.

Tri-methyl-hexadecyl-benzene *v.* HEXADECYL-MESITYLENE.

METHYL-HEXANE *v.* HEPTANE.

METHYL-HEXOSE $C_7H_{14}O_6$ *i.e.* $CH_3.CH(OH).CH(OH).CH(OH).CH(OH).CH(OH).CHO$.

[181°]. Formed by reducing the lactone of rhamnose carboxylic acid with sodium amalgam (Emil Fischer, *B.* 23, 936). Crystallises from methyl alcohol. Hydrogen cyanide yields $C_8H_{15}O_6N$, which on saponification forms methyl-heptonic acid $C_8H_{16}O_3$, the lactone of which crystallises easily, and gives rise, on reduction, to methyl-heptose $CH_3(CH.OH)_5.CHO$, of which the phenyl-hydrazide is sl. sol. water.

Phenyl-hydrazide. V. sol. water.

Osazone. [200° with decomposition].

METHYL-HEXYL-CARBINOL *v.* OCTYL ALCOHOL.

DI-METHYL HEXYLENE DIKETONE $C_{10}H_{18}O_2$ *i.e.* $(CH_3.CO)_2CH.C_5H_{11}$. *Iso-amyl-acetyl-acetone.* (c. 222°). Formed by heating $(CH_3.CO)_2CHNa$ with isoamyl iodide at 180° (Combes, *A. Ch.* [6] 12, 249). Liquid. Decomposed by caustic potash into acetic acid and $CH_3.CO.CH_2.C_5H_{11}$.

Di-methyl hexylene diketone $C_{10}H_{18}O_2$ *i.e.* $CH_3.CO.CH_2.CH_2.CH_2.CH_2.CHMe.CO.CH_3$. *α-methyl-αε-di-acetyl-pentane.* (232°–235°). Formed by decomposing its carboxylic ether with alcoholic potash (Kipping a. Perkin, *C. J.* 55, 346). Colourless mobile oil. Dissolves in a solution of $NaHSO_3$, and is reprecipitated by K_2CO_3.

DI-METHYL HEXYLENE DIKETONE CARBOXYLIC ETHER $C_{13}H_{22}O_4$ *i.e.* $CH_3.CO.CMe(CO_2Et).CH_2.CH_2.CH_2.CH_2.CO.CH_3$. (255°–260°). Formed by the action of NaOEt and $BrCH_2.CH_2.CH_2.CH_2.CO.CH_3$ on methyl-acetoacetic ether (Kipping a. Perkin, *C. J.* 55, 346). Colourless liquid, with faint odour, v. sl. sol. water.

METHYL-HEXYL-GLYOXALINE $C_{10}H_{18}N_2$ *i.e.* $C_6H_{13}.CH\left\langle\begin{matrix}NMe{:}CH\\ |\\ N=CH\end{matrix}\right.$. (262°). S.G. $\frac{16.5}{}$ ·928. Formed by heating hexyl-glyoxaline with a solution of MeI in methyl alcohol (Karcz, *M.* 8, 221). Colourless oil, insol. water, sol. alcohol and ether. Gives the alkaloidal reactions.—$B'_2H_2PtCl_6$: yellow plates, sol. water.

Methylo-iodide B'MeI. [124°]. V. sol. alcohol and ether.

METHYL *n*-HEXYL KETONE $C_8H_{16}O$ *i.e.* $CH_3.CO.CH_2.CH_2.CH_2.CH_2.CH_2.CH_3$. (172°). S.G. $\frac{20}{4}$ ·8185 (Brühl, *A.* 203, 29); $\frac{0}{}$ ·835 (C.). S.V. 186·6 (R. Schiff, *A.* 220, 103). $\mu_\beta = 1·4213$. R_∞ 63·29. H.C. 1,209,510 (Louguinine, *Bl.* [2] 41, 389).

Formation.—1. By distilling sodium ricinoleate with NaOH (Limpricht, *A.* 93, 242; Bouis, *A.* 97, 34).—2. By distilling a mixture of calcium acetate and calcium *n*-heptoate (œnanthate) (Städeler, *J. pr.* 72, 246).—3. From octoic aldehyde by treatment with PCl_5, decomposing the resulting $C_7H_{15}CHCl_2$ by alcoholic KOH, and adding the octinene $C_6H_{13}.C{:}CH$ so formed to cold H_2SO_4, diluting and distilling with water (Béhal, *Bl.* [2] 47, 33; *A. Ch.* [6] 15, 275).—4. Together with ethyl amyl ketone by treating $C_5H_{11}.C{:}C.CH_3$ with H_2SO_4 and water successively (Béhal, *Bl.* [2] 48, 704).—5. 'Oil of wine' contains a methyl hexyl ketone (164°), which yields hexoic and acetic acids on oxidation (Hartwig, Scholl, *J. pr.* [2] 23, 449).—6. By heating octyl alcohol with boracic acid at 170°, and distilling *in vacuo* (Councler, *B.* 11, 1108).

Properties.—Colourless, mobile liquid, smelling like apples and tasting like camphor; sol. alcohol and ether, insol. water. Combines with $NaHSO_3$, forming a compound sol. alcohol, but decomposed by hot water. Does not reduce ammoniacal $AgNO_3$ or Fehling's solution. Chromic acid mixture oxidises it to acetic and hexoic acids (Béhal a. Combes). Nitric acid oxidises it to heptoic acid (Petersen, *A.* 118, 78). PCl_5 forms $C_8H_{16}Cl_2$ (190°–200°) (Dachauer, *A.* 106, 271).

Combinations.—$C_8H_{16}OKHSO_3\ \frac{1}{2}$aq.—$C_8H_{16}ONH_4HSO_3$. V. sol. water (L.).

Oxim $CH_3.C(NOH).C_6H_{13}$. (214°) at 725 mm. (*B.* 21, 509; *cf.* Béhal, *Bl.* [2] 47, 163).

Methyl isohexyl ketone $CH_3.CO.CH_2.C_5H_{11}$. *Isoamyl-acetone.* (170°). Formed by the action of KOH upon di-methyl hexylene diketone $(CH_3.CO)_2CH.C_5H_{11}$ (Combes, *A. Ch.* [6] 12, 249). Limpid liquid, with agreeable odour. Combines with $NaHSO_3$.

Methyl hexyl ketone(?) $Me.CO.C_6H_{13}$ (208°–210° cor.). S.G. $\frac{15}{}$ ·843. Occurs in small quantity (40 g.) among the products of the passage of CO over a mixture of sodic acetate (546 g.) and sodic iso-amylate (746 g.) (Poetsch, *A.* 218, 60).

Methyl hexyl diketone $C_8H_{14}O_2$ *i.e.* $CH_3.CO.CO.CH_2.CH_2Pr$. (165°) (Von Pechmann, *B.* 21, 2140).

DI-METHYL-HEXYL-PYRIDINE $C_{13}H_{21}N$ *i.e.* $C_6H_{13}.C\left\langle\begin{matrix}CH.CMe\\ CH{:}CMe\end{matrix}\right\rangle N$. *n-Hexyl-lutidine.* (250°) at 719 mm. Obtained by distilling its dicarboxylic acid with lime (Jaeckle, *A.* 246, 41). Colourless liquid, with faint blue fluorescence.—$B'_2H_2PtCl_6$. [163°]. Orange prisms.—B'_2AgNO_3. [65°]. White needles, sol. hot water and alcohol.

Hexahydride $C_{13}H_{27}N$ *i.e.* $C_6H_{13}.CH\left\langle\begin{matrix}CH_2.CHMe\\ CH_2.CHMe\end{matrix}\right\rangle NH$. *Hexyl-lupetidine.* (240°) at 715 mm. Obtained by the action of sodium-amalgam on an alcoholic solution of di-methyl-hexyl-pyridine (J.). Colourless oil, not exhibiting fluorescence. Its dilute alcoholic solution gives a dark-brown pp., with mercurous nitrate. Its platinochloride and dichromate could not be obtained in a crystalline state.—B'HCl: long white prisms, v. sl. sol. water.

DI-METHYL-HEXYL-PYRIDINE DICARBOXYLIC ACID $C_{15}H_{21}NO_4$ *i.e.* $C_6H_{13}.C\left\langle\begin{matrix}C(CO_2H).CMe\\ C(CO_2H){:}CMe\end{matrix}\right\rangle N$. *Hexyl-lutidine di-carboxylic acid.* The potassium salt is formed by saponifying its ether with boiling KOHAq (Jaeckle, *A.* 246, 40). The free acid has not been prepared.—PbA″ $1\frac{1}{2}$aq.

Di-ethyl ether Et_2A''. Formed by oxidising its dihydride with nitrous acid. Yellowish-brown oil, forming salts with mineral acids.—$H_2A''H_2PtCl_6$. [141°]. Orange plates.

Dihydride *Di-ethyl ether* $C_6H_{13}.CH\left\langle\begin{matrix}C(CO_2Et){:}CMe\\ C(CO_2Et){:}CMe\end{matrix}\right\rangle NH$. [54°]. Formed by the condensation of heptoic aldehyde (œnanthol) (1 mol.) with acetoacetic ether (2 mols.) and ammonia (1 mol.) (J.). Yellow prisms, crystallising with difficulty from a dilute alcoholic solution.

DI-METHYL-HOMO-CAFFEÏC ACID *v.* *Di-methyl derivative of* (4:3:1)-DI-OXY-PHENYL-CROTONIC ACID.

METHYL-HOMO-FERULIC ACID *v. Di-methyl derivative* of (4:3:1)-Di-oxy-phenyl-crotonic acid.

METHYL-HYDANTOÏC ACID $C_4H_8N_2O_3$ *i.e.* $NH_2.CO.NMe.CH_2.CO_2H$. *Methyl-uramido-acetic acid.*

Formation.—1. Occurs in the urine of a dog whose food is mixed with methyl-amido-acetic acid (Schultzen, *B.* 5, 578).—2. By digesting an aqueous solution of sarcosine with potassium cyanate and ammonium sulphate for two days at 40° (Baumann a. Hoppe Seyler, *B.* 7, 35).—3. By boiling methyl-amido-acetic acid with urea and excess of baryta-water, or by digesting the same mixture for two days at 40° (B. a. H.).—4. By the action of potassium cyanate and H_2SO_4 on methyl-amido-acetic acid (E. Salkowsky, *B.* 7, 116).

Properties.—Transparent plates (from alcohol), m. sol. cold water and cold alcohol, v. sol. hot water and hot alcohol. Acid in reaction. When the concentrated aqueous solution is boiled it is partially converted into methyl-hydantoïn; this dehydration is more rapidly effected by boiling with water and $PbCO_3$ or $BaCO_3$, only traces of the acid then passing into solution. When heated in a sealed tube with a saturated solution of baryta at 140° it yields NH_3, methyl-amido-acetic acid, and CO_2. Moist Ag_2O forms laminæ of silver methyl-hydantoïn.

Salts.—$^{\times}BaA'_2$. Ppd. by adding alcohol to its aqueous solution.—$^{\times}CuA'_2$. Amorphous.

Di-methyl-hydantoïc acid *v.* Acetonuramic acid.

METHYL-HYDANTOÏN $C_4H_6N_2O_2$ *i.e.* $CO{<}^{NMe.CH_2}_{NH\,.\,CO}{>}$. *Anhydride* of *methyl-uramido-acetic acid.* Mol. w. 114. [182°] (F. a. K.); [156°] (E. Salkowsky, *B.* 7, 119); [145°] (N.).

Formation.—1. By heating creatinin with baryta-water at 100° in a sealed tube (Neubauer, *A.* 137, 288).—2. By boiling methyl-hydantoïc acid with water and $PbCO_3$ or $BaCO_3$.—3. By melting methyl-amido-acetic acid with urea (Huppert, *B.* 6, 1278).—4. By the action of cyanogen chloride on melted methyl-amido-acetic acid (Traube, *B.* 15, 2110).—5. By warming caffuric acid with baryta-water (Fischer, *A.* 215, 286).—6. By the reduction of methyl-allantoïn by HI (Hill, *B.* 9, 1091).—7. By heating a mixture of hydantoïn (3 pts.), MeI (6 pts.), methyl alcohol (16 pts.), and KOH (2 pts.), for three hours at 100°, and extracting the product with boiling alcohol (Franchimont a. Klobbie, *R. T. C.* 8, 289).

Properties.—Short prisms, v. sol. boiling water, sl. sol. cold water, v. sol. alcohol, v. sl. sol. ether. May be sublimed. It does not unite with baryta, but its hot solution dissolves Ag_2O, and the alkaline filtrate then deposits $C_4H_5AgN_2O_2$ as groups of thin laminæ. The mercuric compound, obtained in like manner, forms nodular groups of minute needles, very soluble in water. Nitric acid (S.G. 1·5) converts methyl-hydantoïn into the nitramine $CO{<}^{NMe-CH_2}_{N(NO_2).CO}{>}$ which crystallises from alcohol in scales [168°], v. sl. sol. cold water, decomposed by boiling water.

(α)-**Methyl-hydantoïn** *v.* Lactyl-urea.

Di-methyl-hydantoïn $C_5H_8N_2O_2$ *i.e.* $CO{<}^{NH.CMe_2}_{NH.CO}$. [175°]. Formed by slowly adding HCl to commercial potassium cyanide (containing cyanate) covered by acetone. The liquid, after the action is completed, is left to evaporate, and the crystals which separate extracted with ether, and finally sublimed (Urech, *A.* 164, 264). Large prisms, v. sol. water, alcohol, and ether. Slowly converted by boiling baryta-water into acetonuramic acid $NH_2.CO.NH.CMe_2.CO_2H$. By heating in a sealed tube with fuming hydrochloric acid at 160° it is resolved into CO_2, ammonia, and α-amido-iso-butyric acid $CMe_2(NH_2).CO_2H$.—$C_5H_7AgN_2O_2$: crystalline powder, sl. sol. hot water.—$C_5H_8N_2O_2AgNO_3$: large prisms, v. sol. water.

METHYL-HYDANTOÏN CARBOXYLIC ACID $C_5H_6N_2O_4$. Formed by boiling caffuric acid with baryta-water (E. Fischer, *A.* 215, 286). The free acid is decomposed into CO_2 and methyl-hydantoïn when its aqueous solution is warmed.

METHYL-HYDRASTINE $C_{22}H_{23}NO_6$ *i.e.*

$$\begin{array}{l} CH_3O.\dot{C}.C(OMe):\dot{C}.CO{>}O \quad \dot{C}H:C_2(O_2CH_2) \\ \quad HC.CH = C.C = CH.C:C(C_2H_4NMe_2) \end{array}{>}CH$$

[156°]. Formed, together with hydrastine methylo-hydroxide, by the action of alkalis on a solution of hydrastine methylo-chloride. Prepared by adding potash to a hot aqueous solution of hydrastine methylo-iodide until no further ppn. takes place (Freund a. Rosenberg, *B.* 23, 406). Small yellow needles (from alcohol), almost insol. water, sol. chloroform, benzene, CS_2, ether, and dilute alcohol. With sulphomolybdic acid (Fröhde's reagent) it gives a violet colour, changing through blue to green. Forms sparingly soluble double salts with $SnCl_2$, zinc chloride, and $HgCl_2$. Ammonia converts it into the amide $C_{22}H_{26}N_2O_6$ [180°] which forms a crystalline hydrochloride $C_{22}H_{26}N_2O_6HCl$ 2aq, and on boiling with dilute nitric acid yields hemipic acid (Freund a. Heim, *B.* 23, 2902). The formula of this amide may be written

$$\begin{array}{l} C_6H_2(OMe_2)CONH_2 \\ | \\ CO.CH_2.C_6H_2(O_2CH_2).CH_2.CH_2NMe_2 \end{array}$$

and it may also be got by heating hydrastine methylo-iodide with alcoholic ammonia. The corresponding methylamide $C_{23}H_{28}N_2O_6$ [182°], ethylamide $C_{24}H_{30}N_2O_6$ [162°], allylamide $C_{25}H_{30}N_2O_6$ [158°], and amylamide $C_{27}H_{36}N_2O_6$ [171°] have been prepared.

Salts.—B'HCl. [241°]. M. sol. hot water. Decomposed on fusion. A 1 p.c. solution is inactive.—$B'_2H_2PtCl_6$: sl. sol. water.—$B'H_2SO_4$. [250°]. Less soluble than the chloride.—$B'HNO_3$. Decomposes at 250°. V. sl. sol. water.

Methylo-iodide $C_{22}H_{23}NO_6MeI$. Yellow needles, more soluble in water than in alcohol. Decomposes at 250°. On warming with aqueous KOH it gives off trimethylamine.

Methyl-hydrastimide $C_{22}H_{24}N_2O_5$ *i.e.*

$$C_6H_2(OMe)_2{<}^{CO.NH}_{\;\_\_\_\_}{>}C:CH.C_6H_2(O_2CH_2).CH_2.CH_2.NMe_2$$

[192°]. Formed by the action of dilute H_2SO_4 on the amide (Freund a. Heim, *B.* 23, 2899). Yellow needles, insol. water, sl. sol. alcohol.—B'HCl. [227°].—B'HCl *x*aq.—$B'_2H_2PtCl_6$. [205°].

—$B'H_2SO_4$. [218°]. Yellow crystals (from alcohol).—$B'HNO_3$ aq.

Methylo-iodide B'MeI ½aq. [245°].

Methyl-hydrasteïne $C_{22}H_{27}NO_8$. [151°]. Formed by warming hydrastine methylo-chloride with excess of KOHAq; or, better, by warming methyl-hydrastine with strong caustic potash (Freund a. Rosenberg, *B.* 23, 408). Colourless needles (containing aq) (from water), sl. sol. cold water, more sol. hot water and alcohol. Decomposed by long heating at 110°. Very soluble in alkalis, but reppd. by CO_2; insoluble in aqueous Na_2CO_3. It dissolves in aqueous NH_3, but is ppd. on evaporation. It also dissolves in HClAq. In a 5 p.c. hydrochloric acid solution it is inactive. Tertiary base. Coloured reddish-brown by chlorine-water and ammonia. Iodine has no action. Hot conc. HBrAq reconverts it into methyl-hydrastine. Its salts are colourless.—B'HCl aq. [290°]. Compact groups of crystals.

Methyl-hydrastinine. *Methylo-iodide* $C_{13}H_{18}NO_3I$ *i.e.* $CHO.C_7H_4O_2.CH_2.CH_2.NMe_3I$. [267°]. Formed by heating hydrastinine with MeI (Freund, *B.* 22, 2329). Pale-yellow needles (from alcohol or water). AgCl gives $C_{13}H_{18}NO_3Cl$ [213°], which forms white crystals (containing aq).—$(C_{13}H_{18}NO_3Cl)_2PtCl_4$: yellow crystalline pp.

Oxim of the *methylo-iodide* $HO.N:CH.C_9H_8O_2.NMe_3I$. Yellowish needles, decomposed at 250°. V. sol. alkalis and ppd. unchanged by acids. Gives a dark reddish-brown pp. with platinic chloride.

METHYL-HYDRAZINE CN_2H_6 *i.e.* $CH_3.NH.NH_2$. (87° i.V.) at 745 mm. Formed by treating methyl-urea nitrate with $NaNO_2$, reducing the resulting nitroso-methyl-urea [124°] with zinc and dilute acetic acid, and decomposing the product with HCl (Brüning, *B.* 21, 1810; *A.* 253, 7). Mobile liquid with strong ammoniacal odour, soluble in water (heat being evolved), miscible with alcohol and ether. Reduces Fehling's solution.

Salts.—$B'H_2SO_4$. [139·5°]. White needles v. sol. water, sl. sol. alcohol.—B'HCl: v. sol. water and alcohol.—$B'C_6H_2(NO_2)_3OH$. [162°]. Yellow needles, decomposed on fusion.

Di-benzoyl derivative $CH_3N_2HBz_2$. [c. 143°]. Colourless needles (from water); m. sol. hot water, v. sol. alcohol, sl. sol. ether. Does not reduce Fehling's solution.

Picryl derivative $CH_3N_2H_2C_6H_2(NO_2)_3$. [171°]. Obtained from the hydrazine and picryl chloride (chloro-tri-nitro-benzene) in diluted alcoholic solution. Yellow plates; v. sol. alcohol and ether, m. sol. chloroform. Decomposed on fusion.

Oxalyl derivative $CH_3N_2H_2.CO.CO.N_2H_2CH_3$. [221·5°]. Formed by adding an aqueous solution of methyl-hydrazine to oxalic ether. White needles; v. sol. alcohol, m. sol. water, v. sl. sol. ether. Sublimes at about 160° in needles. Reduces Fehling's solution. Nitrous acid forms the nitrosamine $CH_3.N_2H(NO).CO.CO.N_2H(NO).CH_3$ [147°].

Di-methyl-hydrazine $C_2H_8N_2$ *i.e.* $NMe_2.NH_2$. (63°) at 720 mm. S.G. $\frac{11}{}$ ·801. V.D. (H = 1) 30. Prepared by reducing di-methyl-nitros-amino $(CH_3)_2N.NO$ with zinc-dust and acetic acid (Fischer, *B.* 9, 111; Renouf, *B.* 13, 2171). Formed also by reducing di-methyl-nitramine $(CH_3)_2N.NO_2$ (Franchimont, *R. T. C.* 2, 123). Light volatile liquid with ammoniacal odour, v. sol. water, alcohol, and ether. Its haloid salts volatilise without decomposition.

Reactions.—1. CS_2 forms di-methyl-thio-carbazic acid $NMe_2.NH.CS_2H$.—2. *Phenyl-thio-carbimide* (phenyl mustard oil) forms $C_6H_5NH.CS.NH.NMe_2$.—3. *Oxalic ether* produces $NMe_2.NH.CO.CO.NH.NMe_2$. — 4. *Alkyl iodides* unite, forming azonium iodides, such as $NH_2.NMe_3I$.—5. $K_2S_2O_7$ forms $NMe_2.NH.SO_3K$, which crystallises in white plates, v. sol. water. It is split up by hot HClAq into dimethyl-hydrazine and H_2SO_4.—6. HgO oxidises it, forming tetra-methyl-tetrazone $NMe_2.N:N.NMe_2$, a yellow oil (130°) which explodes when heated above its boiling-point. It forms a mirror with ammoniacal $AgNO_3$, even in the cold, and is decomposed by boiling dilute acids into formic aldehyde, NH_2Me, nitrogen, and $NHMe_2$. The tetrazone is a strong base.—7. *Nitrous acid* decomposes it into N_2O and dimethylamine.—8. *Acetophenone* at 100° forms $NMe_2.N:CMePh$, a liquid (165° at 100 mm.). It is split up again by acids into its generators (Reisenegger, *B.* 16, 663).

Salts.—B'HCl.—$B'H_2Cl_2$: hygroscopic crystals.—$B'_2H_2PtCl_6$: orange-yellow prisms, v. sol. water, sl. sol. alcohol.—$B'_2H_2SO_4$. [105°]. White needles.—$B'_2H_2C_2O_4$: colourless plates, v. sol. water and alcohol, sl. sol. ether.

Ethylo-chloride $NH_2.NMe_2EtCl$. Crystallises with difficulty; v. e. sol. water. The ethylo-hydroxide is reduced by zinc-dust and acetic acid to HCl, ammonia, and NMe_2Et.—$(NH_2.NMe_2EtCl)_2PtCl_4$. Crystals.

DI-METHYL-DI-HYDRO-ANTHRACENE *v.* DI-METHYL-ANTHRACENE-DI-HYDRIDE.

METHYL-HYDRO-ETHYL-PYRIDINE *v.* METHYL-ETHYL-PYRIDINE HYDRIDE.

DI-METHYL-HYDRO-HOMO-CAFFEÏC ACID *v. Di-methyl derivative* of (4:3:1)-DI-OXY-PHENYL-ISO-BUTYRIC ACID.

METHYL-HYDRO-HOMO-FERULIC ACID *v. Di-methyl derivative* of (4:3:1)-DI-OXY-PHENYL-ISO-BUTYRIC ACID.

METHYL-DI-HYDRO-PARVOLINE *v.* PENTA-METHYL-PYRIDINE DIHYDRIDE.

METHYL-HYDRO-PYRIDINES *v.* METHYL-PYRIDINE HYDRIDES.

METHYL-HYDRO-QUINALDINE *v.* (*Py.* 3:4)-DI-METHYL-QUINOLINE TETRA-HYDRIDE.

METHYL-HYDRO-QUINOLINES *v.* METHYL-QUINOLINE HYDRIDES.

DI-METHYL-HYDROQUINONE *v. Di-methyl derivative* of HYDROQUINONE.

DI-METHYL-HYDROQUINONE-TRI-METHYL-AMMONIUM-IODIDE *v. Methylo-iodide* of the *di-methyl derivative* of DI-METHYL-AMIDO-HYDROQUINONE.

METHYL-HYDRO-TOLUQUINONE *v. Di-methyl derivative* of HYDROTOLUQUINONE.

METHYL-HYDROXYLAMINE *v. Alkyl derivatives* of HYDROXYLAMINE.

METHYL HYPOPHOSPHATE $Me_4P_2O_6$. S.G. $\frac{15}{}$ 1·109. From MeI and $Ag_4P_2O_6$ (Sänger, *A.* 232, 11). Saponified by water.

Methyl-hypophosphate of calcium $MeCaHP_2O_6$ 5aq. Needles.

METHYLIA. A name formerly used for METHYLAMINE.

METHYL-IMESATIN. Described as *Imide* of *Methyl-isatin* under ISATIN.

METHYL-IMIDAZOLE. A name employed by Wohl and Marckwald (*B.* 22, 1359) to denote the substance usually called METHYL-GLYOXALINE.

METHYL - IMIDAZYL MERCAPTAN *v.* SULPHYDRO-METHYL-GLYOXALINE.

METHYL - IMIDO - DI-METHYL-THIAZOLE
$$\begin{matrix} S.C(NMe) \\ | \\ CH{:}CMe \end{matrix}\Big\rangle NMe.$$
[96°]. Formed by the action of chloro-acetone on di-methyl-urea (Traumann, *A.* 249, 49). White needles (from water), with strong alkaline reaction. Is identical with di-methyl-amido-methyl-thiazole.

METHYL-IMIDO-DI-(β)-NAPHTHYL SULPHIDE $NMe\Big\langle{C_{10}H_6 \atop C_{10}H_6}\Big\rangle S$. [285°]. Formed by heating imido-di-naphthyl sulphide (10 g.) with MeI (5 g.) and MeOH (12 c.c.) for five hours at 150°. Formed also by heating di-(β)-naphthyl-methyl-amine with sulphur (Kym, *B.* 23, 2459). Lemon-yellow plates or needles. Gives a blue colour with H_2SO_4 containing HNO_3.

METHYL -IMIDO - PHENYL - NAPHTHYL SULPHIDE $NMe\Big\langle{C_{10}H_6 \atop C_6\ H_4}\Big\rangle S$. [133°]. Formed by heating $NH\Big\langle{C_{10}H_6 \atop C_6\ H_4}\Big\rangle S$ with MeI and MeOH at 150° (Kym, *B.* 23, 2466). Light greenish-yellow needles, sl. sol. hot spirit, v. e. sol. hot benzene.

METHYL-IMIDO-DI-PHENYL SULPHIDE $C_{13}H_{11}NS$ *i.e.* $S\Big\langle{C_6H_4 \atop C_6H_4}\Big\rangle NMe$. [99·3°]. (c. 363°). Formed by heating imido-di-phenyl sulphide (thiodiphenylamine) with MeI and MeOH in sealed tubes at 110° (Bernthsen, *A.* 230, 88; *B.* 16, 2899). Long white prisms (from alcohol), insol. water, v. sol. ether, benzene, and hot HOAc. Its alcoholic solution is coloured brown by $FeCl_3$. Nitric acid forms a yellow nitro- derivative which, unlike that of imido-di-phenyl sulphide, is insol. NaOHAq. The nitro- derivative may be reduced to an amido- compound which gives a deep bluish-green colour with $FeCl_3$.

Isomeride $C_{13}H_{11}NS$ *i.e.* $S(C_6H_4)_2NMe$ or $C_6H_5.N\Big\langle{C_6H_4 \atop CH_2}\Big\rangle S$ (?). [79°]. Formed by the action of SCl_2 dissolved in petroleum on di-phenyl-methyl-amine $NMePh_2$ (Holzmann, *B.* 21, 2065). Thin yellow scales (from hot benzene-alcohol), insol. water, sl. sol. hot alcohol and ether, v. sol. hot benzene. On heating with copper it yields di-phenyl-methyl-amine.

METHYL-IMIDO-DI-PHENYL SULPHONE $C_{13}H_{11}NSO_2$ *i.e.* $NMe\Big\langle{C_6H_4 \atop C_6H_4}\Big\rangle SO_2$. [222°]. Formed by the action of $KMnO_4$ on methyl-imido-di-phenyl sulphide suspended in water (Bernthsen, *A.* 230, 91). Chains of white needles, often slightly reddish (from alcohol) or small compact prisms (from glacial acetic acid). V. sl. sol. cold alcohol, glacial acetic acid or ether. Insol. acids or alkalis; not affected by boiling KOH or HCl. Boiled with conc. H_2SO_4 it forms a splendid blue liquid, turned pale violet-brown by pouring into water. Its nitro- derivative after reduction gives no colour with $FeCl_3$.

METHYL-INDAZINE $C_8H_8N_2$ *i.e.*
$$C_6H_4\Big\langle{CMe \atop | \atop N}\Big\rangle NH.$$
Quinazole. Methyl-indazole. [113°]. (281° i. V.) at 736 mm. V.D. 4·37 (calc. 4·53). Formed by slowly adding $NaNO_2$ to a paste composed of *o*-amido-acetophenone and HClAq. The resulting diazo-compound is soluble in water, and the liquid is poured into a solution of Na_2SO_3. The product at first contains $CH_3.CO.C_6H_4.NH.NHSO_3Na$, but it gradually loses its reducing power, and deposits needles of
$$C_6H_4\Big\langle{CMe \atop | \atop N}\Big\rangle N.SO_3Na.$$
When these needles are heated with HClAq they yield methyl-indazine and H_2SO_4 (Fischer a. Tafel, *A.* 227, 303). Methyl-indazine is also formed, together with carbonic acid gas, when indazyl-acetic acid
$$C_6H_4\Big\langle{C.CH_2.CO_2H \atop | \atop N.NH}$$
is heated.

Properties.—Colourless needles (from water), m. sol. hot water, v. sol. alcohol, ether, and chloroform, almost insol. conc. NaOHAq. May be sublimed. Does not reduce Fehling's solution. Gives crystalline compounds with metallic salts.

Salts.—B'HCl. [177°]. Needles, v. sol. water and alcohol.—Sulphate: needles.—Picrate: yellow crystalline powder.—Platinochloride: yellow needles.

Nitrosamine $C_8H_7N_3O$ *i.e.*
$$C_6H_4\Big\langle{CMe \atop | \atop N}\Big\rangle N.NO.$$
[60°]. From B'HCl and cold aqueous $NaNO_2$. Yellow needles, v. sol. alcohol, ether, and chloroform.

Di-methyl-indazine $C_9H_{10}N_2$ *i.e.*
$$C_6H_4\Big\langle{CMe \atop | \atop N}\Big\rangle NMe.$$
[80°]. Formed by methylation of the preceding. Colourless plates, v. sol. alcohol, ether, benzene, and hot water.

Di-methyl-ψ-indazine $C_6H_4\Big\langle{CMe \atop NMe}\Big\rangle N$. [36°]. Formed from methyl-*o*-amido-acetophenone by conversion into the nitrosamine $CH_3.CO.C_6H_4.NMe.NO$ and reducing this body with zinc and HOAc (Fischer a. Tafel, *A.* 227, 336). Yellow oil, solidifying on cooling as nearly colourless plates. Very volatile with steam. It forms crystalline compounds with metallic salts.—The chloride forms colourless needles.—The sulphate crystallises in needles, and the picrate in rectangular tables.

METHYL-INDAZINE *v*-**SULPHONIC ACID** $C_8H_8N_2SO_3$ *i.e.*
$$C_6H_4\Big\langle{CMe \atop | \atop N}\Big\rangle N.SO_3H.$$
The sodium salt of this acid is formed as described under methyl-indazine. It is m. sol. cold water, but ppd. on addition of NaOH or NaCl. It does not reduce HgO or Fehling's solution. Boiling conc. HClAq splits it up into $NaHSO_3$ and methyl-indazine.

METHYL-INDAZOLE *v.* METHYL-INDAZINE.

DI-METHYL-INDIGO *v.* INDIGO.

METHYL-ISO-INDILEUCINE *v.* INDIGO.

(*In.* 1)-**METHYL-INDOLE** C_9H_9N *i.e.* $C_6H_4<{CMe \atop NH}>CH$. *Scatole. Skatole.* [95°]. (266° i.V.). V.D. (H = 1) 65·2 (calc. 65·5).

Occurrence.—The chief volatile constituent of human fæces, but not present in that of dogs (Brieger, *J. pr.* [2] 17, 129; *B.* 12, 1986). It occurs among the products of the putrefaction of albuminous substances (Brieger, Nencki, *J. pr.* [2] 17, 98; *H.* 4, 371; E. a. H. Salkowsky, *B.* 12, 651).

Formation.—1. By fusing egg-albumen with KOH (Nencki).—2. By reducing indigo with tin and HCl, and distilling the product with zinc-dust. A mixture of indole and scatole is thus obtained, and these are combined with picric acid. When the picrates are distilled with conc. NaOHAq the indole is destroyed, and the scatole passes over, and may be crystallised from water. The yield is ·3 p.c. Scatole prepared in this way has no fæcal odour (Baeyer, *B.* 13, 2339).—3. By heating aniline-zinc-chloride with glycerine (Fischer a. German, *B.* 16, 710).—4. By adding nitro-cuminic acid (6 pts.) to amido-cuminic acid (obtained by reducing 4 pts. of the nitro-acid), mixing with baryta (10 pts.), drying, and distilling (Fileti, *G.* 13, 358, 378).—5. The phenyl-hydrazide of propionic acid is warmed with $ZnCl_2$, and the product distilled with steam (E. Fischer, *A.* 236, 138).—6. In small quantity in distilling strychnine with lime (Stoehr, *B.* 20, 1108; Löbisch a. Malfatti, *M.* 9, 629).—7. By heating its carboxylic acid (Arnold, *A.* 246, 335).

Preparation from pancreas. — 2,300 grms. pancreas and 500 grms. flesh are freed from fat, cut up and put into a loosely covered pot containing 8 litres of water. The whole is left for 5 months at the ordinary temperature. At the end of the fourth month the odour of skatole appears. The liquid is acidified with acetic acid and distilled. The distillate is acidified with HCl and picric acid is added. Red needles of skatole picrate, $C_9H_9N.C_6H_2(NO_2)_3OH$, separate. This is decomposed by ammonia, and the skatole is distilled over with steam and crystallised from water (Nencki, *J. pr.* [2] 20, 467).

Properties.—Glittering plates of powerful fæcal odour, sl. sol. water. It differs from indole in giving no colour when its solutions are treated with chlorine water. Its solution gives with fuming HNO_3 an opalescence; with KNO_2 and acetic acid a white pp. of the nitrosamine; with CrO_3 a red amorphous pp. in concentrated solutions; and with $FeCl_3$ no colour (Brieger, *J. pr.* [2] 17, 130). It is not attacked by warm dilute HNO_3. It colours pine-wood moistened with HCl red; this is best seen by dropping pine-wood saturated with an alcoholic solution of scatole into cold conc. HClAq (Fischer, *A.* 236, 138).

Reactions.—1. *Potash-fusion* yields the corresponding indole carboxylic acid (Ciamician a. Magnanini, *B.* 21, 673).—2. By passing CO_2 over a mixture of *sodium* and scatole, heated at 240° there is formed indole (*In*-1)-carboxylic acid (C. a. M.).—3. With *chloroform* and NaOEt it yields a chloro-methyl-quinoline $C_{10}H_8ClN$.—4. *Benzoic aldehyde* and $ZnCl_2$ form, slowly at 100°, $C_6H_5.CH(C_9H_8N)_2$ which crystallises from alcohol [142°] (Fischer, *B.* 19, 2989).—5. When administered to animals it appears in the urine in the form of the chromogen of a red pigment and as methyl-indyl sulphuric acid $C_9H_8N.SO_4H$ (?) (Brieger, *H.* 4, 414; Mester, *H.* 12, 130).

Salts.—B'_2HCl. Ppd. in needles when ether is added to its alcoholic solution (Wenzing, *A.* 239, 239). [168°]. Insol. ether, v. sl. sol. water, v. sol. alcohol.—Picrate $B'C_6H_2(NO_2)_3OH$. Red needles.

Acetyl derivative so-called *v.* METHYL-INDYL METHYL KETONE.

Dihydride $C_9H_{11}N$ *i.e.* $C_6H_4<{CHMe \atop NH}>CH_2$. (232° i.V.) at 744 mm. Formed by reducing an alcoholic solution of scatole with zinc-dust and HCl (Wenzing, *A.* 239, 242). Colourless oil, resembling quinoline and piperidine in odour. V. sol. alcohol, ether, and ligroïn. Its alcoholic solution stains pine-wood, moistened with HClAq, orange. It reduces $AgNO_3$ and $FeCl_3$ on warming. It yields a nitrosamine which may be reduced to an oily hydrazine. With phenyl thiocarbimide it forms a compound melting at 125°.—$^xB'HCl$: sol. alcohol and water, insol. ether.—Oxalate: [126°]; insol. ether.—$B'_2H_2PtCl_6$: yellow needles, sl. sol. water, decomposed by hot water.—Picrate: [150°]; yellow granular crystals (from benzene).

(*In.* 2)-Methyl-indole C_9H_9N *i.e.* $C_6H_4<{CH \atop NH}>CMe$. *Methyl-ketole.* [60°]. (272° i.V.) at 750 mm. V.D. 4·75 (calc. 4·54) (Treadwell, *B.* 14, 1466).

Formation.—1. By nitrating benzyl methyl ketone with fuming HNO_3, reducing the resulting [2:1]$C_6H_4(NO_2).CH_2.CO.CH_3$ with zinc-dust and ammonia, and distilling with steam (Baeyer a. Jackson, *B.* 13, 187; 14, 879).—2. Obtained by heating the phenyl-hydrazide of acetone $(CH_3)_2C:N.NHC_6H_5$ (1 pt.) with $ZnCl_2$ (5 pts.) for half an hour at 100° and then for some minutes at 180° (E. Fischer, *B.* 19, 1564; *A.* 236, 124).

Properties.—Needles or plates (from ligroïn), sl. sol. hot water, v. sol. alcohol and ether. Smells like indole. V. sol. cold HClAq, but decomposed on boiling with conc. HClAq. HNO_2 colours its solution yellow, and soon gives a yellow amorphous pp. which does not give Liebermann's reaction. Colours pine-wood, moistened with HClAq, red.

Reactions.—1. $KMnO_4$ oxidises it to acetyl *o*-amido-benzoic acid.—2. *Potash-fusion* yields indole (*In.*2)-carboxylic acid (Ciamician a. Magnanini, *B.* 21, 673).—3. By heating with *sodium* in a stream of CO_2 at 240° there is formed methyl-indole carboxylic acid (Ciamician a. Magnanini, *B.* 21, 671).—4. *Reduced* by tin and HCl to a hydride, although sodium-amalgam does not act upon it.—5. With *chloroform* and NaOEt it yields chloro-methyl-quinoline [71°]. *Bromoform* and NaOEt yield the corresponding bromo-methyl-quinoline (Magnanini, *G.* 17, 246).—6. On heating with conc. HClAq for 7 hours at 225° there is formed aniline and a liquid base $C_{10}H_9N$ (250°) which smells like quinoline and forms the salts $B'_2H_2PtCl_6$ and $B'HAuCl_4$ (Magnanini, *B.* 20, 2609).—7. *Benzoic aldehyde* at 100° forms $C_6H_5CH\left(C<{C_6H_4 \atop CMe}>NH\right)_2$ which separates from acetone in colourless shining crystals

[247°], insol. water, v. sl. sol. hot alcohol and ether. On boiling with Fe_2Cl_6 in HOAc it is converted into di-methyl-rosindole (Fischer, *A.* 242, 373; *B.* 19, 2988).—8. *Nitro-benzoic aldehyde* heated with (*In.* 2)-methyl-indole on the water-bath forms the corresponding $[3:1]C_6H_4(NO_2).CH(C_9H_8N)_2$, small crystals (from acetone), sl. sol. alcohol, ether, and HOAc. This body melts at 263°, and is reduced by zinc-dust and ammonia to $C_6H_4(NH_2).CH(C_9H_8N)_2$ a yellow crystallisable oil (Fischer, *A.* 242, 375).—9. By fusing with *phthalic anhydride* and a little $ZnCl_2$ there is formed an acid $C_{17}H_{13}NO_3$ probably $C_9H_8N.CO.C_6H_4.CO_2H$ which crystallises from alcohol in colourless prisms, insol. water, sl. sol. ether, v. sol. hot alcohol and HOAc (Fischer).—10. On heating with *benzoyl chloride* and a little $ZnCl_2$ the products are di-methyl-rosindole $C_{25}H_{20}N_2$ and benzoyl-methyl-indole.—11. On heating with *zinc chloride* alone, a small quantity of quinoline is formed (Fischer a. Steche, *B.* 20, 819).—12. *Diazo-benzene chloride* and NaOAc form compact red crystals (from petroleum-ether) of $C_6H_5.N:N.C\langle{}^{C_6H_4}_{CMe}\rangle NH$, [116°], insol. water, v. sol. alcohol, ether, and benzene, m. sol. petroleum-ether. This body is split up again, by reduction, into aniline and amido-methyl-indole $C_6H_4\langle{}^{C(NH_2)}_{NH}\rangle CMe$ [113°] (Fischer, *A.* 242, 384).—13. When (*In.* 2)-methyl-indole (1 pt.) is heated with MeI ($2\frac{1}{2}$ pts.) and a little methyl alcohol at 100° for 15 hours, there is produced di-methyl-quinoline dihydride (243°) (Fischer a. Steche, *B.* 20, 818, 2199).

Salts.—B′HI. Formed by passing dry HI into a solution of the methyl-indole in ether (Wagner, *A.* 242, 388). Flocculent pp., very easily decomposed by water and by moist air.—$B'_2H_2PtCl_6$ 3aq: yellow needles, decomposed by water.

Acetyl derivative $C_6H_4\langle{}^{CH}_{NAc}\rangle CMe$. (200°–210° at 40 mm.). Formed in small quantity, together with methyl-indyl methyl ketone (*q.v.*), by heating (*In.* 2)-methyl-indole with Ac_2O and NaOAc. The product is extracted with chloroform, and the extract distilled *in vacuo* (Magnanini, *G.* 18, 95). Pale-yellow liquid. Decomposed by boiling aqueous KOH into KOAc and methyl-indole. Yields indole carboxylic acid on fusion with potash. $KMnO_4$ oxidises it to acetyl-*o*-amido-benzoic acid (Ciamician a. Magnanini, *B.* 21, 673).

(*β*)-*Acetyl derivative v.* METHYL-INDYL METHYL KETONE.

Benzoyl derivative C_9H_8NBz. [82°]. Formed, together with di-methyl-rosindole, by heating (*In.* 2)-methyl-indole with BzCl and a little $ZnCl_2$ on the water-bath (Fischer a. Wagner, *B.* 20, 817). Glittering plates (from alcohol), v. sl. sol. hot water, m. sol. alcohol and ether.

Dihydride $C_9H_{11}N$ *i.e.* $C_6H_4\langle{}^{CH_2}_{NH}\rangle CHMe$. *Hydromethylketole.* (228° i.V.) at 742 mm. Prepared by reduction of (*In.* 2)-methyl-indole with tin and HCl (Jackson, *B.* 14, 883; Wenzing, *A.* 239, 244). Colourless oil with powerful odour. Heavier than water. Strong base. With phenyl-thiocarbimide it forms a compound $C_{16}H_{16}N_2S$, which crystallises from ether in prisms [101°].—$B'_2H_2PtCl_6$: orange-yellow needles; decomposed by water.—Oxalate: [130°]; crystalline.—Picrate: [151°]; crystalline.

Acetyl derivative $C_9H_{10}NAc$. [56°]. From the dihydride and Ac_2O. White needles, insol. water, sol. most other solvents.

Nitrosamine $C_9H_{10}N.NO$. [55°]. Formed by adding $NaNO_2$ to a solution of the hydrochloride of (*In.* 2)-methyl-indole dihydride (Jackson). Yellow crystals (from ligroïn), v. sol. alcohol, ether, and boiling ligroïn. On treatment with tin and HCl, methyl-indole dihydride is regenerated. On reduction with zinc-dust and HOAc it yields the hydrazine $C_9H_{10}N.NH_2$, which crystallises from ligroïn in prisms [41°], and yields a crystalline sulphate and hydrochloride.

(*In.* 3)-Methyl-indole $C_6H_4\langle{}^{CH}_{NMe}\rangle CH$. (240° i.V.) at 720 mm. S.G. $\frac{0}{}$ 1·0707. Obtained by long heating at about 205° from its carboxylic acid [212°], which is formed by the action of HCl on the phenyl-methyl-hydrazide of pyruvic acid (Fischer a. Hess, *B.* 17, 562). Formed also by heating *ω*-chloro-methyl-*o*-amido-styrene $C_6H_4(NHMe).CH:CHCl$ with NaOEt at 135° (Lipp, *B.* 17, 2510).

Properties.—Yellowish liquid, nearly insol. water, v. sol. alcohol, ether, and benzene. Volatile with steam. A chip of pine-wood, dipped in HClAq, is coloured violet-red by its vapour or solution. It dissolves in conc. HClAq, and is reppd. by addition of water. Fuming nitric acid added to (*In*-3)-methyl-indole suspended in water gives a deep red colour and finally a red pp.

Reactions.—1. An alkaline solution of *bromine* (NaOBr) converts it into di-bromo-methyl-oxindole $C_9H_9Br_2NO$, which crystallises in transparent tables, melting at 204°. It is converted by heating with alcoholic potash into methyl-*ψ*-isatin, which is ppd., after boiling off the alcohol, by adding HCl.—2. (*In.* 3)-methyl-indole (2 mols.) heated with benzoic aldehyde (1 mol.) and $ZnCl_2$ for 2 hours on the water-bath forms $C_6H_5.CH(C\langle{}^{C_6H_4}_{CH}\rangle NMe)_2$, which crystallises in colourless prisms [197°], insol. water, sl. sol. alcohol and ether, v. sol. hot acetone and HOAc. It yields a red dye on heating with $FeCl_3$ in HOAc (Fischer, *A.* 242, 377; *B.* 19, 2988).—3. On fusing equal weights of *phthalic anhydride* and (*In.* 3)-methyl-indole with a little $ZnCl_2$ at 100° there is formed $C_6H_4:C_2O_2(C_9H_8N)_2$, which crystallises from acetone in colourless prisms [300°]. It is insol. water and alkalis, v. sl. sol. ether and alcohol, but v. sol. hot acetone (Fischer, *A.* 242, 382; *B.* 19, 2989).—4. Scarcely attacked by MeI at 100°, but at 120° it appears to yield a methyl-quinoline dihydride (Fischer a. Steche, *B.* 20, 2199).

Picrate $C_9H_9NC_6H_2(NO_2)_3OH$. [150°]. Long dark-red prisms or needles, v. sol. benzene, sl. sol. ether. Decomposed by alcohol.

Chloro-derivative v. DI-CHLORO-METHYL-INDOLE.

Dihydride $C_6H_4\langle{}^{CH_2}_{NMe}\rangle CH_2$. (216° i.V.) at 728 mm. Formed by reducing (*In.* 3)-methyl-indole with zinc-dust and conc. HClAq (Wenzing, *A.* 239, 246). Liquid, sl. sol. water, v. sol. alcohol and ether, volatile with steam. Most of its salts dissolve in alcohol and water.—$B'_2H_2PtCl_6$:

yellow needles, decomposed by boiling water.—Oxalate: [105°].—Picrate: [155°]; yellow tables (from benzene).

(*B.* 2)-**Methyl-indole** $\begin{array}{l} CMe{:}CH.C.CH \\ \;| \qquad\quad \| \\ CH\ {:}CH.C.NH \end{array}\!\!>\!CH.$ *Tolindole.* [58·5°]. Formed by heating at 240° its carboxylic acid, which is obtained from the *p*-tolyl-hydrazide of pyruvic ether (Raschen, *A.* 239, 226). Needles (from water), m. sol. hot water, v. sol. alcohol, ether, benzene, and ligroïn. Volatile with steam. Reacts like indole with pine-wood and with nitrous acid.—Picrate $B'C_6H_2(NO_2)_3OH$. [151°]. Red needles (from water).

(*In.* 1,2)-**Di-methyl-indole** $C_{10}H_{11}N$ *i.e.* $C_6H_4{<}^{CMe}_{NH}{>}CMe$. [108°]. (285° i.V.). Formed by heating the phenyl-hydrazide of methyl ethyl ketone with $ZnCl_2$ at 180° (E. Fischer, *B.* 19, 1565; *A.* 236, 126). Formed also by heating bromo-acetyl-propionic acid $CH_3.CO.CHBr.CH_2.CO_2H$ (1 pt.) with aniline (3 pts.) at 100° (Wolff, *B.* 20, 427; 21, 123). Obtained likewise by heating $C_6H_4{<}^{C.CH_2.CO_2H}_{NH}{>}CMe$ at 225° (Fischer).

Properties.—White plates (from dilute alcohol). Smells like indole. V. sl. sol. hot water, v. e. sol. alcohol and ether, sl. sol. cold ligroïn. Dissolves in conc. HClAq but is reppd. on dilution with water. Does not colour pine wood.

Reactions.—1. $NaNO_2$ added to its solution in HOAc forms a nitrosamine [63°], crystallising in yellow needles, v. sl. sol. water, v. sol. alcohol. By zinc-dust and HCl it is re-converted into di-methyl-indole. It exhibits Liebermann's reaction.—2. MeI in MeOH converts it into tri-methyl-quinoline dihydride.

Picrate $B'C_6H_2(NO_2)_3OH$. [157°]. Brown needles (from alcohol).

Dihydride $C_6H_4{<}^{CHMe}_{NH}{>}CHMe$. (231°) at 750 mm. Formed by reducing di-methyl-indole with zinc-dust and HClAq (Stechc, *A.* 242, 371).

(*In.* 2,3)-**Di-methyl-indole** $C_{10}H_{11}N$ *i.e.* $C_6H_4{<}^{CH}_{NMe}{>}CMe$. [56°]. Formed by heating the phenyl-methyl-hydrazide of acetone (1 pt.) with zinc chloride (5 pts.) for 3 hours at 130° (Fischer, *B.* 19, 1565; Degen, *A.* 236, 153). Formed also by heating its carboxylic acid $C_6H_4{<}^{C(CO_2H)}_{N(CH_3)}{>}CMe$ at 200° (D.). White needles, v. sol. alcohol, ether, benzene, and ligroïn, v. sl. sol. water, v. sol. conc. HClAq. May be distilled without decomposition. It gives the pine-wood test very distinctly. Nitrous acid forms a complicated product. The picrate crystallises in dark-red needles. The hydride is v. sol. weak acids.

(*In.* 1,3)-**Di-methyl-indole** $C_6H_4{<}^{CMe}_{NMe}{>}CH$. (230°–255°). Formed by heating the phenyl-methyl-hydrazide of *n*-propionic aldehyde (1 pt.) with $ZnCl_2$ (5 pts.) at 135° (Degen, *A.* 236, 163). Oil.

(*B.* 2-*In*-3)-**Di-methyl-indole** $C_{10}H_{11}N$ *i.e.* $\begin{array}{l} CMe{:}CH.C.CH \\ \;| \qquad\quad \| \\ CH{:}CH.C.NMe \end{array}\!\!>\!CH.$ *Methyl-p-tolindole.* (242°–245°). Formed by heating its carboxylic acid at 225° (Hegel, *A.* 232, 216). Liquid, volatile with steam; v. sol. alcohol, ether, and benzene. Dyes pine-wood, moistened with HCl, red. Fuming HNO_3 gives a red colour and, finally, a pp. The picrate is crystalline.

(*B.* 2, *In.* 2)-**Di-methyl-indole** $C_{10}H_{11}N$ *i.e.* $\begin{array}{l} CMe{:}CH.C.CH \\ \;| \qquad\quad \| \\ CH{:}CH.C.NH \end{array}\!\!>\!CMe.$ *Methyl-p-tolindole.* [114°–117°]. Formed by heating the *p*-tolyl-hydrazide of acetone with $ZnCl_2$ (Raschen, *A.* 239, 227). May be distilled without decomposition. Almost insol. hot water, v. sol. hot alcohol, ether, and benzene.—$B'C_6H_2(NO_2)_3(OH)$. [155°]. Dark-red needles (from benzene).

(*B.* 4, *In.* 2)-**Di-methyl-indole** $C_{10}H_{11}N$ *i.e.* $\begin{array}{l} CH{:}CH.C.CH \\ \;| \qquad\quad \| \\ CH{:}CMe.C.NMe \end{array}\!\!>\!CH.$ *Methyl-o-tolindole.* Obtained by the action of heat on its carboxylic acid, which is derived from the o-tolyl-methyl-hydrazide of pyruvic acid (Hegel, *A.* 232, 220). Liquid, smelling like indole, volatile with steam. Dyes pine-wood, acidified by HCl, violet-red. Behaves like indole towards nitrous acid.

Di-methyl-indole $C_{10}H_{11}N$. (275°). Formed by allowing a solution of the hydrochloride of (α)-di-methyl-dipyrrole in dilute H_2SO_4 to stand for some time in the cold (Dennstedt, *B.* 21, 3439). Liquid, volatile with steam.—Picrate $B'C_6H_2(NO_2)_3OH$. [156°]. Dark-red silky needles (from benzene).

Di-methyl-indole $C_{10}H_{11}N$. (c. 270°). Formed from (β)-di-methyl-dipyrrole in the same way as the preceding isomeride (D.). Liquid. Smells like scatole.—Picrate $B'C_6H_2(NO_2)_3OH$. [149°]. Red silky needles.

(*In.* 1,2,3)-**Tri-methyl-indole** $C_{11}H_{13}N$ *i.e.* $C_6H_4{<}^{CMe}_{NMe}{>}CMe$. (280°). Formed by heating di-methyl-indyl-acetic acid for several hours at 210° (Degen, *A.* 236, 160). Formed also by heating the phenyl-methyl-hydrazide of methyl ethyl ketone with $ZnCl_2$ at 180° (D.). Yellow oil with characteristic odour. Miscible with alcohol and ether. Gives no colour to pine-wood. Picrate $B'C_6H_2(NO_2)_3OH$. [150°]. Dark-red needles (from hot benzene).

(*B.* 4, *In.* 1, 2)-**Tri-methyl-indole** $C_{11}H_{13}N$ *i.e.* $\begin{array}{l} CH{:}CH.C.CMe \\ \;| \qquad\quad \| \\ CH{:}CMe.C.NH \end{array}\!\!>\!CMe.$ [79°]. (283° uncor.). Formed by heating bromo-acetyl-propionic (bromo-levulic) acid $CH_3.CO.CHBr.CH_2.CO_2H$ with o-toluidine (Wolff, *B.* 21, 3362). White plates, v. sol. alcohol, chloroform, and petroleum-ether, v. sl. sol. water. Volatile with steam.—Picrate $B'C_6H_2(NO_2)_3OH$. [152°]. Purple-red scales.

(*B.* 2, *In.* 1,2)-**Tri-methyl-indole** $C_{11}H_{13}N$ *i.e.* $\begin{array}{l} CMe{:}CH.C.CMe \\ \;| \qquad\quad \| \\ CH{:}CH.C.NH \end{array}\!\!>\!CMe.$ [121°]. (297° cor.). Formed by warming β-bromo-acetyl-propionic acid (1 pt.) with *p*-toluidine (3 pts.), and finally heating the mixture to boiling (Wolff, *B.* 21, 3361). Plates, v. sol. alcohol, chloroform, and petroleum-ether, v. sl. sol. water. Does not give the pine-wood reaction. The solution in HOAc, mixed with $FeCl_3$, becomes green on boiling, and

finally blue. Picrate $B'C_6H_2(NO_2)_3OH$. [189°]. Brownish-red needles, v. sol. benzene and alcohol.

Nitrosamine $C_7H_6<\begin{smallmatrix}CMe\\N(NO)\end{smallmatrix}>CMe$. [73°]. Golden-yellow needles, v. e. sol. alcohol and HOAc, sl. sol. water.

Tetra-methyl-indole $C_{12}H_{15}N$. (285°). Light-yellow oil, with characteristic odour (Dennstedt, *B.* 22, 1924). Picrate $B'C_6H_2(NO_2)_3OH$. [100°]. Shining red needles.

METHYL-INDOLE ACETIC ACID *v.* METHYL-INDYL-ACETIC ACID.

(*In.* 1)-**METHYL-INDOLE** (*In.* 2)-**CARBOXYLIC ACID** $C_{10}H_9NO_2$ *i.e.* $C_6H_4<\begin{smallmatrix}CMe\\NH\end{smallmatrix}>C.CO_2H$. *Scatole* (*β*)-*carboxylic acid* [165°]. Formed by saponifying with alcoholic potash its ether which is obtained by boiling with alcoholic hydrogen sulphate (10 p.c.), the phenyl-hydrazide of ethyl-glyoxylic ether $CH_3.CH_2.C(N_2HPh).CO_2H$ (Wislicenus a. Arnold, *B.* 20, 3395; *A.* 246, 335). Formed also by heating scatole with sodium in a current of CO_2 at 240° (Ciamician a. Magnanini, *G.* 18, 61; *B.* 21, 672, 1927; *Rend. Accad. Linc.* [4] 4, 740). Thin white needles (from boiling water), v. sol. alcohol and benzene, v. sl. sol. water. Its alcoholic solution is coloured deep red by $FeCl_3$. On heating above 165° it is split up into CO_2 and scatole [95°].—AgA′: white powder, insol. water.

Ethyl ether EtA′. [134°]. Needles (from alcohol), insol. water, v. e. sol. benzene and ether.

(*In.* 1)-**Methyl-indole carboxylic acid** $C_{10}H_9NO_2$. *Scatole* (*α*)-*carboxylic acid.* [164°]. (Possibly identical with the preceding acid). Occurs among the products of the putrefaction of serum-albumen, and of muscular tissue (H. a. E. Salkowsky, *B.* 13, 191, 2217; *H.* 8, 23; 9, 8). Small plates (from benzene). Decomposed on heating above its melting-point into CO_2 and scatole. V. sl. sol. cold water, v. sol. alcohol and ether, m. sol. benzene. $FeCl_3$ colours its dilute solution (containing HCl) violet on boiling. Nitrous acid colours its dilute solution cherry-red, and presently gives a pp. Bleaching powder colours a dilute solution, acidified by HCl, purple; this reaction, and that with nitrous acid, are not exhibited by (*In.* 1)-indole (*In.* 2)-carboxylic acid. —AgA′. Sparingly soluble pp.

(*In.* 2) **Methyl-indole** (*In.* 1)-**carboxylic acid** $C_6H_4<\begin{smallmatrix}C.CO_2H\\ \| \\ NH.CMe\end{smallmatrix}$. *Methyl-ketole carboxylic acid.* [172°] or [183°]. Prepared by heating (*In.* 2)-methyl-indole (10 g.) mixed with sodium (3·6 g.) in a current of dry CO_2 first at 235° and finally at 315°; the unaltered methyl-indole is removed by steam distillation, and the acid recrystallised from acetone (Ciamician a. Magnanini, *G.* 18, 60; *B.* 21, 672; *Rend. Accad. Linc.* [4] 4, 740). White crystalline powder, completely decomposed at its melting-point into CO_2 and methyl-indole (methyl-ketole); this decomposition is partially effected by merely boiling the aqueous solution. Sl. sol. water and benzene, v. sol. alcohol and acetone. It gives white pps. with lead and mercuric salts, and a green pp. with a cupric salt.—AgA′: white crystalline pp.

(*In.* 3)-**Methyl-indole** (*In.* 1)-**carboxylic acid** $C_6H_4<\begin{smallmatrix}C(CO_2H)\\N(CH_3)\end{smallmatrix}>CH$. [212°]. Obtained by heating the phenyl-methyl-hydrazide of pyruvic acid (1 pt.) with 10 p.c. aqueous HCl (15 pts.) on the water-bath (E. Fischer a. Hess, *B.* 17, 559). White needles, v. sol. hot alcohol, ether, and benzene, sl. sol. hot water, nearly insol. cold water. Its solution in H_2SO_4 is red. By prolonged heating at its melting-point it is split up into CO_2 and (*In.* 3)-methyl-indole. Readily oxidised by $KMnO_4$. An alkaline solution of Br or Cl oxidises it to methyl-*ψ*-isatin and CO_2.

(*B.* 4)-**Methyl-indole** (*In.* 2)-**carboxylic acid** $\begin{smallmatrix}CH:CH.C.CH\\ | \quad\quad \| \\ CH:CMe.C.NH\end{smallmatrix}>C.CO_2H$. [171°]. Formed by saponifying with alcoholic potash its ethyl ether which is obtained by heating the *o*-tolyl-hydrazide of pyruvic ether (1 pt.) with $ZnCl_2$ (1 pt.) at 220° (Raschen, *A.* 239, 228). Needles (from water), v. sol. alcohol, ether, and HOAc.

(*B.* 2)-**Methyl-indole** (*In.* 2)-**carboxylic acid** $\begin{smallmatrix}CMe:CH.C.CH\\ | \quad\quad \| \\ CH\ :CH.C.NH\end{smallmatrix}>C.CO_2H$. [228°]. Formed from its ethyl ether which is obtained by heating the *p*-tolyl-hydrazide of pyruvic ether with $ZnCl_2$ at 220° (Raschen, *A.* 239, 228). Needles (from water), m. sol. hot water, v. sol. alcohol, ether, chloroform, and HOAc. Decomposed on fusion into CO_2 and (*B.* 2)-methyl-indole.

Ethyl ether EtA′. [160°]. Colourless needles or plates.

(*In.* 2, 3)-**Di-methyl-indole** (*In.* 1)-**carboxylic acid** $C_{11}H_{11}NO_2$ *i.e.* $C_6H_4<\begin{smallmatrix}C(CO_2H)\\NMe\end{smallmatrix}>CMe$. [185°]. Formed by saponifying its ether which is obtained by heating the phenyl-methyl-hydrazide of acetoacetic ether with $ZnCl_2$ (Fischer, *B.* 19, 1569; Degen, *A.* 236, 157). Six-sided plates, m. sol. hot alcohol and chloroform, sl. sol. water, ether, benzene, and ligroïn. Splits up at 200° into CO_2 and (*In.* 2-3)-di-methyl-indole. The Na salt is insol. conc. NaOHAq. The Ag salt is insol. NH_3Aq. Colours pine wood.

Ethyl ether EtA′. [95°]. Colourless needles (from alcohol-ligroïn), v. sol. alcohol ether, benzene, and chloroform, sl. sol. ligroïn.

(*B.* 4, *In.* 3)-**Di-methyl indole** (*In.* 2)-**carboxylic acid** $C_{11}H_{11}NO_2$ *i.e.* $\begin{smallmatrix}CH:CH.C.CH\\ | \quad\quad \| \\ CH:CMe.C.NMe\end{smallmatrix}>C.CO_2H$. [210°]. Formed by warming the *o*-tolyl-methyl-hydrazide of pyruvic acid (1 pt.) with phosphoric acid (20 pts. of S.G. 1·17) on the water-bath (Hegel, *A.* 232, 220). Colourless needles (from benzene), v. e. sol. alcohol. Splits up on heating into CO_2 and the corresponding di-methyl-indole. When its alkaline solution is warmed with NaOCl and the product heated with water there is formed di-methyl-*ψ*-isatin $C_6H_3Me<\begin{smallmatrix}CO\\NMe\end{smallmatrix}>CO$ [157°].

(*B.* 2, *In.* 3)-**Di-methyl-indole** (*In.* 2)-**carboxylic acid** $\begin{smallmatrix}CMe:CH.C.CH\\ | \quad\quad \| \\ CH\ :CH.C.NMe\end{smallmatrix}>C.CO_2H$. [221°]. Formed by warming the *p*-tolyl-methyl-hydra-

zide of pyruvic acid (1 pt.) with HCl (20 pts. of 10 p.c.), the acid being ppd. (Hegel, *A.* 232, 216). Needles (from hot alcohol), sl. sol. ether, sol. hot benzene, chloroform, and glacial HOAc, insol. ligroïn. Forms the corresponding di-methyl-indole on heating. A neutral solution of its Na salt gives with NaOCl a yellow crystalline pp. [135°], which on boiling with water is changed to di-methyl-ψ-isatin $C_6H_3Me<\begin{smallmatrix}CO\\NMe\end{smallmatrix}>CO$ crystallising in red needles [148°].

METHYL-INDONAPHTHENE $C_{10}H_{10}$ *i.e.* $C_6H_4<\begin{smallmatrix}CMe\\CH_2\end{smallmatrix}>CH$. *Methyl-indene.* (206°) (Roser); (201°) (Von Pechmann, *B.* 16, 516). Formed by distilling methyl-indonaphthene carboxylic acid with soda-lime (Roser, *A.* 247, 159). Transparent highly refractive liquid, smelling somewhat like naphthalene. Absorbs oxygen from the air, becoming gummy. On heating with conc. HClAq it also becomes gummy, and H_2SO_4 has a like effect. By heating with HIAq at 180° it is converted into a solid body, fusible under water, v. sol. ether, sl. sol. alcohol.

Picric acid compound $C_{10}H_{10}C_6H_2(NO_2)_3OH$. [76°]. Unstable orange powder (Von Miller, *B.* 23, 1882).

METHYL-INDONAPHTHENE CARBOXYLIC ACID $C_{11}H_{10}O_2$ *i.e.* $C_6H_4<\begin{smallmatrix}CMe\\CH_2\end{smallmatrix}>C.CO_2H$. '*Dihydronaphthoic*' *acid.* [200°]. Formed by gently warming benzyl-aceto-acetic ether (1 pt.) with conc. H_2SO_4 (7 pts.), and pouring the product into water (Von Pechmann, *B.* 16, 516; Roser, *B.* 20, 1574; *A.* 247, 158). White needles (from alcohol), almost insol. water, m. sol. hot alcohol and ether. Crystallises from glacial acetic acid in prisms (containing HOAc). May be distilled with slight decomposition, but when boiled for a long time it splits up into CO_2 and methyl-indonaphthene. On oxidation it yields phthalic acid.

Methyl ether ×MeA'. [78°]. Small needles, v. sol. alcohol and ether.

Di-bromide $C_6H_4<\begin{smallmatrix}CMeBr\\CH_2—\end{smallmatrix}>CBr.CO_2H$. [215°]. Formed by exposing the acid to bromine-vapour. White crusts (from ether). On warming with HOAc it gives off HBr and leaves $C_6H_4<\begin{smallmatrix}CMeBr\\CH=\!=\end{smallmatrix}>C.CO_2H$ [245°], which forms a methyl ether melting at 100°.

Methyl ether $C_{10}H_9Br_2CO_2Me$. [157°]. White needles, sl. sol. methyl alcohol.

METHYL-INDONAPHTHENE DIHYDRIDE CARBOXYLIC ACID $C_{11}H_{12}O_2$ *i.e.* $C_6H_4<\begin{smallmatrix}CHMe\\CH_2\end{smallmatrix}>CH.CO_2H$. *Methyl-hydrindonaphthene carboxylic acid.* [80°]. (300°–310°). Formed by the action of sodium-amalgam on an alkaline solution of methyl-indonaphthene carboxylic acid (Roser, *B.* 20, 1574; *A.* 247, 165). Small needles (from hot water), v. sol. alcohol and ether, scarcely volatile with steam. On continued heating above 310° it becomes viscid, but the crystalline acid is reproduced on treating this viscid mass with alkalis.—AgA'.—BaA'_2 2aq: needles (from alcohol), v. sol. water.

METHYL-INDONAPHTHOQUINONE $C_{10}H_8O_2$ *i.e.* $C_6H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>CHMe$. *Methyl-di-keto-hydrindene.* [85°]. (c. 150° at 18 mm.). Formed by the action of sodium on a mixture of ethyl propionate and phthalate (Wislicenus a. Kötzle, *A.* 252, 80). Blunt pyramids (from alcohol) or needles (from light petroleum), sol. ether and hot water. The sodium derivative $C_{10}H_7NaO_2$ crystallises in small dark-red prisms.

Di-oxim $C_6H_4<\begin{smallmatrix}C(NOH)\\C(NOH)\end{smallmatrix}>CHMe$. [117°]. Needles, sol. alcohol, ether, alkalis, and HOAc.

Mono-phenyl-hydrazide $C_6H_4<\begin{smallmatrix}C(N_2HPh)\\CO———\end{smallmatrix}>CHMe$. [164°]. Crystals, v. sol. ether and benzene. Forms a green solution in HOAc.

Di-methyl-indonaphthoquinone $C_{11}H_{10}O_2$ *i.e.* $C_6H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>CMe_2$. [108°]. (c. 250°). Formed by heating methyl-indonaphthoquinone with MeI and MeOH at 100° (W. a. K.). V. sol. alcohol, ether, and benzene.

Phenyl-hydrazide $C_6H_4<\begin{smallmatrix}C(N_2HPh)\\C(N_2HPh)\end{smallmatrix}>CMe_2$. [184°–187°]. Slender yellowish prisms (from alcohol), sol. ether and HOAc. $FeCl_3$ colours its solution in H_2SO_4 intensely dark green.

METHYL INDOPHENINE *v.* INDOPHENINE.

METHYL-INDYL-ACETIC ACID $C_{11}H_{11}NO_2$ *i.e.* $C_6H_4<\begin{smallmatrix}C—CH_2.CO_2H\\ \|\\ NH.CMe\end{smallmatrix}$. [195°–200°]. Formed by warming the phenyl-hydrazide of acetyl-propionic (levulic) acid with $ZnCl_2$ at 125° (E. Fischer, *B.* 19, 1565; *A.* 236, 149). Colourless plates, sl. sol. hot water and chloroform, m. sol. ether, v. sol. hot alcohol, v. e. sol. acetone and hot HOAc. Nitrous acid yields a nitrosamine. At 225° it is split up, slowly into CO_2 and di-methyl-indole. Its picric acid compound crystallises in slender dark-red needles.

Di-methyl-indyl-acetic acid $C_{12}H_{13}NO_2$ *i.e.* $C_6H_4<\begin{smallmatrix}C—CH_2.CO_2H\\ \|\\ NMe.CMe\end{smallmatrix}$. [188°]. Formed by saponification (by alcoholic KOH) of its ether, which is obtained by warming the phenyl-methyl-hydrazide of acetyl-propionic ether with $ZnCl_2$ (Fischer, *B.* 19, 1568; Degen, *A.* 236, 158). Colourless plates, sl. sol. water, ether, and benzene, v. sol. alcohol and chloroform. Its alkaline salts are v. e. sol. water, but ppd. on addition of caustic alkalis. At 210° it is split up into CO_2 and (*In*-1,2,3)-tri-methyl-indole. Does not give the pine-wood reaction.

METHYL INDYL KETONE *v.* (β)-*Acetyl-*INDOLE.

(*In.* 1)-**METHYL-INDYL METHYL KETONE** $C_{11}H_{11}NO$ *i.e.* $C_6H_4<\begin{smallmatrix}CMe\\NH\end{smallmatrix}>C.CO.CH_3$. *Acetyl-scatole.* [148°]. Formed by heating (*In*-1)-methyl-indole (scatole) (1 g.) with AcCl (10 g.) and $ZnCl_2$ ($\frac{1}{2}$ g.) (Magnanini, *G.* 18, 99; *B.* 21, 1938). Long needles (from dilute alcohol), insol. cold water, v. sol. hot alcohol and acetone, m. sol. ether. Volatile with steam. Not affected by KOHAq, but conc. HCl forms scatole. Hot conc. H_2SO_4 gives a purple solution.

Picrate [156°]. Yellow needles, sl. sol. cold, v. sol. hot, benzene.

Oxim $C_6H_4{<}\genfrac{}{}{0pt}{}{CMe}{NH}{\gg}C.C(NOH).CH_3$. [119°]. Small needles, decomposed by acids and alkalis, reproducing the ketone.

(*In.* 2)-**Methyl-indyl methyl ketone**

$$C_6H_4{<}\begin{array}{l}C{<}\begin{array}{l}CO.CH_3\\ \diagdown\end{array}\\ NH\;.\;CMe\end{array}$$ *Acetyl-methyl-ketole.*

[196°]. Formed by heating (*In*-2)-methyl-indole (methyl-ketole) (1 pt.) with Ac_2O (5 pts.) and NaOAc (1 pt.) for six hours with inverted condenser (Jackson, *B.* 14, 879; Fischer, *A.* 242, 379). Colourless needles (from acetone), sl. sol. water, v. sol. alcohol and hot benzene. Dissolves in HClAq. Not decomposed by boiling NaOHAq, but boiling conc. HClAq regenerates the ketone. $KMnO_4$ oxidises it to acetyl-amido-benzoic acid (Magnanini, *G.* 18, 97).

Phenyl-hydrazide $C_{17}H_{17}N_3$ *i.e.*

$$C_6H_4{<}\begin{array}{l}C{<}\begin{array}{l}C(N_2HPh).CH_3\\ \diagdown\end{array}\\ NH\;.\;CMe\end{array}$$. [c. 136°]. Formed

by heating the ketone with phenyl-hydrazine hydrochloride and NaOAc. Colourless plates, m. sol. hot benzene, v. sl. sol. petroleum-ether.

DI-METHYL-INOSITE *v.* DAMBONITE.

METHYL-IODAMINE *v.* METHYLAMINE.

METHYL IODIDE CH_3I. *Iodo-methane.* Mol. w. 142. (42·8°) (Dobriner, *A.* 243, 23); (42·3°) (Perkin, *C. J.* 45, 459). S.G. $\frac{0}{0}$ 2·3346 (D.); $\frac{15}{15}$ 2·2852; $\frac{25}{25}$ 2·2529 (P.). S. ·008 at 15° (Bardy a. Bordet, *A. Ch.* [5] 16, 569). C.E. (0°–10°) ·00118 (D.). S.V. 64·1 (Lossen, *A.* 254, 69); 64·8 (Ramsay); M.M. 9·009 at 19·5°. H.F.p. (gas) + 3420. H.F.v. (gas) 2840 (Thomsen, *Th.*). Obtained by distilling phosphorus (1 pt.) with iodine (8 pts.), dissolved in moist methyl alcohol (14 pts.), or phosphorus (60 g.) with iodine (1000 g.) and methyl alcohol (500 g.) (Dumas a. Péligot, *A.* 15, 30; Pierre, *A.* 56, 147; Landolt, *A.* 84, 44; Hofmann, *C. J.* 13, 69). Prepared also from red phosphorus (10 pts.), MeOH (35 pts.), and I (100 pts.) (Personne, *J.* 1861, 607; Butlerow, *B.* 6, 561), and from KI, MeOH, and gaseous HCl (De Vrij, *J.* 1857, 441). The distillate is washed with water and rectified over $CaCl_2$ and lead oxide. Colourless, slightly combustible liquid. Not attacked by gaseous HCl.

Reactions.—1. *Chlorine* converts it into MeCl.—2. When heated with *zinc* it forms IZnMe. The moist copper-zinc couple forms methane (Gladstone a. Tribe, *C. J.* 26, 682).—3. When heated with alloys of K or Na with As or Sb it yields methides of arsenic or antimony.—4. With Mg and Al it forms methides.—5. When heated in a sealed tube with aqueous NH_3 it forms mono-, di-, and tri-methylamine and NMe_4I.—6. With EtOH at 125° it forms EtI and MeOEt (Busse a. Kraut, *A.* 177, 272).—7. Heated with *water* (15 pts.) at 100° it is converted into methyl alcohol (Niederist, *A.* 196, 350).—8. With H_2S and water it forms $MeI(H_2S)_2$ 23aq (Forcrand, *A. Ch.* [5] 28, 21).—9. *Sulphur* at 160° to 190° forms SMe_3I and other products (Klinger, *B.* 10, 1880).

Hydrate $(MeI)_2aq$. [−4°] (F.); [4·8°] (Villard, *C. R.* 111, 185). Formed by passing a current of moist air through the iodide (Forcrand, *C. R.* 90, 1491).

METHYL-IODOFORM *v.* TRI-IODO-ETHANE.

METHYL-ISATIC ACID *v.* ISATIC ACID.

METHYL-ISATIN *v.* ISATIN.

METHYL-ISATOÏC ACID *v.* ISATOÏC ACID.

METHYL-ISATOID *v.* ISATOID.

METHYL-ITACONIC ACID $C_6H_8O_4$. [166°]. A product of the distillation of methyl-paraconic acid (Fränkel, *A.* 255, 37). Formed also by heating a solution of methyl-citraconic acid at 150° in sealed tubes. Prisms, sol. water, insol. chloroform. When distilled it partially carbonises, and is partially converted into the isomeric methyl-citraconic acid. Nitric acid appears to convert in into methyl-mesaconic acid [195°]. Sodium-amalgam reduces it to ethyl-succinic acid. — $BaA''\frac{1}{2}aq$. — $CaA''aq$. — Ag_2A''.

TETRA-METHYLIUM HYDROXIDE *v.* *Methylo-hydroxide* of TRIMETHYLAMINE.

DI-METHYL-KETINE is TETRA-METHYL-PYRAZINE.

DI-METHYL-KETOL *v.* METHYL-OXYETHYL KETONE.

METHYL-KETOLE *v.* (*In.* 2)-METHYL-INDOLE.

DI-METHYL-KETONE is ACETONE.

Di-methyl di-ketone $C_4H_6O_2$ *i.e.* $CH_3.CO.CO.CH_3$. *Di-acetyl.* (88°). S.G. $\frac{22}{}$ ·9734. S. 25 at 15°. Formed by heating its dicarboxylic acid (ketipic acid) either by itself or with dilute H_2SO_4 (Fittig, *B.* 20, 3179; *A.* 249, 200). Formed also from its mono-oxim (nitroso-methyl-ethyl-ketone) by successive treatment with $NaHSO_3$ and dilute acid: $CH_3.CO.CMe{:}NOH + H_2SO_3 + H_2O$ $= CH_3.CO.COMe + NH_4SO_4H$ (Von Pechmann, *B.* 20, 3162). Most easily prepared by saponifying methyl-aceto-acetic ether with dilute (3 p.c.) alkali, treating the product with $NaNO_2$ and H_2SO_4, removing alcohol by distillation, adding dilute H_2SO_4 (20 vols. of 15 p.c.), and distilling with steam (Von Pechmann, *B.* 21, 1411). Yellow mobile liquid, smelling like acetone and quinone, miscible with alcohol and ether. Decomposed by alkalis or hot alkaline carbonates. Forms metallic derivatives of trimethyl-glyoxaline with ammoniacal solutions of silver nitrate and of cuprous chloride. With alcohol it forms an unstable compound $C_4H_6O_22HOEt$, boiling at 75°. With water it forms a crystalline hydrate $(C_4H_6O_2)_3 2aq$, insol. water, alcohol, and ether. Yields a very unstable compound with SO_2. Combines with $NaHSO_3$.

Reactions.—1. With HCy it forms the nitrile of di-oxy-di-methyl-succinic acid.—2. *Bromine* dissolved in CS_2 forms a di-bromo- derivative $C_4H_4Br_2O_2$ [117°].—3. *Ammonia* forms tri-methyl-glyoxaline $CHMe{<}\begin{array}{l}N{:}CMe\\ \;|\\ N{:}CMe\end{array}$ [133°] (271°).

4. When warmed with *o-tolylene-diamine* acetate it is converted into tri-methyl-quinoxaline $C_6H_3Me{<}\genfrac{}{}{0pt}{}{N{:}CMe}{N{:}CMe}{>}$, which crystallises from light petroleum in prisms [91°] (270°).—5. *Aniline* forms the anilide PhN:CMe.CMe:NPh, which crystallises from alcohol in lustrous sulphur-yellow scales [133°], v. sol. ether, m. sol. alcohol, insol. water.—6. On adding dilute aqueous NaOH or Na_2CO_3 to an aqueous solution of the diketone until it becomes colourless, then at once acidifying with dilute H_2SO_4 and extract-

ing with ether, the product is di-methyl-quinogen $CH_3.CO.CMe:CH.CO.CO.CH_3$, a yellowish bitter syrup, which forms a phenyl-hydrazide $C_8H_{10}(N_2HPh)_3$ [205°], and is converted by excess of alkali into *p*-xyloquinone.—7. Heated with an aqueous solution of *urea* it forms di-methyl-glycolurite $C_6H_{10}N_4O_2$ (Franchimont a. Klobbie, *R. T. C.* 7, 251).—8. Reduced in alkaline solution to a product ($CH_3.CO.CH(OH).CH_3$?), which instantly reduces Fehling's solution in the cold.

Mono-oxim $CH_3.CO.C(NOH).CH_3$. *Iso-nitroso-methyl-ethyl-ketone.* [74°]. (186°). V.D. 3·51 (calc. 3·49). Formed by treating methyl-aceto-acetic ether (1 mol.) with aqueous KOH (3 mols.), followed by nitrous acid (V. Meyer a. Züblin, *B.* 11, 322). Prisms (from chloroform) or plates (from water), v. e. sol. alcohol, ether, and chloroform. Decomposed by heating with dilute HClAq at 140° into ammonia and acetic acid. Boiling conc. HClAq yields HOAc, hydroxylamine, and a little of the dioxim (Schramm, *B.* 16, 177). By boiling with dilute H_2SO_4 it is split up into hydroxylamine and the diketone (Von Pechmann, *B.* 20, 3213). Treatment with aqueous $NaHSO_3$ and dilute H_2SO_4 also forms di-methyl diketone (Von Pechmann, *B.* 20, 3162). Alkaline K_3FeCy_6 oxidises it, even in the cold, to acetic and nitrous acids (Gutknecht, *B.* 12, 2290). On reduction by $SnCl_2$ and HCl, followed by removal of tin by H_2S and addition of alkali, tetra-methyl-pyrazine is obtained. But if the solution is allowed to stand when acid another base is got (Braun, *B.* 22, 559).

Methyl ether of the mono-oxim $CH_3.CO.C(NOMe).CH_3$. (125° uncor.). Colourless oil, lighter than water (Ceresole, *B.* 16, 834).

Di-oxim $CH_3.C(NOH).C(NOH).CH_3$. *Methyl-ethyl-acetoximic acid.* [234°]. Formed by the action of hydroxylamine on the mono-oxim (Schramm, *B.* 16, 179; Auwers a. V. Meyer, *B.* 21, 3527) or on the diketone (Fittig, *A.* 249, 204). Small colourless needles, insol. water, v. sol. alcohol and ether. May be sublimed.

Oxim-phenyl-hydrazide $CH_3.C(NOH).C(N_2HPh).CH_3$. [158°]. Formed from the oxim and phenyl-hydrazine (Von Pechmann a. Wehsarg, *B.* 21, 2997). Large crystals (from alcohol). Its solution in H_2SO_4 is coloured bluish-violet by $FeCl_3$.

Phenyl-hydrazide $CH_3.CO.C(N_2HPh).CH_3$. [133°]. Formed by running a solution of diazobenzene chloride into one of methyl-acetoacetic acid, the reaction being completed by adding a solution of NaOAc (Japp a. Klingemann, *B.* 21, 549; *A.* 247, 218; Von Pechmann, *B.* 21, 1411). Yellow tables (from benzene). Forms a yellow solution in conc. H_2SO_4.

Di-phenyl-di-hydrazide $CH_3.C(N_2HPh).C(N_2HPh).CH_3$. [243°] (Japp); [239°] (Fittig). Formed by treating the mono-phenyl-hydrazide with phenyl-hydrazine (Japp, *A.* 247, 218), or by the action of phenyl-hydrazine on an ethereal solution of di-methyl diketone (Fittig, *A.* 249, 203; Von Pechmann, *B.* 20, 3164). Formed also by heating the phenyl-hydrazide of pyruvic acid (Japp a. Klingemann, *B.* 21, 550). Yellowish needles, almost insol. water, alcohol, and ether, sl. sol. chloroform, m. sol. acetone and hot benzene. Dissolves in cold conc. H_2SO_4 forming a brown solution, which after some time becomes dirty-wine red, appearing green in thin layers. $K_2Cr_2O_7$ in HOAc oxidises it to the 'osotetrazone'

$$\begin{array}{l} CH_3.C:N.NPh \\ \quad | \qquad\ | \\ CH_3.C:N.NPh \end{array}$$

, which crystallises in matted red needles [169°], insol. water, sol. chloroform and benzene, m. sol. ether, sl. sol. acetone and alcohol, almost insol. HOAc. This 'osotetrazone' is reduced to the original diphenyl-dihydrazide by warming with phenyl-hydrazine. HCl converts the 'osotetrazone' into an 'osotriazone'

$$\begin{array}{l} CH_3.C:N\diagdown \\ \quad | \qquad\quad >NPh \\ CH_3.C:N\diagup \end{array}$$

, which is a very weak base, [35°], (c. 255°), insol. water, sol. alcohol and ether (Von Pechmann, *B.* 21, 2759).

DI-METHYL-DI-KETONE DICARBOXYLIC ACID $C_6H_6O_6$ *i.e.* $CO_2H.CH_2.CO.CO.CH_2.CO_2H$. *Di-keto-adipic acid. Ketipic acid. Ketipatic acid. Oxalyl di-acetic acid.* Obtained by warming its ethyl ether with cold conc. HClAq (Fittig a. Daimler, *B.* 20, 203; *A.* 249, 183). White amorphous powder, insol. or v. sl. sol. cold water, alcohol, chloroform, CS_2, benzene, and petroleum-ether. On heating alone or with dilute H_2SO_4 it is converted into dimethyl diketone.

Ethyl ether Et_2A''. [77°]. Prepared by warming oxalic ether with chloro-acetic ether and amalgamated granulated zinc at 80° for three days. The mass is extracted with water and the insoluble portion treated with dilute H_2SO_4, and the solution so obtained extracted with ether. The ether is distilled off, and the ketipic ether left recrystallised from alcohol (Fittig a. Daimler). Formed also by the action of NaOEt and oxalic ether on acetic ether (Wislicenus, *B.* 20, 589; *A.* 246, 328). Colourless plates or prisms, insol. cold water, v. sol. ether and chloroform, m. sol. hot alcohol, benzene, and CS_2. Decomposed by boiling water. $FeCl_3$ colours its alcoholic solution deep red.

Reactions.—1. *Bromine* added to a warm solution of the ether in CS_2 forms $CO_2Et.CBr_2.CO.CO.CBr_2.CO_2Et$ [119°], which is converted by ammonia into oxamide and di-bromo-acetamide [156°]. Bromine added to a solution of ketipic ether in cooled CS_2 forms $CO_2Et.CHBr.CO.CO.CHBr.CO_2H$, which is deposited in colourless plates [70°].—2. *Chlorine* passed into a boiling solution of the ether in chloroform forms $CO_2Et.CCl_2.CO.CO.CCl_2.CO_2Et$ [93°], which is also produced by chlorinating di-oxy-quinone dicarboxylic ether (Böniger, *B.* 22, 1285).—3. *Phenyl-hydrazine* forms a phenyl-hydrazide $CO_2Et.CH_2.C(N_2HPh).C(N_2HPh).CH_2.CO_2Et$ crystallising from chloroform in light-yellow needles [160°–180°].

DI-METHYL-KETOXIM *v.* ACETOXIM.

METHYL-LEPIDONE *v.* OXY-DIMETHYL-QUINOLINE.

METHYL-PARA-LEUCANILINES *v.* METHYL-TRI-AMIDO-TRI-PHENYL-METHANES.

METHYL-LUTIDONE *v.* OXY-TRI-METHYL-PYRIDINE.

METHYL-PSEUDO-LUTIDO-STYRIL *v.* OXY-TRI-METHYL-PYRIDINE.

DI-METHYL-MALEIC ACID $C_6H_8O_4$ *i.e.* $CO_2H.CMe:CMe.CO_2H$. *Pyrocinchonic acid. Di-methyl-fumaric acid. Di-methyl-ethylene di-carboxylic acid. Butylene dicarboxylic acid.*

Formation.—1. Its anhydride is formed by the dry distillation of cinchonic acid $C_7H_8O_6$ (Weidel a. Schmidt, *B.* 12, 1151; Weidel a. Brix, *M.* 3, 608).—2. The anhydride is formed by distilling the mother-liquor from the preparation of terebic acid by oxidation of turpentine with HNO_3 (Roser, *B.* 15, 1318).—3. By heating the lactone $CH_3.C(CO_2H).CH(CO_2H).CH_2.CO$ at 180°
|———————O———|
(Rach, *A.* 234, 39).—4. Together with di-chloro-di-methyl-succinic acid $CO_2H.CClMe.CClMe.CO_2H$ by the action of reduced silver upon di-α-chloro-propionic acid (Otto a. Beckurts, *B.* 18, 825).—5. By the action of reduced silver upon di-chloro-di-methyl-succinic acid (O. a. B.).—6. The anhydride is formed by treating either 'anti' or 'para' di-methyl-succinic acid in the fused state with bromine (Bischoff a. Voit, *B.* 23, 646).

Properties.—The free acid is unstable; on adding an acid to its salts the anhydride is at once ppd. The sodium salt gives a dark-red colouration with $FeCl_3$, and crystalline pps. with $Pb(NO_3)_2$ and $HgCl_2$.

Salts.—$Na_2A''\frac{1}{2}aq$: white crystalline solid. —$Na_2A''1\frac{1}{2}aq$.—CaA'': small needles, less sol. hot water than cold (Roser).—$CaA''aq$: small white plates (O. a. B.).—BaA'': white glistening plates, more sol. cold water than hot.—Ag_2A'': sparingly soluble pp., decomposed on heating into Ag_2O and the anhydride.

Methyl ether Me_2A''. Colourless oil.

Ethyl ether Et_2A''. (240°). Oil. Formed by treating the anhydride with alcohol and HCl.

Anhydride $\begin{matrix} CMe.CO \\ \| \\ CMe.CO \end{matrix}\!\!>\!O$. [96°]. (223°). V.D. 4·2 (calc. 4·3). Formed as above. Crystallises in glistening white leaflets or trimetric tables (from water); $a:b:c = \cdot626:1:1\cdot521$ or $\cdot201:\cdot332:1$. V. sol. alcohol, ether, and benzene, sl. sol. cold water. The aqueous solution is acid and has a sweet but burning taste. Volatile with steam. Readily sublimes. Not attacked by HNO_3. Chromic acid mixture oxidises it to acetic acid and CO_2. Reduced by sodium-amalgam to *s*-di-methyl-succinic acid [194°] and two isomeric acids [241°] and [120°], the last acid being methyl-ethyl-malonic acid (Otto a. Rössing, *B.* 20, 2736). Conc. HIAq at 220°, and zinc filings in water or ammonia also reduce it to *s*-di-methyl-succinic acid. The anhydride is not attacked by PCl_5 or AcCl. It is dissolved by aqueous alkalis, forming the sodium salt of the acid. Potash fusion yields oxalic acid. By heating with bromine and water at 100° there is formed di-bromo-acetic acid. When it is dissolved in benzene and shaken with phenyl-hydrazine in the cold the anhydride forms the compound $CH_3.C(CO.N_2H_2Ph):CMe.CO.O.N_2H_4Ph$, which, when shaken with HClAq, regenerates the anhydride, but when heated at 115° yields CO_2, phenyl-hydrazine, and $\begin{matrix} CMe.CO.NH \\ \| \qquad\quad | \\ CMe.CO.NPh \end{matrix}$ [129°], which crystallises from dilute alcohol in yellow monoclinic prisms, and yields di-methyl-maleïc acid when warmed with KOHAq or HClAq (Otto a. Holst, *J. pr.* [2] 42, 67).

Chloride $\begin{matrix} CMe.COCl \\ \| \\ CMe.COCl \end{matrix}$. (220°–230°). Formed by the action of PCl_5 on the anhydride (O. a. H.). Yellow oil. When acted upon by the Na salt it yields the anhydride. NH_3 converts it into the imide. Phenyl-hydrazine forms the compound $\begin{matrix} CMe.CO \\ \| \\ CMe.CO \end{matrix}\!\!>\!N.NHPh$ [187°] isomeric with the body melting at 129° (*v. supra*).

Imide $\begin{matrix} CMe.CO \\ \| \\ CMe.CO \end{matrix}\!\!>\!NH$. [118°]. Formed by heating the anhydride with alcoholic NH_3. Triclinic plates, m. sol. hot water, v. sol. alcohol. May be sublimed.—$^{x}B'_2H_2PtCl_6$.

Anilide $\begin{matrix} CMe.CO \\ \| \\ CMe.CO \end{matrix}\!\!>\!NPh$. [96°]. Formed by heating the anhydride with aniline at 180°. Prisms (from alcohol).

METHYL-MALONIC ACID $C_4H_6O_4$ *i.e.* $CH_3.CH(CO_2H)_2$. *Iso-succinic acid.* Mol. w. 118. [130°]. H.C.v. 365,100. H.C.p. 364,800. H.F. 218,200 (Stohmann, Kleber, a. Langbein, *J. pr.* [2] 40, 207). S.H. (0°–50°) ·3372 (Hess, *P.* [2] 35, 410).

Formation.—1. By decomposing α-cyano-propionic acid with potash (Wichelhaus, *Z.* 1867, 247; Byk, *J. pr.* [2] 1, 19).—2. From sodium-malonic ether and MeI (Züblin, *B.* 12, 1112).

Preparation.—By acting on potassium α-bromo-propionate with pure aqueous KCy, and saponifying the product by boiling with aqueous KOH (Cohn, *A.* 251, 335).

Properties.—Long prisms or tables (by sublimation). Decomposed on distillation into CO_2 and propionic acid. $FeCl_3$ gives no pp. in neutral solutions. Fuming HNO_3 decomposes it into tri-nitro-ethane, CO_2 and acetic acid (Franchimont, *R. T. C.* 5, 281). Electrolysis of a concentrated solution of its potassium salt yields hydrogen, CO_2, and oxygen.

Salts.—$NaHA''\frac{1}{2}aq$.—$Na_2A''2aq$.—KHA''.—$K_2A''aq$. — $CaA''\frac{1}{2}aq$. — $CaA''aq$. Solubility: Miczynsky (*M.* 7, 269).—$BaA''\,2aq$.—$ZnA''\,3aq$. —$PbA''\frac{1}{2}aq$. — Ag_2A'': heavy granular pp. gradually becoming crystalline.

Methyl ether Me_2A''. (179°). S.G. $\frac{15}{}$ 1·107. When treated with HNO_3 (S.G. 1·5) it gives a small quantity of $CH_3.C(NO_2)(CO_2Me)_2$.

Ethyl ether Et_2A''. (196·5° cor.) (Krestownikoff, *B.* 10, 409); (199°) (Perkin, *C. J.* 45, 510). S.G. $\frac{22}{15}$ 1·021 (Conrad a. Bischoff, *A.* 204, 146); $\frac{15}{15}$ 1·0213; $\frac{25}{25}$ 1·0130 (P.).

Di-amide $CH_3.CH(CO.NH_2)_2$. [206°]. Formed, together with methyl carbonate, by treating the compound $CH_3.C(NO_2)(CO_2Me)_2$ (*v. supra*) with ammonia (Franchimont, *R. T. C.* 8, 286). V. sl. sol. alcohol.

Di-methyl-di-amide $CH_3.CH(CO.NHMe)_2$. [154°]. Formed by the action of methylamine on the ether (Franchimont, *R. T. C.* 4, 204). Small needles (from benzene), v. sol. water and alcohol, sl. sol. ether and benzene. Fuming HNO_3 decomposes it, forming CO_2 and N_2O.

Di-methyl-malonic acid $CMe_2(CO_2H)_2$. *Isopyrotartaric acid.* Mol. w. 132. [186°]. H.C. 515,300. H.F. 230,700 (Stohmann, Kleber, a. Langbein, *J. pr.* [2] 40, 208). S.H. (0°–50°) ·310 (Hess, *P.* [2] 35, 410).

Formation.—1. By heating bromo-isobutyric acid with KCy and decomposing the resulting nitrile with potash or HClAq (Markownikoff, *B.* 6, 1440; *A.* 182, 324).—2. By boiling di-methyl-barbituric acid with potash (Conrad a. Guthzeit, *B.* 14, 1644).—3. From methyl-malonic acid, NaOEt, and MeI (Thorne, *C. J.* 39, 543).—4. By oxidising β-acetyl-di-α-methyl-propionic acid with nitric acid (3 pts. of S.G. 1·4 and 1 pt. water) (Anschütz, *A.* 247, 105).

Properties.—Transparent four-sided monoclinic prisms, sl. sol. alcohol, v. sol. water and ether. Sublimes in white needles, even at 100°. Split up on melting into CO_2 and isobutyric acid. Not attacked by boiling dilute HNO_3, and scarcely at all by boiling chromic acid mixture.

Salts.—$^{\times}Na_2A''$: small efflorescent needles, sl. sol. water.—$^{\times}BaA''$: stellate groups of thin needles.—$^{\times}CaA''$: nodules, m. sol. cold water, deposited on warming its solution.—$^{\times}MgA''$: crystalline, v. sol. water.—$PbA''\frac{1}{2}aq$: insoluble pp., changing to shining scales on boiling.—$ZnA''aq$. S. ·68 at 24°. Monoclinic pyramids (Thorne).—$ZnA''3aq$. S. ·94 (Markownikoff).—Ag_2A'': small needles, insol. water.

Ethyl ether Et_2A''. (194·5°) (Thorne); (196·5° cor.) (Perkin, *C. J.* 45, 511). S.G. $\frac{25}{15}$ ·9965 (T.); $\frac{15}{15}$ 1·0015; $\frac{25}{25}$ ·9936 (P.). M.M. 9·268 at 14·4°.

Amide $(CH_3)_2C(CO.NH_2)_2$. [197°]. From the ether and alcoholic NH_3 at 120° (Thorne).

Amic acid $CO_2H.CMe_2.CO.NH_2$. [85°]. A product of the oxidation of mesitylic acid

$$CMe_2\left\langle\begin{array}{l}CH_2.CMe.CO_2H\\ \quad\quad |\\ CO\,.\,NH\end{array}\right.$$

by $KMnO_4$ and H_2SO_4 (Pinner, *B.* 15, 580). At 135° it decomposes, giving off CO_2. Boiling KOHAq forms NH_3 and di-methyl-malonic acid. The potassium salt $KA'2aq$ crystallises in prisms, v. e. sol. water, m. sol. alcohol.

Di-methyl-di-amide $CMe_2(CO.NHMe)_2$. [123°]. Long needles (from benzene), v. e. sol. water and alcohol, sl. sol. ether, m. sol. benzene (Franchimont, *R. T. C.* 4, 206). Fuming HNO_3 attacks it, forming N_2O, methyl nitrate, and dimethylmalonic acid.

Tetra-methyl-di-amide $CMe_2(CO.NMe_2)_2$. [80°]. (276°). Long prisms (from ligroïn), v. e. sol. water, alcohol, and benzene. Fuming HNO_3 forms di-methyl-malonic acid and di-methyl-nitramine.

DIMETHYL-MALONYL-UREA *v.* DI-METHYL-BARBITURIC ACID.

METHYL-MANDELIC ACID *v. Methyl derivative* of MANDELIC ACID and OXY-TOLYL-ACETIC ACID.

Tetra-methyl-mandelic acid *v.* OXY-DURYL-ACETIC ACID.

METHYL-MELAMINE *v. Methyl-cyanuramide* in the article CYANIC ACIDS.

METHYL MERCAPTAN CH_4S *i.e.* $CH_3.SH$. *Methyl sulphydrate.* (5·8°) at 752 mm. (Klason, *B.* 20, 3407); (20°) (Gregory, *A.* 15, 239); (21°) (Obermeyer, *B.* 20, 2919). H.F.p. 5,950. H.F.v. 6,370 (Thomsen, *Th.*). Occurs in human excrement (Nencki, *M.* 10, 863). Obtained by distilling $KMeSO_4$ with KHS. Prepared by diluting with ice a cold mixture of MeOH (500 c.c.) and H_2SO_4 (750 c.c.), adding (2·75 kilos. of) $Na_2CO_3\,10aq$, and evaporating until most of the Na_2SO_4 has separated. The mother-liquor is mixed with a solution of potash (500 g.) in water (1,000 c.c.) previously saturated with H_2S. The mixture is distilled from a water-bath, and the gases evolved are passed first through a concentrated aqueous solution of KOH (50 g.) and then into a solution of KOH (350 g.) in water (700 c.c.). A small quantity of lead acetate is added to the last solution to ppt. H_2S, and the methyl mercaptan is then liberated by HCl, dried, and distilled. The yield is fair (200 g. of MeSH and 40 g. of Me_2S) (Klason, *B.* 20, 3407).

Properties.—Thin, colourless, highly refractive liquid with very repulsive odour. Yields a crystalline hydrate.

Salts.—$Hg(SMe)_2$. [175°]. Obtained by treating HgO with MeSH, or by passing the gas through an aqueous solution of $HgCy_2$. V. sl. sol. water.—$Pb(SMe)_2$: minute tables.—$Bi(SMe)_3$: minute yellow needles.—AgSMe: yellow crystalline pp.

Reference.—PER-CHLORO-METHYL MERCAPTAN.

DI-METHYL-MESIDINE $C_{11}H_{17}N$ *i.e.* $C_9H_{11}NMe_2$. (214°). S.G. ·908. Formed by methylation of mesidine (Hofmann, *B.* 5, 718; Klobbie, *R. T. C.* 6, 33). By treatment with H_2SO_4 and HNO_3 (S.G. 1·5) it is converted into $C_6Me_3(NO_2)_2.NMeNO_2$ [138°].—$B'_2H_2PtCl_6$.

METHYL-METHANE *v.* ETHANE.

Di-methyl-methane *v.* PROPANE.

Tri-methyl-methane *v.* ISO-BUTANE.

Tetra-methyl-methane *v.* PENTANE.

METHYL - PENTAMETHENYL TRIHYDRIDE DICARBOXYLIC ACID $C_8H_{10}O_4$ *i.e.*

$$CO_2H.CH\left\langle\begin{array}{l}C(CH_3)\\ CH_2.CH_2\end{array}\right\rangle C.CO_2H.$$

[188°]. Obtained by saponifying its ether which is among the products resulting from the distillation of di-methyl butylene diketone dicarboxylic (di-acetyl-adipic) ether with KOH (Perkin, jun., *C. J.* 57, 227, 233). Glistening needles or groups of plates, v. sol. hot water, alcohol, and acetone, sl. sol. cold light petroleum, benzene, CS_2, and chloroform.

Reactions.—1. Its aqueous solution decolourises *bromine* in the cold, and on evaporating to a syrup it gives off HBr.—2. HBrAq in sealed tubes at 110° forms $C_6H_{11}Br$, a light-brown oil, probably bromo-methylpentamethylene.—3. *Sodium-amalgam* has no action.

Salts.—$^{\times}(NH_4)A''$: gelatinous.—Ag_2A'': heavy white pp. which darkens in daylight.—$AgHA''$: slender needles, v. sol. hot water.

METHYL-PENTAMETHENYLYL METHYL KETONE TRIHYDRIDE $C_8H_{12}O$ *i.e.*

$$CH_2\left\langle\begin{array}{l}CH_2.CMe\\ \quad\quad \|\\ CH_2.C.CO.CH_3\end{array}\right.$$

Methyl dihydropentene methyl ketone. (191°). Formed by the action of boiling alcoholic potash on di-methyl butylene diketone dicarboxylic (di-acetyl-adipic) ether (Marshall a. Perkin, jun., *C. J.* 57, 232, 241). Colourless mobile oil, smelling like peppermint. Lighter than water. V. sol. alcohol and ether. Readily reacts with phenyl-hydrazine. May be

reduced to the alcohol $C_8H_{16}O$, whence HI at 250° yields C_8H_{16}.

Oxim $C_8H_{12}(NOH)$. [85°]. Formed by the action of hydroxylamine hydrochloride on the ketone dissolved in methyl alcohol. Thick colourless prisms, v. sol. alcohol, ether, acids, and alkalis. May be distilled with slight decomposition. — $(C_8H_{13}NO)_2H_2PtCl_6$: tufts of orange crystals, v. sol. boiling alcohol; decomposing at 192°.

METHYL-METHRONIC ACID $C_9H_{10}O_5$ *i.e.*

$$CO\begin{cases}CH(CH_3).CH.CO_2H \\ \quad\quad\quad | \\ C(CO_2H){:}CMe\end{cases} \text{ or } CO\begin{cases}CH_2\text{——}C(CH_3).CO_2H \\ \quad\quad\quad | \\ C(CO_2H).CMe\end{cases}.$$

Di-methyl-keto-pentene dicarboxylic acid. [198°]. Formed by heating acetoacetic ether, sodium pyruvate, and Ac_2O at 140°, and saponifying the resulting ether with baryta or NaOH (Fittig, *A.* 250, 195). White needles, v. sol. HOAc, ether, hot alcohol, and hot water, sl. sol. cold water, CS_2, and benzene, almost insol. petroleum-ether. At 250° it is split up into CO_2 and methyl-uvic acid $C_8H_{10}O_3$ [98°], which on prolonged boiling yields

$$CO\begin{cases}CH(CH_3).CH_2 \\ \quad\quad\quad | \\ CH\text{═══}CMe\end{cases} \text{ or } CO\begin{cases}CH_2.\ CH.CH_3 \\ \quad\quad | \\ CH{=}CMe\end{cases},$$

an oil, boiling at 119°.

S a l t s.—$BaA''2aq$: small needles, v. e. sol. water.—$CaA''\,3aq$: small prisms.—Ag_2A'': silky nodules, sl. sol. water.

Mono-ethyl ether $EtHA''$. Obtained by boiling the di-ethyl ether with alcoholic potash. Yellow syrup, sl. sol. water.—$Ba(EtA'')_2aq$: yellow gummy pp., v. e. sol. water and alcohol.—$Ca(EtA'')_2\,2aq$: needles, m. sol. water, v. sol. hot alcohol.—$AgEtA''$: flocculent pp., sl. sol. water, v. sol. alcohol and ether.

Di-ethyl ether Et_2A''. (280° uncor.). Heavy oil, miscible with alcohol and ether.

METHYL-TETRAMETHYLENE C_5H_{10} *i.e.* $CH_2{<}^{CH_2}_{CH_2}{>}CHMe$. (c. 40°). Formed by the action of sodium on αδ-di-bromo-pentane dissolved in toluene (Colman a. Perkin, *C. J.* 53, 201). Very volatile oil. Does not combine with conc. HIAq.

METHYL-PENTAMETHYLENE C_6H_{12} *i.e.* ${<}^{CH_2.CH_2}_{CH_2.CH_2}{>}CHMe$? Formed by the action of finely-divided sodium on αε-di-bromo-hexane dissolved in toluene (Perkin, *C. J.* 53, 214). Oil, not attacked by HI.

METHYL - PENTAMETHYLENE CARBOXYLIC ACID $C_7H_{12}O_2$ *i.e.*

$$CH_2\begin{cases}CH_2.CHMe \\ \quad\quad | \\ CH_2.CH.CO_2H\end{cases}.$$

(220°). S.G. $\frac{15}{15}$ 1·0205; $\frac{20}{20}$ 1·0174; $\frac{25}{25}$ 1·0144. M.M. 6·914. Formed by heating methyl-pentamethylene dicarboxylic acid a little above its melting-point (Colman a. Perkin, jun., *C. J.* 53, 194). Colourless oil. Bromine at 110° attacks it with evolution of HBr.—BaA'_2: syrup.—AgA'': white amorphous pp.

Methyl-pentamethylene dicarboxylic acid $C_8H_{12}O_4$ *i.e.* $CH_2\begin{cases}CH_2.CHMe \\ \quad\quad | \\ CH_2.C(CO_2H)_2\end{cases}$. [175°]. Obtained by boiling its ether with alcoholic potash (C. a. P.). Prisms (from ether), or plates (from water), v. sol. alcohol, ether, and hot water, m. sol. cold water.—Ag_2A': white pp.

Ethyl ether Et_2A''. (244°). Obtained from $CH_3.CHBr.CH_2.CH_2.CH_2Br$, malonic ether and NaOEt. Thick oil.

METHYL - HEXAMETHYLENE CARBOXYLIC ACID $C_8H_{14}O_2$ *i.e.* $CH_2{<}^{CH_2.CHMe}_{CH_2.CH_2}{>}CH.CO_2H$. *o-Toluic acid hexahydride*? (236°). S.G. $\frac{4}{4}$ 1·0079; $\frac{10}{10}$ 1·0033; $\frac{20}{20}$ ·9966. M.M. 7·975. Formed by decomposing the dicarboxylic acid by heat (Perkin, jun., *C. J.* 53, 208, 213). It is also one of the products of the electrolysis of methyl-hexamethylenyl methyl ketone carboxylic ether by alcoholic potash. Colourless oil.—AgA': white pp.

Methyl - hexamethylene dicarboxylic acid $C_9H_{14}O_4$ *i.e.* $CH_2{<}^{CH_2.CHMe}_{CH_2.CH_2}{>}C(CO_2H)_2$. [147°]. Obtained by hydrolysing its ether with alcoholic potash (Perkin, *C. J.* 53, 207). Crystalline powder, v. sol. ether, alcohol, and hot water, sl. sol. cold water.—Ag_2A'': white amorphous pp.

Ethyl ether Et_2A''. (c. 263°). Obtained from $CH_3.CHBr.CH_2.CH_2.CH_2.CH_2Br$, malonic ether, and NaOEt (Perkin, jun., *C. J.* 53, 206). Thick oil, with unpleasant odour.

METHYL-TETRAMETHYLENE-KETONE *v.* TETRAMETHYLENYL METHYL KETONE.

METHYL - TRI - METHYLENE KETONE CARBOXYLIC ACID *v.* TRI-METHYLENYL METHYL KETONE CARBOXYLIC ACID.

METHYL-PENTAMETHYLENE METHYL KETONE *v.* METHYL-PENTAMETHYLENYL METHYL KETONE.

TETRA-METHYL-ν-TRIMETHYLENE-DI-PYRROLE $C_{15}H_{22}N_2$ *i.e.*

$$\begin{matrix}HC{:}CMe \\ | \\ HC{:}CMe\end{matrix}{>}N.C_3H_6.N{<}\begin{matrix}CMe{:}CH \\ | \\ CMe{:}CH\end{matrix}.$$

[77°]. Formed by heating acetonyl-acetone (2 mols.) and tri-methylene-diamine (1 mol.) in conc. alcoholic solution at 120°. Crystalline solid. Sol. alcohol and ether, insol. water (Paal a. Schneider, *B.* 19, 3157).

DI-METHYL - TRI - METHYLENE - TRI-SULPHONE $C_3H_4(CH_3)_2S_3O_6$. [330°–340°]. Two bodies of this formula are produced when 1 g. tri-methylene-tri-sulphone in 10 c.c. of 5 p.c. caustic soda is heated with an equal volume of methyl iodide. These two substances crystallise together in glittering needles. By further methylation the hexamethyl derivative is formed (E. Baumann a. R. Camps, *B.* 23, 72).

Tetra-methyl-di-methylene disulphone $CMe_2{<}^{SO_2}_{SO_2}{>}CMe_2$. *Di-isopropylidene di-sulphone.* [220°–225°]. Obtained from acetone (1 pt.) by heating it with P_2S_3 (1 pt.) at 125° for 7 hours, distilling with steam, and oxidising the resulting 'duplo'-thio-acetone $S_2(CMe_2)_2$ with $KMnO_4$ (Autenrieth, *B.* 20, 373). Slender white needles, v. sol. alcohol and ether, sl. sol. hot water. Not attacked by HNO_3 and H_2SO_4, nor by boiling dilute aqueous KOH.

METHYL-PENTAMETHYLENYL-METHYL-CARBINOL $C_8H_{16}O$ *i.e.*

$$\begin{matrix}CH_2.CHMe \\ | \\ CH_2.CH_2\end{matrix}{>}CH.CH(OH).CH_3.$$

(180°). Ob-

tained by reducing the corresponding ketone in ethereal solution with sodium (Marshall a. Perkin, jun., *C. J.* 57, 247). Colourless liquid, with strong odour of menthol, sl. sol. water, v. sol. alcohol and ether. On boiling with Ac_2O it yields a strongly refracting acetyl derivative with agreeable odour. Excess of solution of hydriodic acid (S.G. 1·96) forms a heavy oily iodide
$$\begin{matrix} CH_2.CHMe \\ | \\ CH_2.CH_2 \end{matrix} > CH.CHI.CH_3$$
(155°–160° at 90 mm.), which smells like *sec*-hexyl iodide, and is slightly decomposed on distillation.

METHYL-HEXAMETHYLENYL-METHYL-CARBINOL $C_9H_{18}O$ *i.e.*
$$CH_2 < \begin{matrix} CH_2.CHMe \\ CH_2.CH_2 \end{matrix} > CH.CH(OH).CH_3.$$
Hexahydride of o-*tolyl-methyl-carbinol*. (195°–200°). Formed by reducing tetrahydro-tolyl methyl ketone in ethereal solution with sodium (Kipping a. Perkin, jun., *C. J.* 57, 22). Thick, colourless liquid, smelling like menthol, sl. sol. water, miscible in alcohol and ether. When mixed with conc. HIAq it dissolves with evolution of heat and separation of the corresponding iodide.

METHYL-PENTAMETHYLENYL METHYL KETONE $C_8H_{14}O$ *i.e.*
$$CH_2 < \begin{matrix} CH_2.CHMe \\ | \\ CH_2.CH.CO.CH_3 \end{matrix}.$$
(171°). S.G. $\frac{4}{4}$ ·9222; $\frac{10}{10}$ ·9174; $\frac{15}{15}$ ·9136; $\frac{25}{25}$ ·9070. M.M. 8·019. Obtained as one of the products of the hydrolysis of its carboxylic ether by alcoholic potash (Colman a. Perkin, *C. J.* 53, 198). Colourless oil, smelling of peppermint. Readily combines with phenyl-hydrazine and with hydroxylamine. Dissolves with difficulty in a solution of $NaHSO_3$.

Methyl-hexamethylenyl methyl ketone
$$CH_2 < \begin{matrix} CH_2.CHMe \\ CH_2.CH_2 \end{matrix} > CH.CO.CH_3.$$
o-*Tolyl methyl ketone hexahydride*. (198°). Obtained as one of the products of the hydrolysis of its carboxylic ether by alcoholic potash (Perkin, *C. J.* 53, 213). Colourless oil, smelling, when in small quantities, like new-mown hay.

METHYL-TRIMETHYLENYL METHYL KETONE CARBOXYLIC ACID $C_7H_{10}O_3$ *i.e.*
$$\begin{matrix} CHMe \\ | \\ CH_2 \end{matrix} > C(CO_2H).CO.CH_3.$$
Propylene-aceto-acetic acid. Obtained by saponifying its ether, which is produced by treating acetoacetic ether with NaOEt and propylene bromide (Perkin, jun., *B.* 17, 1443). Thick oil, splitting off CO_2 when heated.—AgA': amorphous powder, sl. sol. water.

Ethyl ether EtA'. (210°–215°) at 720 mm.

Methyl-pentamethylenyl methyl ketone carboxylic ether
$$CH_2 < \begin{matrix} CH_2.CHMe \\ | \\ CH_2.C(CO_2Et).CO.CH_3 \end{matrix}.$$
(238°). Obtained by the action of $a\delta$-di-bromo-pentane on sodium-aceto-acetic ether (Colman a. Perkin, jun., *C. J.* 53, 197). Thick, colourless oil. On hydrolysis with alcoholic potash it yields the corresponding ketone as well as the acid.

Methyl-hexamethylenyl methyl ketone carboxylic ether
$$CH_2 < \begin{matrix} CH_2.CHMe \\ CH_2.CH_2 \end{matrix} > C(CO_2Et).CO.CH_3.$$
Hexahydro-o-tolyl methyl ketone carboxylic ether. (257°). Formed by the action of di-bromo-hexane $CH_3.CHBr.CH_2.CH_2.CH_2.CH_2Br$ and NaOEt on aceto-acetic ether (Perkin, *C. J.* 53, 212). Colourless oil with disagreeable odour. Yields on hydrolysis methyl-hexamethylenyl methyl ketone as well as its carboxylic acid.

METHYL-MORPHINE *v.* CODEÏNE.

(α)-METHYL-NAPHTHALENE $C_{11}H_{10}$ *i.e.*
$$C_6H_4 < \begin{matrix} CMe:CH \\ | \\ CH:CH \end{matrix}.$$
Mol. w. 142. (242° i.V.) (S.); (232°) (F. a. R.). S.G. $\frac{11\cdot5}{}$ 1·029. Occurs, together with (β)-methyl-naphthalene, in the fraction of coal-tar oil boiling between 200° and 300° (Schulze, *B.* 17, 844).

Formation.—1. By the action of sodium on a mixture of MeI and (α)-bromo-naphthalene (Fittig a. Remsen, *A.* 155, 114).—2. By distilling colophony, gum-benzoïn, or aldehyde-resin with zinc-dust (Ciamician, *B.* 11, 269; *M.* 1, 193).—3. By distilling (α)-naphthyl-acetic acid with lime (Boessneck, *B.* 16, 1546).

Properties.—Colourless liquid, not solid at −18°. Boiling conc. HNO_3 oxidises it to (α)-naphthoic acid.

Picric acid compound $C_{11}H_{10}C_6H_2(NO_2)_3OH$. [117°]. Long, slender orange needles (from alcohol).

(β)-Methyl-naphthalene $C_{10}H_7(CH_3)$ *i.e.*
$$C_6H_4 < \begin{matrix} CH:CMe \\ | \\ CH:CH \end{matrix}.$$
[33°]. (242° i.V.). Occurs in the fraction of coal-tar oils boiling at 200°–300°. The oil is shaken with NaOH and with H_2SO_4, to remove phenols and bases, and fractionally distilled. By cooling the fraction 239°–242° to 0° the (β)-methyl-naphthalene separates out, leaving the liquid (α)-methyl-naphthalene (Schulze, *B.* 17, 842, 1203; Reingruber, *A.* 206, 367). Could not be obtained from (β)-bromo-naphthalene MeI and Na (Brunel, *B.* 17, 1179). White plates; insol. water; sol. alcohol, ether, and benzene; volatile with steam. Completely decomposed on oxidation. Yields, on chlorination at 245°, $C_{10}H_7.CH_2Cl$ [47°].

Picric acid compound: [115°]; yellow needles.

Di-methyl-naphthalene $C_{12}H_{12}$ *i.e.* $C_{10}H_6Me_2$. (110° at 6 mm.); (c. 265°) at 760 mm. S.G. $\frac{0}{}$ 1·0283; $\frac{12}{0}$ 1·0199 (C. a. C.); $\frac{20}{}$ 1·0176 (G.); $\frac{16\cdot4}{}$ 1·0180 (Nasini, *G.* 15, 84). R_∞ 87·25 (N.).

Formation.—1. From di-bromo-naphthalene [81°], sodium, and MeI (Mono, *B.* 13, 1517).—2. By heating santonin, or the dimethyl-naphthol derived therefrom, to redness with zinc-dust (Cannizzaro a. Carnelutti, *G.* 12, 410).—3. By heating dimethyl-naphthol hydride with sulphide of phosphorus (Cannizzaro, *G.* 13, 393).

Preparation.—Di-bromo-naphthalene dissolved in toluene is heated with MeI and sodium, the product is heated to 150° to remove MeI and toluene, and the residue extracted with ether. The extract is fractionally distilled, and the fraction 260°–270°, after rectification under 12 mm. pressure, is heated with sodium at 100° to remove any unaltered di-bromo-naphthalene. The di-methyl-naphthalene is finally obtained pure by means of its compound with picric acid (Giovanozzi, *G.* 12, 147).

Properties.—Colourless, highly refractive oil, not solid at −18°. With bromine it appears to form $C_{12}H_{12}Br_6$ and $C_{12}H_9Br_3$.

Picric acid compound; [139°]. Orange needles; sol. alcohol and ether.

Hexahydride $C_{12}H_{18}$. S.G. $\frac{19.4}{4}$ ·922. R_∞ 86·14 (Nasini a. Bornheimer, *G.* 15, 93). Formed by treating the di-methyl-naphthalene with HIAq and phosphorus (Zuco, *G.* 15, 81).

Di-methyl-naphthalene $C_{12}H_{12}$ (265°). Occurs in coal-tar (Emmert a. Reingruber, *A.* 211, 365). Not solid above −18°.

Picric acid compound $C_{12}H_{12}C_6H_2(NO_2)_3OH$. [118°]. Orange prisms.

Trimethyl-naphthalene $C_{13}H_{14}$ *i.e.* $C_{10}H_5Me_3$ (275°). Obtained (according to Maschke, *C.C.* 1886, 824) by heating di-methyl-(β)-naphthylamine methylo-iodide at 320°, and distilling the resinous product with steam.

Picric acid compound: [133°].

References.—Bromo- and Chloro-methyl-naphthalenes.

(α)-METHYL-NAPHTHALENE SULPHONIC ACID $C_{10}H_6Me.SO_3H$. Obtained by sulphonating (α)-methyl-naphthalene (Fittig a. Remsen, *A.* 155, 115).—BaA'_2: sl. sol. water.

(β)-Methyl-naphthalene sulphonic acid $C_{10}H_6Me.SO_3H$. Obtained by sulphonating (β)-methyl-naphthalene (Reingruber, *A.* 206, 377). Syrup.—BaA'_2: amorphous mass.

Di-methyl-naphthalene sulphonic acid $C_{10}H_5Me_2.SO_3H$. Obtained by the action of H_2SO_4 at 120° on the di-methyl-naphthalene derived from di-bromo-naphthalene [81°] (Giovanozzi, *G.* 12, 147). Deliquescent scales.—KA'aq: iridescent laminæ.

Di-methyl-naphthalene sulphonic acid $C_{10}H_5Me_2.SO_3H$. Obtained by heating the di-methyl-naphthalene of coal-tar with fuming H_2SO_4 (Emmert a. Reingruber, *A.* 211, 365).—×BaA'_2: sl. sol. water.

Di-methyl-naphthalene di-sulphonic acid $C_{10}H_4Me_2(SO_3H)_2$. Formed at the same time as the preceding, from which it differs in having an easily soluble barium salt (E. a. R.).

METHYL-NAPHTHAQUINOLINE *v.* Methyl-naphthoquinoline.

(*In.* 2)-METHYL (α)-NAPHTHINDOLE $C_{13}H_{11}N$ *i.e.* $C_{10}H_6<\genfrac{}{}{0pt}{}{CH}{NH}>CMe$. [132°]. Obtained by heating (1 pt. of) the (α)-naphthyl-hydrazide of acetone with $ZnCl_2$ (2 pts.) at 180° (Schlieper, *A.* 239, 237). Slender needles (from water); v. sol. alcohol and ether. Colours pine-wood, acidified by HCl, bluish-violet. $FeCl_3$ imparts a cherry-red colour to its solution in HOAc, and on adding water a pp. is formed.

Picrate: [168°]; dark-red needles (from hot benzene).

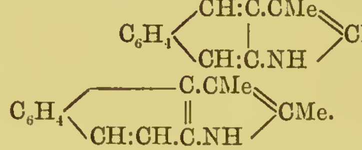
(*In.* 2)-Methyl-(β)-naphthindole $C_{10}H_6<\genfrac{}{}{0pt}{}{CH}{NH}>CMe$. (314°–320° at 223 mm.). Prepared by heating the (β)-naphthyl-hydrazide of acetone with $ZnCl_2$ at 175°, dissolving the fused mass in water, and extracting with ether (Schlieper, *A.* 236, 182). Liquid; v. sl. sol. water, v. sol. alcohol, ether, and benzene. Colours acidified pine-wood violet. $NaNO_2$ added to the acetic acid solution gives a brown pp.

Picrate: [176°]; reddish-brown needles (from hot benzene).

Dihydride $C_{13}H_{13}N$ *i.e.* $C_{10}H_6<\genfrac{}{}{0pt}{}{CH_2}{NH}>CHMe$. (190°–200° at 20 mm.). Obtained by treating methyl-(β)-naphthindole with zinc-dust and HClAq, until it ceases to give the pine-wood reaction, then adding NaOH and extracting with ether. Yellow oil, which in an ethereal solution exhibits blue fluorescence. Forms soluble crystalline salts with mineral acids. Reduces $AgNO_3$ on warming. Gives an oily nitrosamine.

(*In.* 1, 2)-Di-methyl-(α)-naphthindole $C_{14}H_{13}N$ *i.e.* $C_{10}H_6<\genfrac{}{}{0pt}{}{NH}{CMe}>CMe$. [150°]. Formed by heating bromo-acetyl-propionic (bromo-levulic) acid $CH_3.CO.CHBr.CH_2.CO_2H$ (2 pts.) with (α)-naphthylamine (7 pts.) (Wolff, *B.* 21, 3365). White granules or prisms (from alcohol), v. sol. ether and benzene, m. sol. cold alcohol and HOAc, insol. water. Its solution in conc. HClAq is ppd. by water. $FeCl_3$ colours its solution in HOAc cherry-red, whilst $K_2Cr_2O_7$ give a deep-blue colour.

(*In.* 1, 2)-Di-methyl-(β)-naphthindole



or [132°]. (above 360°). Prepared by the action of bromo-acetyl-propionic acid on (β)-naphthylamine (Wolff, *B.* 21, 3363). Plates (from alcohol), v. e. sol. ether and benzene, m. sol. cold alcohol and HOAc, insol. water. $FeCl_3$ colours its solution in boiling HOAc green. The concentrated alcoholic solution exhibits violet fluorescence.

Picrate: [175°]; dark-brown needles.

(*In* 1, 2)-Di-methyl-(β)-naphthindole $C_{10}H_6<\genfrac{}{}{0pt}{}{CMe}{NH}>CMe$. [126°]. Possibly identical with the preceding body. Formed by heating (*In* 1, 2)-methyl-(β)-naphthindyl-acetic acid at 210° (E. Fischer a. Steche, *A.* 242, 370). Six-sided plates, insol. water, v. sol. alcohol and HOAc. $FeCl_3$ gives a blue colouration to its solution in HOAc. Yields a crystalline nitrosamine. Reacts with MeI forming di-methyl-(β)-naphtho-quinoline dihydride.

Picrate: dark-red crystals.

Dihydride $C_{14}H_{15}N$ *i.e.* $C_{10}H_6<\genfrac{}{}{0pt}{}{CHMe}{NH-}>CHMe$. Obtained by reducing the di-methyl-(β)-napthindole with zinc-dust and HCl. Oil, turning red on oxidation. Forms a crystalline platinochloride, decomposed by boiling water.

(*In* 1, 2)-METHYL-(β)-NAPHTHINDYL-ACETIC ACID $C_{15}H_{13}NO_2$ *i.e.* $C_{10}H_6<\genfrac{}{}{0pt}{}{CMe}{NH}>C.CH_2.CO_2H$. [210°]. *Di-methyl-naphthindole ω-carboxylic acid.* Formed by heating the (β)-naphthyl-hydrazide of β-acetyl-propionic ether with $ZnCl_2$ at 135° (Steche, *A.* 242, 368). Small crystals containing $\frac{1}{2}C_3H_6O$ (from acetone), v. sl. sol. water, benzene, and chloroform, v. sol. alcohol, ether, acetone, and HOAc. Loses CO_2 on heating.—AgA': white pp. which yields a silver mirror on boiling with water.

METHYL-NAPHTHOCOUMARIN *v.* *Anhydride* of Oxy-naphthyl-crotonic acid.

METHYL-(α)-NAPHTHOFURFURANE
$C_{13}H_{10}O$ *i.e.* $C_6H_4\left\langle\begin{matrix}\text{C—O}\\ \| \\ \text{CH:CH.C.CMe}\end{matrix}\right\rangle\text{CH}$. [35°]. (298°). Obtained by distilling its carboxylic acid alone or with KOH (Hantzsch a. Pfeiffer, *B.* 19, 1304). Very volatile with steam. Reduces $AgNO_3$ on boiling. Its solution in H_2SO_4 becomes green, and finally violet, on warming; on dilution with water it becomes green again.

Methyl-(β)-naphthofurfurane
$C_6H_4\left\langle\begin{matrix}\text{C.CMe}\\ \| \\ \text{CH:CH.C — O}\end{matrix}\right\rangle\text{CH}$. [59°]. Obtained by distilling its carboxylic acid alone or with soda-lime (H. a. P.). Resembles the preceding isomeride.

METHYL - (α) - NAPHTHOFURFURANE CARBOXYLIC ACID $C_{14}H_{10}O_3$ *i.e.*
$C_6H_4\left\langle\begin{matrix}\text{C — O}\\ \| \\ \text{CH:CH.C.CMe}\end{matrix}\right\rangle\text{C.}CO_2H$. [245°]. By the action of chloro-aceto-acetic ether on sodium (α) - naphthol there is formed $C_{10}H_7O.CHAc.CO_2Et$, and this ether is then mixed with H_2SO_4, and the product poured into water. The ppd. ether is then saponified by alcoholic potash (Hantzsch a. Pfeiffer, *B.* 19, 1301). Needles (from HOAc), which may be sublimed; v. sl. sol. alcohol and ether, almost insol. water.

Ethyl ether EtA′. [108°]. Flat needles (from alcohol), v. sol. ether and hot alcohol.

Methyl-(β)-naphthofurfurane carboxylic acid
$C_6H_4\left\langle\begin{matrix}\text{C.CMe}\\ \| \\ \text{CH:CH.C — O}\end{matrix}\right\rangle\text{C.}CO_2H$. [254°]. Formed in the same manner as the preceding isomeride, which it greatly resembles, by using sodium (β)-naphthol (H. a. P.).—NaA′ 4aq: blue fluorescent needles.

(β)-METHYL-(α)-NAPHTHOL
$C_{11}H_{10}O$ *i.e.* $C_{10}H_6Me.OH$. [89°]. Formed as a by-product, together with phenyl-butylene, by distilling (α)-phenyl-methyl-paraconic acid $C_6H_5.\underline{CH.CH(CO_2H).CHMe.CO}$ (Fittig a. L. $\qquad$ O $\qquad$ Liebmann, *A.* 255, 263). Long slender elastic needles, v. sl. sol. water. $FeCl_3$ gives a white pp. Bleaching powder produces a green pp. which becomes yellow. On distillation with zinc-dust (β)-methyl-naphthalene is formed.

(β)-Methyl-(α)-naphthol $C_{10}H_6Me.OH$. [92°]. Formed by distilling (β)-phenyl-methyl-paraconic acid (Fittig a. Liebmann, *A.* 255, 272). Long elastic white needles (from boiling water), volatile with steam. $FeCl_3$ gives a white pp. which becomes yellow on standing. Bleaching powder forms a green pp., quickly becoming yellow. On distillation with zinc-dust it yields (β)-methyl-naphthalene.

Di-methyl-naphthol $C_{10}H_5Me_2.OH$. [136°]. Obtained by heating santonous or isosantonous acid with $Ba(OH)_2$ above 360°. The product is dissolved in water, and on passing CO_2 through the solution di-methyl-naphthol is ppd. together with $BaCO_3$, which is removed by HClAq (Cannizzaro a. Carnelutti, *G.* 12, 406). Glistening needles (from alcohol), v. sl. sol. water, sol. alcohol and ether. Begins to sublime at 100°. Chromic acid in HOAc oxidises it to $C_{12}H_{12}O_2$, crystallising in tables [105°], which may be reduced to di-methyl-naphthol by HI and phosphorus. On heating to redness with zinc-dust it yields di-methyl-naphthalene identical with that obtained from di-bromo-naphthalene [81°].

Methyl ether $C_{12}H_{11}.OMe$. [68°]. Prisms, sol. alcohol and ether.

Ethyl ether $C_{12}H_{11}.OEt$. Viscid liquid.

Acetyl derivative $C_{12}H_{11}.OAc$. [78°]. Laminæ.

Dihydride $C_{12}H_{14}O$. [113°]. Obtained by saponification of its propionyl derivative, which is one of the products of the dry distillation of santonous acid. Separated from accompanying di-methyl-naphthol by frequent crystallisation from light petroleum (Cannizzaro, *G.* 13, 390). Glistening white needles, v. sol. ether and alcohol, insol. water. Volatile with steam. P_2S_5 converts it into di-methyl-naphthalene.

(*Py.* 3)-METHYL-(α)-NAPHTHOQUINOLINE
$C_{10}H_6\left\langle\begin{matrix}\text{CH:CH}\\ \alpha \quad | \\ \text{N : CMe}\end{matrix}\right.$. *α-Naphthoquinaldine.* (above 300°). Heavy liquid. Formed by heating (α)-naphthylamine with paraldehyde and HCl. Its salts have a blue fluorescence in dilute solution.—$B'_2H_2Cl_2PtCl_4$ 2aq: concentric needles.—$B'_2H_2Cr_2O_7$: yellow crystals (Doebner a. Miller, *B.* 17, 1711).

(*Py.* 1)-Methyl-(β)-naphthoquinoline $C_{14}H_{11}N$ *i.e.* $C_{10}H_6\left\langle\begin{matrix}\text{CMe:CH}\\ | \\ \text{N = CH}\end{matrix}\right.$. [c. 112°]. Formed, together with (β)-naphtho-acridine and a base $C_{24}H_{20}N_2$, by the action of a mixture of methylal, acetone, and HCl upon (β)-naphthylamine (Reed, *J. pr.* [2] 35, 316).—Picrate $B'C_6H_2(NO_2)_3OH$.

(*Py.* 3)-Methyl-(β)-naphthoquinoline
$C_{10}H_6\left\langle\begin{matrix}\text{CH:CH}\\ \beta \quad | \\ \text{N : CMe}\end{matrix}\right.$. (β)-*Naphthoquinaldine.* [82°]. (above 300°). Formed by heating (β)-naphthylamine with paraldehyde and HCl (Doebner a. Miller, *B.* 17, 1711; Seitz, *B.* 22, 254). Large colourless needles. V. sol. alcohol and ether, sl. sol. water. With chloral it forms a crystalline compound $C_{13}H_8N.CH_2.CH(OH).CCl_3$ [185°].

Salts.—$B'_2H_2Cl_2PtCl_4$ 2aq: yellow, sparingly soluble needles.—$B'_2H_2Cr_2O_7$: small yellow needles, sl. sol. hot water.—B′HCl 2aq: slender needles, sl. sol. cold water.—$B'HNO_3$ aq: slender needles, becoming rose-coloured in air.—$B'H_2SO_4$ 2aq: very slender needles, v. e. sol. hot water.—$B'C_6H_2(NO_2)_3OH$. [221°]. Minute needles, v. sl. sol. boiling water, v. sol. HOAc.

Methylo-iodide B′MeI. [241°–247°]. Straw-coloured needles, v. sol. boiling water, sl. sol. alcohol.

(*Py.* 3)-Methyl-(β)-naphthoquinoline
$C_{10}H_6\left\langle\begin{matrix}\text{CH:CH}\\ | \\ \text{N : CMe}\end{matrix}\right.$. [92°]. Possibly identical with the preceding isomeride. Formed by heating (*Py.* 1, 3)-oxy-methyl-naphthoquinoline to redness with zinc-dust (Knorr, *B.* 17, 544). Crystalline. May be distilled. Its acid solutions fluoresce blue when dilute, green when concentrated.—$B'_2H_2PtCl_6$: sl. sol. hot dilute HClAq.

(*Py.* 1, 3)-**Di-methyl-(α)-naphthoquinoline**
$$C_{10}H_6\left\langle\begin{matrix}CMe:CH\\ |\\ N{=\!=}CMe\end{matrix}\right. \quad i.e.\quad C_6H_4\left\langle\begin{matrix}C.N{=\!=}CMe\\ \|\qquad\quad |\\ CH:CH.C.CMe.CH\end{matrix}\right. .$$
[44°]. (361°). Formed by heating at 100° a mixture of (α)-naphthylamine with ethylidene-acetone, derived from acetone and paraldehyde (Reed, *J. pr.* [2] 35, 312). Formed also by heating (α)-naphthylamine (1 mol.) with acetyl-acetone (1 mol.), and heating the product with H_2SO_4 at 100° (Combes, *C. R.* 106, 1536). Needles (from petroleum-ether); v. e. sol. ether, insol. 90 p.c. alcohol. Somewhat volatile with steam. Its solution in H_2SO_4 is coloured purple by $K_2Cr_2O_7$. The solutions of its salts fluoresce violet (C.). The hydrated platinochloride is violet; after drying *in vacuo* it melts at 260° (C.).—$B'C_6H_2(NO_2)_3OH$. [223°]. Needles.

(*Py.* 1, 3)-**Di-methyl-(β)-naphthoquinoline**
$$C_{15}H_{13}N \quad i.e.\quad C_{10}H_6\left\langle\begin{matrix}CMe:CH\\ |\\ N{=\!=}CMe\end{matrix}\right. \quad viz.$$
$$C_6H_4\left\langle\begin{matrix}C.CMe:CH\\ \|\qquad |\\ CH:CH.C.N{=\!=}CMe\end{matrix}\right. .$$ [127°]. (above 300°).
Formed from (β)-naphthylamine hydrochloride by heating at 100° with ethylidene-acetone, the product of the condensation of paraldehyde with acetone in presence of hydrochloric acid, as follows: $C_{10}H_7NH_2 + Me.CO.CH:CHMe = C_{15}H_{13}N + H_2O + H_2$ (Reed, *J. pr.* [2] 35, 299). Flat needles (from ether); v. sl. sol. boiling water; hardly volatile with steam. $KMnO_4$ oxidises it to (β)-di-methyl-phenyl-pyridine dicarboxylic acid. It does not yield a nitrosamine.

Salts.—Picrate $B'C_6H_2(NO_2)_3OH$. [215°]. — $B'H_2Cr_2O_7$. [c. 115°]. — $B'_2H_2PtCl_6$ 2½aq. — $B'H_2SO_4$.—$B'HNO_3$. [181°].—B'_2HBr_5. [207°].— $B'HBr$ 2aq.

Methylo-iodide B'MeI: needles.

Sulphonic acid $C_{15}H_{12}(SO_3H)N$ 1½aq: minute needles, insol. water and alcohol.

Disulphonic acid $C_{15}H_{11}(SO_3H)_2N$ 4½aq: needles, v. e. sol. water and alcohol.—$CuH_2A''_2$ 5aq.—BaA'' 7aq. Potash fusion produces $C_{15}H_{11}(OH)(SO_3H)N$.

Di-methyl-(β)-naphthoquinoline $C_{15}H_{13}N$. [67°]. (380°). Obtained by heating (β)-naphthylamine with acetyl-acetone and H_2SO_4 at 100° (Combes, *C. R.* 106, 1537). Its yellow sulphonic acid $C_{15}H_{13}NSO_3$ is also ppd. on adding ammonia to the aqueous extract of the product. The base forms a greenish-yellow platinochloride, decomposing at 220° without melting.

DI-METHYL-(β)-NAPHTHOQUINOLINE DI-HYDRIDE $C_{15}H_{15}N$ *i.e.* $C_{10}H_6\left\langle\begin{matrix}CMe:CMe\\ |\\ NH\,.\,CH_2\end{matrix}\right.$. [115°].
Formed by heating (*In.* 1, 2)-di-methyl-(β)-naphthindole with MeI in sealed tubes for 15 hours at 100° (Fischer a. Steche, *B.* 20, 820; *A.* 242, 364). Plates; v. sl. sol. water, v. sol. ether, alcohol, and mineral acids; volatile with steam. With nitrous acid it yields a crystalline nitrosamine.—B'HI. Needles (from water); sl. sol. water and alcohol.—The platinochloride is sl. sol. water and alcohol.

METHYL-NAPHTHYLAMINE v. NAPHTHYL-METHYL-AMINE.

Methyl-di-naphthyl-amine v. DI-NAPHTHYL-METHYL-AMINE.

DI-METHYL-NAPHTHYLENE-DIAMINE v. NAPHTHYLENE-DI-METHYL-DI-AMINE.

METHYL-NARCEÏNE v. NARCEÏNE.

METHYL-NARINGENIC ACID v. *Methyl derivative* of *p*-COUMARIC ACID.

METHYL-NICOTINE v. NICOTINE.

METHYL-NICOTINIC ACID v. METHYL-PYRIDINE CARBOXYLIC ACID.

METHYL-NITRAMINE v. METHYLAMINE.

METHYL NITRATE $CH_3.NO_3$ *i.e.* $CH_3.O.NO_2$. Mol. w. 77. (65°). S.G. $\frac{15}{15}$ 1·2167; $\frac{25}{25}$ 1·2032. M.M. 2·057 (Perkin, *C. J.* 55, 682). S.V. 69·3 (Lossen, *A.* 254, 73). Obtained, together with methyl nitrite, by distilling wood-spirit with $NaNO_3$ and H_2SO_4 (Dumas a. Péligot, *A. Ch.* [2] 58, 37). Prepared by distilling methyl alcohol (200 c.c.) with urea nitrate (40 g.) and HNO_3 (150 c.c. of S.G. 1·31) free from nitrous acid. When two-thirds have passed over, an additional quantity of MeOH (170 c.c.) and HNO_3 (110 c.c.) may be added and the distillation continued (Carey Lea, *Am. S.* [2] 33, 227). The process may also be conducted in a continuous manner (*v.* ETHYL NITRATE).

Properties.—Colourless liquid, exploding when struck or when its vapour is heated. With solid KOH it yields Me_2O (Berthelot, *A.* 113, 80). When diluted with MeOH ($\frac{1}{6}$ vol.) and treated with a current of gaseous NH_3 it gives methylamine nitrate and $NMe_4.NO_3$ with only traces of di- and tri-methylamine. Aqueous ammonia forms $NMeH_2$ (13 pts.), NMe_4NO_3 (10 pts.), and a small quantity (1 pt.) of the bases NMe_2H and NMe_3 (Duvillier a. Malbot, *A. Ch.* [6] 10, 284).

METHYL NITRITE CH_3NO_2 *i.e.* $CH_3.O.NO$. Mol. w. 61. (−12°). S.G. (liquid) $\frac{15}{}$ ·991. Produced by treating methyl alcohol with nitric acid and copper turnings or arsenious acid (Strecker, *C. R.* 39, 53; *A.* 91, 82). The product is passed through a receiver at 0° and the gas after purification by passing through potash, a solution of ferrous sulphate, and dry $CaCl_2$, is condensed at −40°. It may also be prepared from methyl alcohol, $NaNO_2$ and H_2SO_4.

Properties.—Gas, smelling like nitrous ether. Burns with a green-edged flame.

METHYL-NITRO-AMIDE v. METHYLAMINE.

METHYL-NITRO-ANILINE v. NITRO-METHYL-ANILINE.

METHYL-NITRO-BENZAMIDE v. *Amide* of NITRO-TOLUIC ACID.

METHYL-NITROLIC ACID $CH_2N_2O_3$ *i.e.* $CH(NO_2):NOH$ or $CH_2(NO_2)(NO)$. Mol. w. 90. [64°]. Prepared by dissolving nitro-methane (15 g.) in water, adding a solution of KNO_2 (8 g.), cooling to 0°, and adding a very dilute ice-cold solution of H_2SO_4 (4 g.). Caustic potash solution is added till the liquid turns red, and then more dilute H_2SO_4. The liquid is then shaken with a little $CaCO_3$ and extracted with ether (Tscherniak, *B.* 8, 114; *A.* 180, 166). The result is very uncertain (V. Meyer a. Constam, *A.* 214, 335).

Properties.—Long needles (from ether). Decomposes slowly in the cold, rapidly at 64°, into formic acid, NO_2, and nitrogen. By boiling dilute H_2SO_4 it is resolved into formic acid and N_2O. Sodium-amalgam reduces it to methyl-azaurolic acid CH(NOH).N:N.CH:NOH an amorphous powder which is violently gasified above 100°.

DI-METHYL-NITROSAMINE *v.* DI-METHYL-AMINE.

METHYL NITROSO-ETHYL KETONE *v.* *Mono-oxim* of DI-METHYL-DIKETONE.

TETRA-METHYL-NITROSO-PHENYLENE-DIAMINE *v.* NITROSO-PHENYLENE-TETRA-METHYL-DIAMINE.

METHYL NONYL KETONE *v.* METHYL ENNYL KETONE.

METHYL-NOROPIANIC ACID *v.* OPIANIC ACID.

METHYL *n*-OCTYL KETONE $C_{10}H_{20}O$ *i.e.* $CH_3.CO.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_3$. [4°]. (214°) (J.); (211°) (K.). S.G. $\frac{17.5}{17.5}$ ·8294; $\frac{4}{4}$ ·838; $\frac{20}{4}$ ·825 (K.). Formed by boiling heptyl-aceto-acetic ether with dilute alkalis (Jourdain, *A.* 200, 106). Formed also by distilling a mixture of barium acetate and barium ennoate (Krafft, *B.* 15, 1695). Liquid, with pleasant odour, insol. water, solidifying in a freezing mixture. Forms a crystalline compound with $NaHSO_3$.

Methyl octyl ketone $C_{10}H_{20}O$ *i.e.* $CH_3.CO.CH_2.CHMe.C_5H_{11}$. *Heptyl-acetone.* (197°). Formed by the action of baryta-water on *n-sec*-heptyl-aceto-acetic ether (Venable, *B.* 13, 1651). Colourless liquid, lighter than water.

METHYL OCTYL OXIDE $C_9H_{20}O$ *i.e.* $CH_3.O.C_8H_{17}$. (173°). S.G. $\frac{0}{0}$ ·8014. S.V. 219·8. C.E. (0°–10°) ·00101 (Dobriner, *A.* 243, 3).

METHYL-OCTYL-PHENYL-AMINE *v.* OCTYL-TOLYL-AMINE.

METHYL-OCTYL-THIOPHENE $C_{13}H_{22}S$ *i.e.* $S<\begin{matrix}CMe{=\!=}CH\\C(C_8H_{17}):CH\end{matrix}>$. [10°]. (272°). Formed by the action of sodium upon an ethereal solution either of MeI and iodo-octyl-thiophene or of octyl bromide and iodo-methyl-thiophene (Schweinitz, *B.* 19, 648). Bromine forms $C_{13}H_{21}BrS$ [20°].

METHYL OXALATE *v.* *Methyl ether* of OXALIC ACID.

METHYL-OXALACETIC ETHER $C_9H_{14}O_5$ *i.e.* $CO_2Et.CO.CHMe.CO_2Et$. *Oxaloxyl-propionic ether.* (138° at 23 mm.). Formed by the action of NaOEt on an ethereal solution of oxalic and propionic ethers (Wislicenus a. Arnold, *B.* 20, 3394; *A.* 246, 329). Formed also from sodium oxalacetic ether and MeI at 100°. Colourless oil, v. sol. alcohol and ether. Its alcoholic solution gives a red colouration with $FeCl_3$. Split up by boiling alcoholic potash into oxalic and propionic acids. Boiling dilute H_2SO_4 yields ethyl-glyoxylic acid.

Salt.—$CO_2Et.CO.CNaMe.CO_2Et$. Does not crystallise from alcohol.

Phenyl-hydrazide $CO_2Et.C(N_2HPh).CHMe.CO_2Et$. [100°]. Small plates, v. sol. ether and benzene. Its solution in conc. H_2SO_4 is coloured reddish-violet by $FeCl_3$. At 120° it gives off alcohol, forming a derivative of pyrazole.

METHYL-OXALYL-UREA *v.* PARABANIC ACID.

METHYL-OXAMIC ACID *v.* OXALIC ACID.

METHYL-OXAMIDE *v.* OXALIC ACID.

METHYL-OXANTHRANOL *v.* OXANTHRANOL.

METHYL-OXAZOLE DIHYDRIDE C_4H_7NO *i.e.* $\begin{matrix}CH_2.O\\|\\CH_2.N\end{matrix}\!\!>\!CMe$. Formed, in small quantity, by the action of Ac_2O and NaOAc on bromo-ethylamine $Br.CH_2.CH_2.NH_2$ (Gabriel, *B.* 22, 2221; 23, 2502). Oil, with sweet smell, somewhat like quinoline.—$B'C_6H_2(NO_2)_3OH$. [149°]. Yellow plates.

METHYL-OXETHYL- *v.* METHYL-OXYETHYL-.

DI-METHYL-OXETONE *v.* *Anhydride* of DI-γ-OXY-DI-BUTYL DIKETONE.

DI-METHYL OXIDE C_2H_6O *i.e.* $(CH_3)_2O$. *Methyl ether.* Mol. w. 46. (–24°) (Regnault, *J.* 1863, 70). V.D. 1·617. S. (gas) 37 at 18°. H.F.p. 49,640 (Thomsen), 56,800 (Berthelot, *A. Ch.* [5] 23, 185). H.F.v. 48,190 (T.). H.C.p. 344,200 (B.). Formed by heating MeOH with H_2SO_4 (Dumas a. Péligot, *A.* 15, 12; Kane, *A.* 19, 166) or with B_2O_3 (Ebelmen, *A.* 57, 328). Formed also, together with NMe_4Cl and NMe_3HCl, by heating NH_4Cl with excess of MeOH (Weith, *B.* 8, 458). Prepared by heating MeOH (13 pts.) with H_2SO_4 (20 pts.) at 140°. The gas is passed through aqueous KOH to remove SO_2, CO_2, and MeOH, and then into conc. H_2SO_4 which absorbs 600 vols. It is obtained by dropping the solution in H_2SO_4 into an equal volume of warm boiled water, and is dried by passing through tubes containing $CaCl_2$ (Erlenmeyer a. Kriechbaumer, *B.* 7, 699; *cf.* Tellier, *Ar. Ph.* [3] 10, 57).

Properties.—Gas. Combines with HCl forming Me_2OHCl which boils at 2°.

References.—CHLORO- and DI-IODO-DI-METHYL OXIDE.

METHYL-OXINDOLE C_9H_9NO *i.e.* $C_6H_4<\begin{matrix}CH_2\\NMe\end{matrix}>CO$. *Oxy-methyl-indole.* [88°]. Obtained from methyl-indole carboxylic acid by the action of NaOBr, the resulting di-bromo-methyl-oxindole being suspended in alcohol and reduced by sodium-amalgam (Colman, *C. J.* 55, 7; *A.* 248, 120). White needles, sl. sol. cold water and light petroleum, v. sol. alcohol, ether, acetone and benzene. Dissolves in hot alkalis without change. Partially decomposes when heated much above its melting-point. Does not react with phenyl-hydrazine. Bromine-water gives a crystalline pp. Nitrous acid converts it into $C_6H_4<\begin{matrix}C(NOH)\\NMe\end{matrix}>CO$, the oxim of methyl-ψ-isatin.

Di-chloro-methyl-oxindole $C_6H_4<\begin{matrix}CCl_2\\NMe\end{matrix}>CO$. [147°]. Formed by adding a solution of sodium methyl-indole carboxylate to a cold solution of NaOCl (Colman). Colourless needles, v. sol. hot alcohol and acetone, m. sol. ether. Not decomposed at 210°.

Bromo-methyl-oxindole $C_6H_4<\begin{matrix}CHBr\\NMe\end{matrix}>CO$ [134°]. Formed, together with methyl-oxindole, by reducing di-bromo-methyl-oxindole with sodium-amalgam. Lustrous white plates, v. sl. sol. cold water, v. sol. hot alcohol. Not decomposed by boiling aqueous KOH.

Di-bromo-methyl-oxindole $C_6H_4<\begin{matrix}CBr_2\\NMe\end{matrix}>CO$. [204°]. Formed by the action of NaOBr on methyl-indole carboxylic acid (Fischer, *B.* 17, 564). Yellowish-white tables, v. sol. alcohol, insol. cold water. Melts at 204° when quickly heated, but 180° when slowly heated. Converted by boiling water into methyl-ψ-isatin. Phenyl-

hydrazine gives the phenyl-hydrazide of methyl-ψ-isatin.

Di-methyl-oxindole $C_{10}H_{11}NO$ *i.e.* $\left[5{:}3{:}\begin{matrix}1\\2\end{matrix}\right]C_6H_2(CH_3)_2<\begin{matrix}CH_2\\NH\end{matrix}>CO$. *Carbomesyl. Anhydride of amido-di-methyl-phenyl-acetic acid.* [232°]. Prepared by reduction of (2:5:3:1)-nitro-di-methyl-phenyl-acetic acid with tin and HCl (Wispeh, *B.* 16, 1580). Sublimable. White needles. Sol. hot alcohol and hot benzene. sl. sol. hot water and cold alcohol and ether, insol. cold water.

Methyl-di-oxindole $C_6H_4<\begin{matrix}CH(OH)\\NMe\end{matrix}>CO$. *Di-oxy-methyl-indole.* [151°]. Formed by reducing methyl-ψ-isatin with sodium-amalgam or with zinc and HCl (Colman, *C. J.* 55, 8; *A.* 248, 121). Needles or prisms (from benzene); m. sol. water, alcohol, and benzene. Oxidising agents reconvert it into methyl-ψ-isatin.

METHYL-OXY-BENZOYL-GLYCOCOLL *v.* ANISURIC ACID.

METHYL OXYBUTENYL KETONE DI-CARBOXYLIC ACID ANHYDRIDE $C_8H_8O_5$ *i.e.* $CH_3.CO.CH<\begin{matrix}C(CO_2H)\\CO.O\end{matrix}>CMe$. *Isocarbopyrotritaric acid.* Obtained from its ether by boiling with 20 p.c. aqueous NaOH, and ppg. with dilute H_2SO_4 (Knorr, *B.* 22, 163). Possesses great reducing power. Decomposes at 200°–209°, leaving an oil $C_7H_8O_3$, which solidifies on cooling. This is composed of two bodies, one being an acid v. sl. sol. most solvents and melting at 175°, the other crystallising from ether in long prisms [60°], and giving an acid solution in water. Water forms acetonyl-acetone.

Ethyl ether EtA′. [110°]. (c. 280° at 15 mm.). Obtained by heating di-acetyl-succinic ether at 170°–180°, pyrotritaric and carbopyrotritaric ethers being also formed (Knorr, *B.* 22, 159). Slender needles (from hot water), v. sl. sol. water and dilute acids, v. sol. alkalis, ether, chloroform, and hot alcohol. Possesses great reducing power. $FeCl_3$ gives a fine blue colour to its solution. With phenyl-hydrazine it yields di-oxy-di-phenyl-di-methyl-dipyrazyl

$$\begin{array}{l}N.NPh.CO\quad CO.NPh.N\\ \|\qquad\quad |\qquad\ \ |\qquad\quad \|\\ C(CH_3).CH—CH——CMe\end{array}$$

. Hydroxylamine appears to form the corresponding di-oxy-di-methyl-dioxazyl

$$\begin{array}{l}N.O.CO\ \ CO.O.N\\ \|\qquad |\qquad |\qquad \|\\ CMe.CH.CH——CMe\end{array}$$

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DI-METHYL-DI-OXY-BUTYLENE DI-KETONE $CH_3.CO.CMe(OH).CMe(OH).CO.CH_3$. [96°]. Formed by reducing di-methyl diketone with zinc-dust and dilute H_2SO_4 (Von Pechmann, *B.* 21, 1411). Needles (from ligroïn). Reduces Fehling's solution in the cold. $FeCl_3$ re-converts it into Me.CO.CO.Me.

METHYL OXY-BUTYL KETONE $C_6H_{12}O_2$ *i.e.* $CH_3.CO.CH_2.CH_2.CH_2.CH_2OH$. *Acetyl-butyl-alcohol.* (227°). S.G. $\frac{4}{4}$ ·997; $\frac{15}{15}$ ·989; $\frac{25}{25}$ ·982. M.M. 6·502 at 18·5°. Obtained by boiling the anhydride of its carboxylic acid with water, CO_2 being evolved (Perkin, jun., *C. J.* 51, 717). Thick oil with sweet burning taste. Does not reduce Fehling's solution or ammoniacal $AgNO_3$ in the cold, but reduces both these reagents on warming. Yields an oily phenyl-hydrazide. Warm conc. HNO_3 gives a dark-pink colour. Iodine and KOH give iodoform. Chromic acid mixture oxidises it to acetic and succinic acids.

METHYL OXY-BUTYL KETONE ANHYDRIDE $C_6H_{10}O$ *i.e.* $O<\begin{matrix}CH_2.CH_2\\CMe{:}CH\end{matrix}>CH_2$. *Methyl-furidane dihydride.* '*Acetyl-tetramethylene.*' '*Tetramethylene methyl ketone.*' *Anhydride of aceto-butyl alcohol.* (109°). S.G. $\frac{4}{4}$ ·9227; $\frac{15}{15}$ ·9127; $\frac{25}{25}$ ·9050. M.M. 6·074 at 22·5°. Formed by distilling its carboxylic acid at 150° (Perkin, jun., *C. J.* 51, 723; *B.* 19, 2558). Colourless mobile liquid with ethereal odour. On prolonged standing in presence of water it is converted into methyl oxy-butyl ketone.

Methyl oxy-butyl ketone anhydride carboxylic acid $C_7H_{10}O_3$ *i.e.* $O<\begin{matrix}CH_2.CH_2.CH_2\\CMe{:}C(CO_2H)\end{matrix}>$. [119°]. Obtained by saponifying its ether with alcoholic potash (Perkin, jun., *C. J.* 51, 715). Colourless needles, v. sol. hot benzene, alcohol, chloroform, and light petroleum, v. e. sol. water. Decomposes above 119° into CO_2 and the preceding body. When heated with aqueous NH_3 at 200° it yields CO_2, methyl oxy-butyl ketone, and a volatile base (probably a derivative of pyridine). Bromine-vapour gives $C_7H_6BrO_3$, a thick syrup. Conc. HBrAq yields methyl bromo-butyl ketone.

Salts.—NH_4A': white crystalline solid, v. sol. water.—CuA'_2 aq: light-green powder, v. sl. sol. water, decomposed at 90°–100°.—AgA′: white crystalline solid, v. sol. water, decomposed on boiling with water or exposure to light.

Ethyl ether EtA′. [9°]. (227°). V.D. 6·21. M.M. 10·069 at 23·7°. S.G. $\frac{15}{15}$ 1·069; $\frac{25}{25}$ 1·0626. μ_A 1·4697. μ_D 1·4772. Formed by heating a mixture of NaOEt with aceto-acetic ether and trimethylene bromide (Perkin, jun., *C. J.* 51, 709). Colourless oil, with a disagreeable camphor-like odour. Does not react with phenyl-hydrazine. Does not contain an atom of hydrogen displaceable by sodium. With PCl_5 it forms $C_9H_{13}O_2Cl$, a colourless oil (212°–215°).

Methyl oxy-butyl ketone anhydride dicarboxylic acid $C_8H_{10}O_5$ *i.e.*

$$O<\begin{array}{l}CH_2.\ CH_2.\ CH_2\\ \qquad\qquad\ \ |\\ C(CH_2.CO_2H){:}C.CO_2H\end{array}$$

. [185°–190°]. Obtained by saponification of its ethers by boiling alcoholic potash (Perkin, jun., *C. J.* 51, 744). Colourless hexagonal plates, v. sol. hot water and hot alcohol, sl. sol. acetic ether, benzene, and ether. Decomposes on fusion, giving off CO_2, and leaving a red liquid.

Mono-ethyl ether

$$O<\begin{array}{l}CH_2.\ CH_2.\ CH_2\\ \qquad\qquad\ \ |\\ C(CH_2.CO_2H){:}C.CO_2Et\end{array}$$

. [114°]. Obtained by treating the di-ethyl ether with conc. alcoholic potash in the cold. Transparent four-sided triclinic needles, $a{:}b{:}c = ·774{:}1{:}·337$; $\alpha = 89°\ 40'$; $\beta = 98°\ 18'$; $\gamma = 89°\ 50'$. V. sol. alcohol and ether, sl. sol. hot water.—AgEtA″: white curdy pp., sl. sol. water.

Di-ethyl ether Et_2A''. (239° at 150 mm.). Obtained by the action of NaOEt on a mixture of trimethylene bromide and acetone di-carboxylic ether $CO_2Et.CH_2.CO.CH_2.CO_2Et$ (Perkin, jun., *C. J.* 51, 739). Thick, colourless oil, with disagreeable odour.

METHYL-OXY-CONIINE *v.* CONIINE.

METHYL-OXY-ETHYL-AMIDO-PHENOL. *Methyl ether* $C_{10}H_{15}NO_2$ *i.e.* [2:1]$C_6H_4(OMe).NMe.CH_2.CH_2OH$. *Methyl-oxy-ethyl-anisidine.* (290°). Formed by the action of $C_6H_4(OMe).NHMe$ on ethylene chlorhydrin (Knorr, *B.* 22, 2098). Liquid.

Anhydride $C_6H_4\left\langle\begin{array}{l}O-CH_2\\ \quad\;\;\,|\\ NMe.CH_2\end{array}\right.$. *Methyl-quinazoxine dihydride.* (261°). Formed by boiling the methyl ether with caustic soda (Knorr, *B.* 22, 2098). Liquid, with irritating smell, volatile with steam, very easily oxidised by contact with air.—B'HCl. [162°]. Short four-cornered plates (from alcohol).

METHYL-OXY-ETHYL-AMINE C_3H_9NO *i.e.* $CH_3.NH.CH_2.CH_2OH$. (130°–140°). Formed from ethylene chlorhydrin (1 mol.) and methyl-amine (1 mol.) (Knorr, *B.* 22, 2088). Oil, with strong ammoniacal smell, v. sol. water, alcohol, and ether.—Aurochloride. [110°–120°]. Anhydrous prisms, v. sol. water.

Methyl-di-oxy-di-ethyl-amine $C_5H_{13}NO_2$ *i.e.* $CH_3.N(CH_2.CH_2OH)_2$. (250°–255°). Formed by heating ethylene chlorhydrin with excess of aqueous methylamine at 100° (Morley, *B.* 13, 222). Formed also by the action of ethylene chlorhydrin on the preceding body (Knorr, *B.* 22, 2081). Viscid oil, v. sol. water, not volatile with steam.—B'HCl: thick syrup.—$B'_2H_2PtCl_6$: orange-red prisms.—Aurochloride: v. sol. water.

Methylo-chloride $C_6H_{16}NO_2Cl$ *i.e.* $ClNMe_2(CH_2.CH_2OH)_2$. Formed by heating ethylene chlorhydrin with a solution of dimethyl-amine at 100° (Morley, *B.* 13, 223). Formed also from di-methyl-oxy-ethyl-amine and ethyl-ene chlorhydrin (Knorr, *B.* 22, 2089). Thick syrup.—$(C_6H_{16}NO_2Cl)_2PtCl_4$ aq. [218°]. Small yellow crystals, v. sol. water, sl. sol. alcohol.—Aurochloride: [233°]; small plates, v. sol. hot water.

Anhydride $CH_3.N\left\langle\begin{array}{l}CH_2.CH_2\\ CH_2.CH_2\end{array}\right\rangle O$. *Methyl-pyroxazine tetrahydride.* (117°). Formed by heating methyl-di-oxy-di-ethyl-amine with SO_3 (K.). Mixes with water, alcohol, and ether. Readily combines with MeI.—Hydrochloride: [205°]; long hygroscopic prisms.—Platino-chloride: needles (from dilute alcohol), v. sol. water.—Aurochloride: [183°]; small needles, m. sol. water.

Methylo-iodide of the anhydride. Long needles. With Ag_2O it yields a methylo-hydroxide, which is split up by heat into alde-hyde and di-methyl-oxy-ethyl-amine.

Methylo-chloride of the anhydride. Crystalline mass. Forms a platinochloride crys-tallising from alcohol in needles, and an auro-chloride, both being v. sol. water.

Di-methyl-oxy-ethyl-amine $C_4H_{11}NO$ *i.e.* $NMe_2.CH_2.CH_2OH$. *Di-methyl-ethyl-alkine.* (130°). Prepared from dimethylamine and ethylene chlorhydrin (Ladenburg, *B.* 14, 2408). Formed also by heating 'methyl-morphi-methine' (*v.* MORPHINE) with Ac_2O at 160°–190° (Knorr, *B.* 22, 1114). Liquid.—B'_2HAuCl_4: needles, sol. hot water.—$B'_2H_2PtCl_6$: easily soluble prisms.

Acetyl derivative $C_4H_{10}AcNO$. Forms an aurochloride $B'HAuCl_4$, crystallising in plates.

Methylo-hydroxide v. NEURINE.

TRI-METHYL-OXYETHYL-AMMONIUM HYDROXIDE *v.* NEURINE.

METHYL-OXYETHYL ANILINE $C_9H_{13}NO$ *i.e.* $C_6H_5.N(CH_3)(C_2H_4.OH)$. *Methyl-phenyl-ethyl-alkine.* (218° at 110 mm.). S.G. $\frac{0}{}$ 1·0806. Obtained by heating methyl-aniline with ethylene-chlorhydrin at 100° (Laun, *B.* 17, 675). Colourless oil. Weak base. By exposure to air it is oxidised to a thick blue syrup.

Methylo-iodide B'MeI: colourless plates or tables.

Methylo-periodide $B'MeI_3$: [87°]; greenish glistening plates.

METHYL α-OXY-ETHYL KETONE $C_4H_8O_2$ *i.e.* $CH_3.CO.CH(OH).CH_3$. (142°). *Ketoxy-butane.* Formed by reducing di-methyl diketone with zinc and H_2SO_4 (Von Pechmann, *B.* 22, 2214; 23, 2421). Colourless liquid, miscible with water. Reduces Fehling's solution. Reacts with phenyl hydrazine, with formation of the compounds $CH_3.C(N_2HPh).CH(OH).CH_3$ [84°] and $CH_3.C(N_2HPh).C(N_2HPh).CH_3$.

METHYL-OXY-ETHYL-PYRIDINE *v.* TROP-INE.

METHYL-OXY-ETHYL-*p*-TOLUIDINE $C_{10}H_{15}NO$ *i.e.* $CH_2OH.CH_2.NMe.C_6H_4Me$. (290°–300°). Formed from oxy-ethyl-toluidine and MeI at 60° (Demole, *A.* 173, 129). Liquid.—B'HI.—$B'_2H_2PtCl_6$.

Methylo-iodide B'MeI. Liquid. Yields $B'_2Me_2PtCl_6$ and $B'MeAuCl_4$.

METHYL-OXY-GLUTARIC ACID *v.* OXY-METHYL-GLUTARIC ACID.

TRI-METHYL-TRI-OXY-HYDROBENZ-AMIDE *v.* ANISHYDRAMIDE.

TETRA-METHYL-OXY-TRIMETHYLENE-DIAMINE $C_7H_{18}N_2O$ *i.e.* $HO.CH(CH_2.NMe_2)_2$. *Tetra-methyl-oxy-propylene-diamine. Tetra-methyl-allyl-alkine.* (170°–185°). Formed by heating *s*-dichlorhydrin $CH_2Cl.CH(OH).CH_2Cl$ with dimethylamine in a sealed tube at 60° (Berend, *B.* 17, 510). The liquid is rendered alkaline by KOH and extracted with chloroform. Liquid, v. e. sol. water.—$B'_2H_2PtCl_6$: yellow plates, m. sol. water.

DI-METHYL-TRI-OXY-PHENYL-BENZYL-KETONE *v.* ANISOÏN.

DI-METHYL-OXY-PROPYL-AMINE $C_5H_{13}NO$. (126°). Prepared by the action of dimethylamine on propylene chlorhydrin at 100° (Morley, *C. R.* 91, 333; Ladenburg, *B.* 14, 2407). Liquid.—$B'_2H_2PtCl_6$: prisms, v. sol. water.

Methylo-chloride B'MeCl. Prepared by heating aqueous trimethylamine with propylene chlorhydrin at 100° (Morley, *C. R.* 91, 333; *B.* 13, 1805). Colourless, very hygroscopic crystals, turning brown in light. Forms a platinochloride $B'_2Me_2PtCl_6$, crystallising in yellow feathery plates, insol. alcohol and ether, v. sol. water.

Methylo-hydroxide B'MeOH. From the chloride and moist Ag_2O. Alkaline syrup. De-composed on distillation into NMe_3 and propylene glycol (Morley, *C. J.* 41, 389).

Di-methyl-dioxypropyl-amine $C_5H_{13}NO_2$ *i.e.* $NMe_2.CH_2.CH(OH).CH_2(OH)$. *Di-methyl-propyl-glycolline.* (217°). Formed by heating di-methyl-amine with glycerin chlorhydrin (Roth, *B.* 15, 1153). Colourless oil. Sol. water, alco-hol, and ether.—$B'_2H_2Cl_2PtCl_4$.

Methylo-chloride $C_6H_{16}NO_2Cl$ *i.e.* $NMe_3Cl.CH_2.CH(OH).CH_2(OH)$. From glycerin chlorhydrin and NMe_3 at 100° (V. Meyer, *B.* 2, 186; Hanriot, *A. Ch.* [5] 17, 99). Crystals, v. e. sol. water. — $(C_6H_{16}NO_2Cl)_2PtCl_4$: tables. — $C_6H_{16}NO_2AuCl_4$. [190°]. Orange crystals.

METHYL-OXYPROPYL-ANILINE $C_{10}H_{15}NO$ *i.e.* $C_6H_5.N(CH_3)C_3H_6.OH$. *Methyl-phenyl-propyl-alkine.* (262°). Colourless liquid. Formed by heating methyl-aniline with propylene chlorhydrin (Laun, *B.* 17, 678).

METHYL β-OXYPROPYL KETONE $C_5H_{10}O_2$ *i.e.* $CH_3.CO.CH_2.CH_2.CH_2OH$. *Acetyl-propyl alcohol.* (145°) at 100 mm.; (209°) at 729 mm. V.D. 2·25 (calc. 3·53). S.G. $\frac{15}{15}$ 1·0051; $\frac{25}{25}$ ·9990. M.M. 5·544 at 25°. Formed by boiling trimethylene methyl ketone carboxylic acid (derived from aceto-acetic ether, sodium, and ethylene bromide) with water, CO_2 being evolved (Perkin, jun., *C. J.* 51, 829). Formed also by boiling bromo-ethyl aceto-acetic ether with aqueous HCl. Thick syrup, miscible with water, v. sol. alcohol and ether. Decomposed by heat into water and its anhydride, which reunite in the cold; does not reduce cold ammoniacal silver nitrate, but reduces it on warming. Gives with phenyl-hydrazine solution an oily precipitate of $C_{11}H_{14}N_2$ or $CH_2\left\langle\begin{array}{l}CMe{:}N\\ CH_2.CH_2\end{array}\right\rangle NC_6H_5$. Oxidised by $K_2Cr_2O_7$ and H_2SO_4 to acetyl-propionic (levulic) acid (Colman a. Perkin, *C. J.* 53, 189; 55, 352; Lipp, *B.* 22, 1196). Reduced by sodium-amalgam to $CH_3.CH(OH).CH_2.CH_2.CH_2OH$ (Perkin, jun., a. Freer, *B.* 19, 2566). With $NaHSO_3$ it forms $CH_3.C(C_3H_6OH)(OH).SO_3Na\,1\frac{1}{2}aq$: needles, v. sol. water and alcohol.

Acetyl derivative $CH_3.CO.C_3H_6OAc$ (214° i.V.) at 728 mm. S.G. $\frac{0}{0}$ 1·0356. V.D. 5·02 (calc. 4·98). Liquid, m. sol. water, v. e. sol. alcohol and ether.

Benzoyl derivative $CH_3.CO.C_3H_6OBz$. (297°).

Anhydride $CH_3.C\left\langle\begin{array}{l}CH.CH_2\\ \quad\ \ |\\ O\ .\ CH_2\end{array}\right.$. (72°–75°).

Formed by slow distillation of the ketone. Water converts it into the flocculent isomeride $CH_2{:}C\left\langle\begin{array}{l}CH_2.CH_2\\ \quad\ \ |\\ O\ .\ CH_2\end{array}\right.$ (111°) at 718 mm., which reddens pine-wood moistened by HCl *v.* METHYLENE-FURFURANE TRIHYDRIDE.

Methyl ω-oxy-propyl ketone $C_5H_{10}O_2$ *i.e.* $CH_3.CO.CH(OH).CH_2.CH_3$. (153°); (77° at 35 mm.). S. G. $\frac{17.5}{4}$ ·972. Formed by reducing methyl ethyl diketone with zinc and dilute H_2SO_4 (Von Pechmann, *B.* 23, 2421). Colourless liquid with sweet smell; sol. water, but separated from the solution by NaCl or NaOH. Readily oxidised to $CH_3.CO.CO.C_2H_5$. Reduced by sodium-amalgam to $CH_3.CH(OH).CH(OH).C_2H_5$ (187°), which is oxidised by bromine-water in sunlight to $CH_3.CO.CO.C_2H_5$. Excess of phenyl hydrazine forms $CH_3.C(N_2HPh).CO.C_2H_5$ [103°].

Methyl α-oxy-propyl ketone $C_5H_{10}O_2$ *i.e.* $CH_3.CO.CH_2.CH(OH).CH_3$. (128°). Formed by adding chloro-acetic ether to sodium under ether, decomposing the resulting sodium compound by HCl, reducing by zinc-dust the ether $C_8H_{13}ClO_4$ (157° at 45 mm.) which is then formed, and boiling the product $C_8H_{14}O_4$ (106° at 14 mm.), with dilute HCl, when it splits up into CO_2, alcohol, and the oxy-ketone (Fittig, *B.* 21, 2138). Colourless mobile liquid, miscible with water. Forms compounds with $NaHSO_3$, and with phenyl-hydrazine.

Methyl ω-oxy-isopropyl ketone. *Oxim of the nitrate* $(CH_3)_2C(ONO_2).C(NOH).CH_3$. *Pentane nitroso-nitrate.* Formed by the action of amyl nitrite and nitric acid on amylene $(CH_3)_2C{:}CH.CH_3$ (38°) dissolved in HOAc (Wallach, *A.* 248, 162). Monoclinic crystals, $a{:}b{:}c$ = ·977:1:1·449; β = 83° 32′ (from benzene), or needles (from HOAc).

METHYL-OXY-QUINIZINE *v.* OXY-PHENYL-METHYL-PYRAZOLE.

METHYL-OXY-QUINOLINE *v.* OXY-METHYL-QUINOLINE.

METHYL-OXY-SUCCINIC ACID *v.* OXY-METHYL-SUCCINIC ACID.

METHYL-PARABANIC ACID *v.* PARABANIC ACID.

METHYL-PARACONIC ACID *v.* *Anhydride* of OXY-ETHYL-SUCCINIC ACID.

TETRA-METHYL-PARALEUCANILINE *v.* TETRA-METHYL-TRI-AMIDO-TRI-PHENYL-METHANE.

METHYL PENTADECYL KETONE $C_{17}H_{34}O$ *i.e.* $CH_3.CO.C_{15}H_{31}$. [48°]. (246°) at 110 mm.; (320° uncor.) at 760 mm. S.G. (liquid) $\frac{48}{}$ ·814. Prepared by distilling a mixture of barium palmitate and barium acetate (Krafft, *B.* 12, 1671). On oxidation it gives pentadecoic acid.

Methyl pentadecyl ketone $CH_3.CO.CH(C_7H_{15})_2$. *Di-n-heptyl-acetone.* (300°–304°). S.G. $\frac{17}{17}$ ·826. Formed by boiling di-heptyl-acetoacetic ether with dilute aqueous KOH (Jourdain, *A.* 200, 115). Oil, smelling of peppermint. Forms a crystalline compound with $NaHSO_3$.

METHYL-PENTANE *v.* HEXANE.

DI-METHYL-PENTENYLAMINE $C_7H_{15}N$ *i.e.* $CH_2{:}CH.CH_2.CH_2.CH_2.NMe_2$. This constitution is assigned by Merling to Ladenburg's di-methyl-piperidine, *v.* DI-METHYL-PYRIDINE HEXAHYDRIDE.

Di-methyl-pentenylamine. *Methylo-hydroxide* $C_5H_9NMe_3OH$. Formed from amylene bromide and trimethylamine at 55° (Schmiedeberg a. Harnack, *J.* 1867, 805). — $(C_5H_9NMe_3Cl)_2PtCl_4$ aq. Irregular laminæ.

(β)-METHYL-PENTHIOPHENE C_6H_8S *i.e.* $S\left\langle\begin{array}{l}CH{:}CMe\\ CH{:}CH\end{array}\right\rangle CH_2$. (134°). S.G. $\frac{19}{19}$ ·9938. Formed by distilling sodium α-methyl-glutarate $CO_2Na.CHMe.CH_2.CH_2.CO_2Na$ (5 g.) with P_2S_3 (10 g.) at 180°–250° (Krekeler, *B.* 19, 3270). Colourless oil. When successively mixed with a solution of isatin in HOAc and conc. H_2SO_4 it gives a dark-green colour, and, on adding water, a green pp. Phenanthraquinone and H_2SO_4 (Laubenheimer's reagent) give a dark-violet colour. Phenyl-glyoxylic acid yields a violet dye. Alkaline $KMnO_4$ (·3 p.c.) produces acetic and oxalic acid. Nitric acid forms a nitro-derivative, and bromine a bromo- derivative.

Methyl-penthienyl methyl ketone $C_8H_{10}SO$ *i.e.* $SC_5H_4Me.CO.CH_3$. (234°).

Oxim $SC_5H_4Me.C(NOH).CH_3$. [68°].

METHYL-PHENACYL-ANILIDE *v.* α-PHENYL-AMIDO-PHENYL ETHYL KETONE.

METHYL - PHENACYL - BROMIDE *v.* α-Bromo-phenyl ethyl ketone.

METHYL-PHENANTHRIDENE *v.* Phenyl-indole.

METHYL-PHENANTHROLINE $C_{13}H_{10}N_2$ *i.e.*

CH: N.C.CH:CH.C.CH:CH
| || || | . [65°]. (above
CH:CH.C———C . N:CMe

360°). Formed, together with an isomeride, when *m*-amido-(*Py.* 3)-methyl-quinoline (100 g.) is boiled with o-nitro-phenol (75 g.), glycerin (320 g.), and H_2SO_4 (270 g.). The product is diluted with water and evaporated to remove o-nitrophenol. The resinous mass that is ppd. on adding NaOH is extracted with benzene, and the dark oily mixture of bases so obtained treated with HCl. The hydrochlorides are washed with alcohol, dissolved in water, decomposed by NH_3, and the bases again extracted with benzene. From the crystalline mixture of bases left after evaporating the benzene, ether extracts methyl-phenanthroline only (Gerdeissen, *B.* 22, 246).

Properties.—White needles (containing 3 aq). Melts at 50° when hydrated, 65° when anhydrous. Sol. boiling water, alcohol, and ether; v. sol. cold benzene. On oxidation with $KMnO_4$ it yields phenanthroline carboxylic acid $C_{12}H_7N_2.CO_2H$ [209°], which decomposes at 210° into CO_2 and phenanthroline.

Salts.—B'HCl aq: small snow-white needles, sl. sol. cold, v. sol. hot, water, m. sol. alcohol, insol. ether.—$B'H_2SO_4$ aq: slender silky needles (from alcohol).—$B'_2H_2Cr_2O_7$: red prisms (from hot water).—$B'H_2PtCl_6$ aq: flesh-coloured crystalline pp., insol. hot water, sl. sol. alcohol.—Picrate $B'C_6H_2(NO_2)_3OH$. [217°]. Transparent yellow needles (from boiling alcohol).

Ethylo-iodide B'EtI 2aq. [100°–110°]. Glittering brown crystals. Yields the platinochloride $B'EtClH_2PtCl_6$ (?) which forms orange-red crystals.

Isomeride $C_{13}H_{10}N_2$ *i.e.*

CH : N . C.CH:C. N : CMe
| || | | . [109°]. Occurs in the
CH:CH.C.CH:C.CH:CH

preparation of the preceding, from which it differs in being insol. ether (G.). Crystallises from alcohol in concentric groups of satiny needles (containing 4aq). Melts at 82° when hydrated and 109° when anhydrous. The anhydrous base is a light white powder, v. sol. warm benzene and hot dilute alcohol, insol. cold ether, v. sl. sol. hot ether.

Methyl-phenanthroline

CH:N . C———C . N : CMe
| || || | . [76°]. Prepared
CH:CH.C.CH:CH.C.CH:CH

from *o*-amido-(*Py.* 3)-methyl-quinoline, glycerin, o-nitro-phenol, and H_2SO_4 (Gerdeissen). Crystals (containing 2aq). Melts at 53° when hydrated, and at 76° when anhydrous. V. e. sol. hot benzene, v. sol. chloroform, m. sol. HOAc, sl. sol. ether and light petroleum. Decomposed on distillation.

Methyl-phenanthroline

CH : N . C.CMe:CH.C.CH:CH
| || || | . [96°]. (above
CH:CH.C ——— C . N : CH

300°). Prepared by boiling *m*-tolylene-diamine hydrochloride (40 g.) with nitrobenzene (30 g.), glycerin (100 g.), and H_2SO_4 (100 g.); and purified by means of the chromate (Skraup a. Fischer, *M.* 5, 523). Short prisms (containing 5aq), more soluble in cold than in hot water; v. sol. alcohol. Its solutions give a white crystalline pp. with $AgNO_3$ and a blue crystalline pp. with cupric acetate. Chromic acid mixture oxidises it to the corresponding phenanthroline carboxylic acid.

Salts.—B'HCl 4aq: transparent needles.—$B'_2H_2Cr_2O_7$: red, sparingly soluble needles.—$B'_2H_2PtCl_6$ 2aq: yellow crystalline pp.—Picrate [253°].

DI-METHYL-PHENANTHROLINE TETRAHYDRIDE

      CH_2:CMe.C——— C . N : CH_2
$C_{14}H_{16}N_2$ *i.e.* | || || | .
      CH_2 : N . C.CH:CH.C.CMe:CH_2

Formed by the action of acetic aldehyde or paraldehyde upon *m*-phenylene-diamine hydrochloride. The resulting base is ppd. by ammonia, dissolved in aqueous HCl, and ppd. by platinic chloride as $B'_2H_2PtCl_6$ (Schiff, *A.* 253, 323).

METHYL-PHENAZINE $C_{13}H_{10}N_2$ *i.e.*

$C_6H_4\langle$ N | N $\rangle C_6H_3Me$. [117°]. (350°). Formed by heating tolylene-o-diamine with pyrocatechin in sealed tubes at 210° (Merz, *B.* 19, 725). Formed also by eliminating the two NH_2 groups by means of the diazo- reaction, from the oxidation product ($C_{13}H_{14}N_4$) of phenylene-*p*-diamine and tolylene-*m*-diamine (Bernthsen a. Schweitzer, *B.* 19, 2604; *A.* 236, 345). Needles (by sublimation), v. sl. sol. water and ligroïn, v. sol. alcohol and ether. Its solution in conc. H_2SO_4 is blood-red. It dissolves in conc. HClAq, but the base is ppd. again on dilution.—Salts.—$B'_2H_2PtCl_6$ 6aq: yellow laminæ (from water).—$B'_2H_2PtCl_6$ 3aq (from dilute alcohol).—Picrate $B'C_6H_2(NO_2)_3OH$. [168°]. Yellow nodules which blacken on fusion.

METHYL-PHENTRIAZINE $C_8H_7N_3$ *i.e.*

$C_6H_4\langle$ N.CMe | || N.N $\rangle$. [89°]. (250°–255°). Formed by the action of sodium-amalgam on acetyl *o*-nitro-phenyl-hydrazine in alcohol, the solution being kept acid with HOAc, and the temperature below 30° (Bischler, *B.* 22, 2806). Crystals, partially decomposed on distillation. V. sol. cold water, v. e. sol. alcohol, sl. sol. hot ligroïn.

Bromo-methyl-phentriazine $C_8H_6BrN_3$ *i.e.*

CBr:CH.C.N.CMe
| || | || . [115°]. Formed from
CH: CH.C.N.N

acetyl-*p*-bromo-o-nitro-phenyl-hydrazine by like treatment (Bischler a. Brodsky, *B.* 22, 2818). Golden plates, sl. sol. cold, v. sol. hot, water.

(α) - **METHYL - PHENTETRAZINE DIHYDRIDE** $C_7H_8N_4$ *i.e.* $C_6H_4\langle$ NH . N || NMe.N $\rangle$. [62°].

Formed by the action of sodium nitrate on a very dilute hydrochloric acid solution of *o*-amido-phenyl-methyl hydrazine (Hempel, *J. pr.* [2] 41, 176). Colourless plates, v. sol. ether and benzene, sl. sol. alcohol and petroleum ether. Sol. hot conc. NaOHAq. Conc. HNO_3 at 80°–100° yields a product [127°] crystallising from alcohol in golden-yellow prisms and needles.

TRI-METHYL PHENENYL TRIKETONE $C_{12}H_{12}O_3$ *i.e.* $C_6H_3(CO.CH_3)_3$. [163°]. *Tri-acetyl-benzene.* Formed by the action of NaOEt in ether on a mixture of acetone (1 mol.) and allyl formate (1 mol.). Sodium aceto-acetic aldehyde slowly separates, and is then dissolved in ice-cold water and neutralised by HOAc. The free aceto-acetic aldehyde changes to tri-acetyl-benzene and water (Claisen a. Stylos, *B.* 21, 1145). Small needles, sl. sol. water, alcohol, and ether, v. sol. HOAc. Oxidised by HNO_3 to trimesic acid.

METHYL - (αβ) - PHEN - NAPHTHAZINE $C_{17}H_{12}N_2$ *i.e.* $C_6H_4\left\langle\begin{array}{l}CH{:}CH.C.N.C.CH{:}CMe\\ \qquad\qquad C.N.C.CH{:}CH\end{array}\right.$ [142°]. Formed by the action of (β)-naphtho-quinone on tolylene-diamine in HOAc (Hinsberg, *A.* 237, 342).

Methyl-(ββ)-phen-naphthazine $C_6H_4\left\langle\begin{array}{l}CH{:}C.N.C.CH{:}CMe\\ CH{:}C.N.C.CH{:}CH\end{array}\right.$. [180°]. Formed by oxidation of a mixture of (β)-naphthol and tolylene o-diamine with alkaline K_3FeCy_6 (Witt, *C. N.* 49, 404). Pale straw-coloured needles, forming an intense red solution in H_2SO_4.

METHYL-PHENOL *v.* Cresol.

Di-methyl-phenol *v.* Xylenol.

Tri-methyl-phenol $C_6H_2Me_3.OH$ [1:2:3:5]. *Hemimellithenol. Hemellithenol.* [81°]. Formed by fusing hemimellithene sulphonic acid with KOH (O. Jacobson, *B.* 19, 2518). Needles (from ether). Gives no pp. with $FeCl_3$.

Tetra-methyl-phenol $C_6HMe_4.OH$ [1:2:3:4:5]. [81°] (L.); [87°] (T.); (249° uncor.) (L.); (266° i.V.) (T.). Formed by the action of nitrous acid on the corresponding $C_6HMe_4.NH_2$ [66°] (Limpach, *B.* 21, 644), or by fusing *c*-tetra-methyl-benzene sulphonic acid with potash (Töhl, *B.* 21, 907). Long white needles (from very dilute alcohol), v. e. sol. alcohol and ether, m. sol. petroleum ether. Volatile with steam. Bromine forms $C_{10}H_{12}Br.OH$ [151°].

Acetyl derivative $C_{10}H_{13}OAc$. [57°]. Prisms.

Tetra-methyl-phenol $C_6H(CH_3)_4.OH$. [81°]. Formed by the action of nitrous acid on tetra-methyl-phenyl-amine [14°] (Hofmann, *B.* 17, 1916). White crystals. Yields a quinone on distillation with MnO_2 and H_2SO_4.

Ethyl ether $C_6H(CH_3)_4OEt$: (236°); liquid. Formed by the action of alcohol upon the sulphate of tetra-methyl-diazo-benzene (Hofmann, *B.* 17, 197).

Penta-methyl-phenol $C_6(CH_3)_5.OH$. [125°]. (267°). Formed by the action of nitrous acid upon penta-methyl-phenyl-amine (Hofmann, *B.* 18, 1826). Fine white needles. Volatile with steam. Soluble in alcohol. Sparingly soluble in alkalis.

Methyl ether $C_6(CH_3)_5.OCH_3$: [64°]; long needles.

METHYL-DIPHENYL $C_{13}H_{12}$ *i.e.* $C_6H_5.C_6H_4Me$ [3:1]. *Phenyl-tolyl.* (275°). S.G. $\frac{0}{0}$ 1·031. Formed by the action of MeCl upon melted diphenyl in presence of Al_2Cl_6 (Adam, *Bl.* [2] 47, 689; 49, 98; *A. Ch.* [6] 15, 239). Limpid colourless liquid, not solidified at −21°. V. e. sol. methyl alcohol and acetone. Not attacked by $KMnO_4$ either in neutral or alkaline solution. Chromic acid oxidises it to diphenyl *m*-carboxylic acid [161°]. Bromine at 150° forms $C_{12}H_9.CH_2Br$ which when treated with KOEt yields $C_{12}H_9.CH_2OEt$ whence dry gaseous HI liberates phenyl-benzyl-alcohol.

o-**Methyl-diphenyl** $C_{13}H_{12}$ *i.e.* $C_6H_5.C_6H_4Me$[2:1]. (259°). Appears to be formed by treating bromo-benzene mixed with liquid bromo-toluene with sodium (Barbier, *B.* 7, 1548).

p-**Methyl-diphenyl** $C_6H_5.C_6H_4Me$[4:1]. (263°–267°). S.G. $\frac{27}{}$ 1·015. Formed by the action of sodium on an ethereal solution of bromo-benzene and *p*-bromo-toluene (Carnelley, *C. J.* 29, 13). Formed also by passing a mixture of benzene and toluene through a red-hot tube (Carnelley, *C. J.* 37, 701). Solidifies at −2°. Dilute nitric acid oxidises it to diphenyl carboxylic acid. Chromic acid forms terephthalic acid.

Di-methyl-diphenyl $C_{14}H_{14}$ *i.e.* $C_{12}H_8Me_2$. (284°–290°). S.G. $\frac{0}{}$ 1·025. Formed by the action of methyl chloride on diphenyl in presence of Al_2Cl_6 (Adam). Colourless liquid, not solidified at −21°. Oxidised by CrO_3 in HOAc yielding an infusible diphenyl dicarboxylic acid which cannot be sublimed.

Other di-methyl-diphenyls are described as Ditolyls.

s - **DI - METHYL - PHENYLACETAMIDINE** $C_{10}H_{14}N_2$ *i.e.* $C_6H_5.CH_2.C(NHMe)(NMe)$. Formed by the action of alcoholic methylamine on the hydrochloride of phenylacetic imido-ether $C_6H_5.CH_2.C(OEt)(NH)$ (Luckenbach, *B.* 17, 1426). Crystalline solid, v. sol. alcohol.—B'HCl: six-sided prisms. — $B'_2H_2PtCl_6$: small glistening crystals, sol. alcohol, sl. sol. water.

u-**Di-methyl-phenylacetamidine** $C_6H_5.CH_2.C(NMe_2)(NH)$. Formed in the same manner as the preceding, using dimethylamine (L.).—$B'_2H_2PtCl_6$: small needles, sl. sol. water, m. sol. alcohol.

DI-METHYL-PHENYL-ACETIC ACID [5:3:1]$C_6H_3(CH_3)_2.CH_2.CO_2H$. *Mesityl-acetic acid.* [100°] (W.); [97°] (Robinet, *Bl.* [2] 40, 316). (273° at 735 mm.). Formed by the saponification of the nitrile obtained by heating mesityl bromide with KCN (Wispek, *B.* 16, 1578). Long white prisms. Sol. alcohol, ether, and hot water, v. sl. sol. cold water.

Salts.—A'K aq: silky needles.—A'_2Ba 4aq: transparent prisms.—A'_2Ca 3aq: easily soluble thick needles.—A'_2Mg 5aq: long silky needles.—A'Ag: long thin needles.

Tetra-methyl-phenyl-acetic acid $C_{12}H_{16}O_2$ *i.e.* $C_6HMe_4.CH_2.CO_2H$ [5:4:3:2:1]. [125° uncor.]. Formed by reducing the corresponding tetra-methyl-mandelic acid with HI (Claus a. Föhlisch, *J. pr.* [2] 38, 234). Slender needles (from hot water), v. sol. alcohol, ether, and chloroform.—CaA'_2 3aq: silky needles.

TRI-METHYL-PHENYL-AMIDO-CROTONIC ACID *v.* ψ-Cumyl-amido-crotonic acid.

Tetra-methyl-phenyl-amido-crotonic acid *Ethyl ether* $C_6HMe_4.NH.CMe{:}CH.CO_2Et$. [101°]. Obtained by the action of tetra-methyl-phenyl-amine (prepared from ψ-cumidine) on acetoacetic ether (Conrad a. Limpach, *B.* 21, 1655). Large white prisms (from alcohol and ether). At 280°–285° it yields oxy-tetra-methyl-phenyl-di-methyl-pyridine carboxylic acid $C_6HMe_4N\left\langle\begin{array}{l}CMe{:}C(CO_2H)\\ CMe{:}CH\end{array}\right\rangle CO$. [145°].

METHYL-PHENYL-AMINE *v.* TOLUIDINE and METHYL-ANILINE.

Di-methyl-phenyl-amine *v.* XYLIDINE and DI-METHYL-ANILINE.

Tri-methyl-phenyl-amine *v.* MESIDINE and ψ-CUMIDINE.

Tetra-methyl-phenyl-amine $C_6HMe_4(NH_2)$[1:2:3:4:5]. [66°]. (260° uncor.). Obtained by heating isocumidine hydrochloride with MeOH at 250° to 260° under pressure (Limpach, *B.* 21, 644). Nacreous leaflets (from water). May be sublimed. The corresponding $C_6HMe_4(OH)$ melts at 81°.

Formyl derivative [144°]; silky needles (from water).

Acetyl derivative [170°]; silky needles.

Tetra-methyl-phenyl-amine $C_6HMe_4NH_2$ [1:2:3:5:6]. *Isoduridine.* [24°]. (255°). Formed by heating the hydrochlorides of ψ-cumidine or mesidine with MeOH at 300° (Hofmann, *B.* 17, 1912; Nölting a. Baumann, *B.* 18, 1149; Limpach, *B.* 21, 646).—B'HCl.—$B'_2H_2PtCl_6$.

Formyl derivative [183°]; long silky needles.

Acetyl derivative $C_6HMe_4.NHAc$. [215°].

Tetra-methyl-phenyl-amine $C_6HMe_4.NH_2$. *Duridine.* [14°]. (253°). S.G. $\frac{24}{}$ ·978. A product of the action of MeOH on xylidine hydrochloride at a high temperature (Hofmann, *B.* 17, 1913).—B'HCl.—$B'_2H_2PtCl_6$.

Penta-methyl-phenyl-amine $C_6(CH_3)_5.NH_2$. *Amido-penta-methyl-benzene.* [152°]. (278°). Prepared by heating dimethyl-ψ-cumidine with methyl iodide under pressure at 240°–250° (Hofmann, *B.* 18, 1821). Large colourless needles. V. sol. alcohol and ether, insol. water. On oxidation by arsenic acid in conjunction with aniline it yields a homologue of rosaniline. MeI at 100° forms C_6Me_5NHMe [61°], which is not further acted on by MeI, even at 170°.

Salts.—B'HCl: long thin needles, easily soluble in hot water, sl. sol. cold.—$B'_2H_2Cl_2PtCl_4$: sparingly soluble trimetric tables.—The *acetate* is very soluble; the *nitrate* forms sparingly soluble needles; the *sulphate* and *oxalate* very sparingly soluble small scales.

Acetyl derivative $C_6(CH_3)_5.NHAc$ [213°]; needles.

METHYL-DI-PHENYL-AMINE $C_{13}H_{13}N$ *i.e.* NPh_2Me. *Di-phenyl-methyl-amine.* (282°) (G.). (292°) at 741 mm. (Brühl, *A.* 235, 21). S.G. $\frac{24}{4}$ 1·0476. Formed by methylation of diphenylamine (Bardy, *Z.* 1871, 649; Girard, *Bl.* [2] 23, 2). Liquid. Gives a violet colour with HNO_3. Fuming HClAq at 150° resolves it into MeCl and diphenylamine (Gnehm, *B.* 8, 1040). By passing through a red-hot tube it is converted into diphenylamine, carbazole, benzonitrile, aniline, benzene, methane, hydrogen, nitrogen, and other products (Graebe, *A.* 174, 181). Nitrous acid passed into its alcoholic solution yields $NMePh.C_6H_4.N_2.C_6H_4.NMePh$. Boiling nitric acid forms a compound which crystallises from alcohol in yellow prisms [234°].

Derivatives.—TRI-BROMO- and BROMO-DI-NITRO-, METHYL-DIPHENYLAMINE.

METHYL-PHENYL-ANTHRACENE *v.* PHENYL-METHYL-ANTHRACENE.

METHYL-PHENYL-CARBAMIC ACID *v.* TOLYL-CARBAMIC ACID.

Di-methyl-phenyl-carbamic acid *v.* XYLYL-CARBAMIC ACID.

Tri-methyl-phenyl-carbamic acid. *Ethyl ether* $C_6H_2Me_3.NH.CO_2Et$. *ψ-Cumyl-carbamic ether.* [91·5°]. Formed by the action of chloroformic ether $ClCO_2Et$ on *ψ-cumidine* (Frentzel, *C. C.* 1888, 1361). P_2O_5 converts it into the cyanate $C_6H_2Me_3NCO$ (221°), polymerised by PEt_3 or KOAc into the cyanurate [234°].

Tri-methyl-phenyl-carbamic acid. *Ethyl ether* $C_6H_2Me_3NH.CO_2Et$. *Mesityl-urethane.* [62°]. Formed from mesidine and $ClCO_2Et$ (Eisenberg, *B.* 15, 1016). Long colourless needles, volatile with steam, sol. alcohol and ether.

TETRA-METHYL-PHENYL-CARBAMINE $C_6H(CH_3)_4.NC$ [51°]. White crystals. Formed by heating tetra-methyl-phenyl-amine [14°] with chloroform and alcoholic KOH. It is changed into the nitrile by distillation (Hofmann, *B.* 17, 1914).

Penta-methyl-phenyl-carbamine $C_6(CH_3)_5.NC$. [128°]. Formed by heating penta-methyl-phenyl-amine with chloroform and alcoholic NaOH (Hofmann, *B.* 18, 1824). Colourless crystals. V. sol. alcohol. At a few degrees above its melting-point it is transformed into the nitrile with evolution of heat.

METHYL-TRI-PHENYL-CARBINOL-CARBOXYLIC ACID *v.* DI-PHENYL-TOLYL-CARBINOL-CARBOXYLIC ACID.

METHYL-PHENYLENE-DIAMINE *v.* PHENYLENE-METHYL-DIAMINE.

Di-methyl-phenylene-diamine *v.* PHENYLENE-DI-METHYL-DIAMINE.

Tri-methyl-phenylene-diamine $C_9H_{14}N_2$ *i.e.* $C_6HMe_3(NH_2)_2$[1:2:4:3:5]. [84°]. Formed from nitro-ψ-cumidine by reduction (Mayer, *B.* 20, 970). Long needles, v. sol. benzene. $FeCl_3$ colours its solution deep red.

Isomerides *v.* DI-AMIDO-MESITYLENE and DI-AMIDO-ψ-CUMENE.

Tetra-methyl-phenylene-diamine $C_{10}H_{16}N_2$ *i.e.* $^{\times}C_6Me_4(NH_2)_2$ [1:2:4:5:3:6]. Formed by reducing di-nitro-*s*-durene with zinc and HOAc (Nef, *A.* 237, 4). Pearly plates, v. sol. chloroform and alcohol, m. sol. ether. Its solutions are coloured green by atmospheric oxidation. $FeCl_3$ yields duroquinone. The hydrochloride is sl. sol. conc. HClAq.

Tetra-methyl-phenylene-diamine $C_6Me_4(NH_2)_2$ [1:2:4:3:5:6]. *Prehnitylene-diamine.* [140°]. Formed by reducing $C_6Me_4(NH_2)(NO_2)$ with tin and HCl (Töhl, *B.* 21, 906). Plates (from water), or needles (from alcohol); v. e. sol. alcohol, sl. sol. ether and ligroïn.—$B''H_2Cl_2$ aq: plates, v. e. sol. water, v. sl. sol. conc. HClAq. Coloured dark red by $FeCl_3$.

METHYL-DIPHENYLENE KETONE OXIDE *v.* PHENYLENE-TOLYLENE KETONE OXIDE.

DI-METHYL PHENYLENE-DIVINYL DI-KETONE $C_{14}H_{14}O_2$ *i.e.* $C_6H_4(CH:CH.CO.CH_3)_2$. [156°]. Formed by the action of NaOHAq on a mixture of acetone (10 pts.) and terephthalic aldehyde (1 pt.) (Loew, *A.* 231, 379). Needles, almost insol. water, alcohol, and ether, v. sol. chloroform, v. e. sol. acetone. With conc. H_2SO_4 it yields a deep-red solution.

METHYL-PHENYL-ETHYL-ALKINE *v.* METHYL-OXYETHYL-ANILINE.

METHYL PHENYL-ETHYL KETONE v. BENZYL-ACETONE.

METHYL-PHENYL-GLYOXYLIC ACID v. TOLYL-GLYOXYLIC ACID.

Di-methyl-phenyl-glyoxylic acid v. XYLYL-GLYOXYLIC ACID.

Tetra-methyl-phenyl-glyoxylic acid [6:5:3:2:1] $C_6HMe_4.CO.CO_2H$. [124°]. Formed by oxidising the ketone $C_6HMe_4.CO.CH_3$ with cold aqueous $KMnO_4$ (Claus a. Foecking, *B.* 20, 3102). White scales, sl. sol. water, v. sol. alcohol and ether. Reduced by sodium-amalgam to tetra-methyl-mandelic acid $C_6HMe_4.CH(OH).CO_2H$.—KA′ 5aq: crystalline, v. e. sol. water.—CaA'_2 9aq: nodules.—$BaA'_2$3aq: nodules.—AgA′: white pp.

Tetra-methyl-phenyl-glyoxylic acid [6:4:3:2:1] $C_6HMe_4.CO.CO_2H$. Formed by oxidising the corresponding duryl methyl ketone with cold aqueous $KMnO_4$ (C. a. F.). Yellow liquid, sl. sol. water, v. sol. alcohol and ether. Solidifies when strongly cooled. Sodium-amalgam reduces it in alcoholic solution to the corresponding tetra-methyl-mandelic acid.—NaA′ 5aq: white crystalline crusts.—BaA'_2 5aq: nodules.—CaA'_2 3aq: granules.—CuA'_2 5aq: green crystals, v. sol. water.—PbA'_2: white pp., v. sl. sol. water.—AgA′: white pp., insol. water.

Tetra-methyl-phenyl-glyoxylic acid $C_{12}H_{14}O_3$ *i.e.* [5:4:3:2:1] $C_6HMe_4.CO.CO_2H$. Formed by oxidising the corresponding tetra-methyl-phenyl methyl ketone (Claus, *J. pr.* [2] 38, 232). Oil.—BaA'_2 4aq: needles. — CaA'_2 4aq: needles. — CuA'_2 3aq.

Penta-methyl-phenyl-glyoxylic acid $C_{13}H_{16}O_3$ *i.e.* $C_6Me_5.CO.CO_2H$. [122°]. Formed by the action of $AlCl_3$ on a mixture of penta-methyl-benzene and $ClCO.CO_2Et$ (Jacobsen, *B.* 22, 1218). Formed also by oxidising $C_6Me_5.CO.CH_3$ with alkaline $KMnO_4$. Prisms, v. sl. sol. cold water, v. sol. alcohol.—NaA′ 3aq: plates, m. sol. cold water.—BaA'_2 5aq: nodules, v. sl. sol. cold water.—CuA'_2 5aq: needles.

HEXA-METHYL-DI-PHENYL-GUANIDINE $C_{19}H_{25}N_3$ *i.e.* $HN:C(NH.C_6H_2Me_3)_2$. *Di-mesityl-guanidine.* [218°]. Formed by heating $SC(NH.C_6H_2Me_3)_2$ with alcoholic NH_3 and lead oxide (Eisenberg, *B.* 15, 1014). Minute prisms, sol. alcohol and ether, insol. water.

Ennea-methyl-tri-phenyl-guanidine $C_{28}H_{35}N_3$ *i.e.* $C_6H_2Me_3N:C(NH.C_6H_2Me_3)_2$. [225°]. Formed by heating hexa-methyl-di-phenyl-thio-urea with alcoholic mesidine and lead oxide (E.). Small crystals, sol. alcohol, insol. water.

METHYL-PHENYL-HYDRAZINE v. PHENYL-METHYL-HYDRAZINE.

Tri-methyl-phenyl-hydrazine $C_9H_{14}N_2$ *i.e.* [1:2:4:5].$C_6H_2Me_3.NH.NH_2$. *ψ-Cumyl-hydrazine.* [120°]. Formed by boiling its sodium sulphonate with water (Haller, *B.* 18, 91). Needles (from ether); insol. water and alkalis, v. sol. alcohol and ether. With aceto-acetic ether it yields oxy-tetra-methyl-phenyl-pyrazole.

Sodium sulphonate $C_6H_2Me_3.NH.NH.SO_3Na$. Formed by warming diazo-ψ-cumene chloride with Na_2SO_3 and reducing the resulting $C_6H_2Me_3.N_2.SO_3Na$ with zinc-dust and HOAc (Haller). White plates (containing 1½aq.), sl. sol. cold water and alcohol, v. sol. hot water.

METHYL-PHENYL-DI-KETONE v. PHENYL-METHYL-DI-KETONE.

TRI-METHYL-PHENYL MERCAPTAN $C_9H_{12}S$ *i.e.* $C_6H_2Me_3.SH$. *Mesityl sulphydrate. Thiomesitol.* (229°). S.G. 1·0192. Formed by reducing mesitylene sulphochloride with zinc and H_2SO_4 (Holtmeyer, *Z.* 1867, 686). Liquid, volatile with steam; v. sol. alcohol, ether, and benzene.—$Hg(S.C_6H_2Me_3)_2$: white silky needles.

HEXA-METHYL-DI-PHENYL-METHANE $C_{19}H_{24}$ *i.e.* $CH_2(C_6H_2Me_3)_2$. *Di-mesityl-methane.* [c. 130°]. Formed by the action of H_2SO_4 on a mixture of $CH_2(OAc)_2$ and mesitylene dissolved in HOAc (Baeyer, *B.* 5, 1098). Monoclinic prisms (from ether).

Methyl-tri-phenyl-methane v. DI-PHENYL-TOLYL-METHANE.

TETRA-METHYL-PHENYL-DI-METHYL-AMINE $C_{12}H_{19}N$ *i.e.* $C_6HMe_4.NMe_2$. (237°). Formed from tetra-methyl-phenyl-amine [14°] by treatment with MeI and alcoholic soda (Hofmann, *B.* 17, 1914). Colourless liquid.—$B'_2H_2PtCl_6$: crystalline.

Penta-methyl-phenyl-methyl-amine $C_{12}H_{19}N$ *i.e.* $C_6(CH_3)_5.NHMe$. *Methyl-amido-penta-methyl-benzene.* [61°]. Colourless scales. Formed by heating penta-methyl-phenyl-amine with methyl iodide.—$B'_2H_2Cl_2PtCl_4$: needles (Hofmann, *B.* 18, 1824).

Penta-methyl-phenyl-di-methyl-amine $C_6(CH_3)_5.NMe_2$. *Di-methyl-amido-penta-methyl-benzene.* [54°]. Colourless scales. Formed by digesting penta-methyl-phenyl-amine with methyl iodide in presence of an alkali. Its methylo-iodide could not be obtained. — $B'_2H_2Cl_2PtCl_4$: needles (Hofmann, *B.* 18, 1824).

TETRA-METHYL-PHENYL-METHYL-CARBINOL [6:4:3:2:1] $C_6HMe_4.CH(OH).CH_3$. *Duryl-methyl-carbinol.* (above 300°). Formed by reducing duryl methyl ketone with zinc and HCl (Claus a. Foecking, *B.* 20, 3099). Pale-yellow liquid.

Tetra-methyl-phenyl-methyl-carbinol [6:5:3:2:1] $C_6HMe_4.CH(OH).CH_3$. [72°]. Formed by reducing *s*-duryl methyl ketone (C. a. F.). White plates.

METHYL-PHENYL METHYL KETONE v. TOLYL METHYL KETONE.

Di-methyl-phenyl methyl ketone v. XYLYL METHYL KETONE.

Tetra-methyl-phenyl methyl ketone $C_{12}H_{16}O$ *i.e.* [5:4:3:2:1] $C_6HMe_4.CO.CH_3$. *c-Duryl methyl ketone.* (260°). Formed from *c*-durene, AcCl, and $AlCl_3$ (Claus, *J. pr.* [2] 38, 231). Brownish, strongly refracting, oil, insol. water, sol. alcohol and ether. Oxidised by $KMnO_4$ to tetra-methyl-phenyl-glyoxylic and *c*-tetra-methyl-benzoic acids.

Phenyl-hydrazide [129°]. Plates.

Tetra-methyl-phenyl methyl ketone [6:4:3:2:1] $C_6HMe_4.CO.CH_3$. (254°). Formed from *u*-durene, AcCl, and $AlCl_3$ in CS_2 (Claus a. Foecking, *B.* 20, 3097). Colourless oil, v. sol. alcohol and ether. Volatile with steam. Reduced by zinc-dust and alcoholic KOH to the carbinol. Oxidised by $KMnO_4$ to tetra-methyl-phenyl-glyoxylic acid.

Phenyl-hydrazide. Needles, decomposing at 215°.

Oxim. [148°]. Plates.

Tetra-methyl-phenyl methyl ketone [6:5:3:2:1] $C_6HMe_4.CO.CH_3$. [63°]. (251°).

Formed by the action of $AlCl_3$ upon *s*-durene mixed with AcCl in CS_2 (C. a. F.). Plates.

Phenyl-hydrazide. Crystals, decomposing at 225°.

Penta-methyl-phenyl methyl ketone $C_{13}H_{18}O$ *i.e.* $C_6Me_5.CO.CH_3$. [85°]. (286°). Formed by the action of $AlCl_3$ on a mixture of penta-methyl-benzene and AcCl dissolved in CS_2 (Jacobsen, *B.* 22, 1218). Pearly plates, v. sol. alcohol, ether, and HOAc. Oxidised by $KMnO_4$ to penta-methyl-phenyl-glyoxylic acid.

DI-METHYL-PHENYL-PHOSPHINE *v.* PHENYL-DI-METHYL-PHOSPHINE.

METHYL-TRI-PHENYL-PHOSPHONIUM IODIDE *v. Methylo-iodide* of TRI-PHENYL-PHOSPHINE.

TRI-METHYL-PHENYL-PHTHALIDE

$C_{17}H_{16}O_2$ *i.e.* $C_6H_4 \langle {}^{CO}_{CH\,.\,C_6H_2Me_3} \rangle O$. *Mesityl-phthalide. Phenyl-mesityl-carbinol carboxylic anhydride.* [164°]. Formed by treating an alcoholic solution of [5:3:1:2] $C_6H_2Me_3.CO.C_6H_4.CO_2H$ with zinc and HCl (Gresly, *A.* 234, 237). Short thick needles.

Tri-methyl-phenyl-phthalide $C_{17}H_{16}O_2$. *ψ-Cumyl-phthalide.* [140°]. Prepared as above, using the derivative of ψ-cumene instead of that of mesitylene (G.). Small needles.

Methyl-di-phenyl-phthalide *v.* DI-PHENYL-TOLYL-CARBINOL CARBOXYLIC-ANHYDRIDE.

METHYL-PHENYL-PSEUDO-PICOLO-STYRIL *v.* OXY-PHENYL-DI-METHYL-PYRIDINE.

METHYL-PHENYL-PROPYL-ALKINE *v.* METHYL-OXYPROPYL-ANILINE.

HEXA-METHYL-DI-PHENYL DISULPHIDE $C_{18}H_{22}S_2$ *i.e.* $(C_6H_2Me_3)_2S_2$. *Mesityl disulphide.* [125°]. Formed by atmospheric oxidation of tri-methyl-phenyl mercaptan in alkaline solution (Holtmeyer, *Z.* 1867, 688). Light-yellow laminæ or tables; insol. water, sol. alcohol, ether, and benzene.

OCTA-METHYL-DI-PHENYL SULPHONE *v.* DI-DURYL SULPHONE.

Deca-methyl-di-phenyl sulphone $C_{22}H_{30}SO_2$ *i.e.* $C_6Me_5.SO_2.C_6Me_5$. [98·5°]. Formed by the action of $ClSO_3H$ on penta-methyl-benzene (Jacobsen, *B.* 20, 896). Very long, slender needles (from ligroïn); v. sol. alcohol. Yields penta-methyl-benzene when heated with conc. HClAq at 170°, and in smaller quantity when distilled.

TRI-METHYL-PHENYL-THIO-CARBAMIC ETHER $C_{12}H_{17}NSO$ *i.e.* $C_6H_2Me_3NH.CS.OEt$ or $C_6H_2Me_3N{:}C(SH).OEt$. *Mesityl-thio-urethane.* [88°]. Formed by heating the corresponding thiocarbimide with alcohol at 140° (Eisenberg, *B.* 15, 1015). Slender needles; sol. alcohol, ether, and warm alkalis.

TRI-METHYL-PHENYL THIOCARBIMIDE $C_6H_2Me_3.NCS$. *Mesityl mustard oil.* [64°]. Formed by heating mesidine with CS_2 and some alcoholic potash (Eisenberg, *B.* 15, 1012). Long needles; sol. alcohol and ether.

Tetra-methyl-phenyl-thiocarbimide $C_{11}H_{13}NS$ *i.e.* $C_6HMe_4.NCS$. [65°]. Formed by boiling tetra-methyl-phenyl-amine [14°] with CS_2 and a little KOH (Hofmann, *B.* 17, 1915). Crystalline solid.

Penta-methyl-phenyl thiocarbimide $C_{12}H_{15}NS$ *i.e.* C_6Me_5NCS. [86°]. Formed, together with the corresponding thio-urea, by boiling penta-methyl-phenyl-amine with CS_2 (Hofmann, *B.* 18, 1827). Needles (from alcohol); volatile with steam.

TRI-METHYL-PHENYL THIO-UREA $C_{10}H_{14}N_2S$ *i.e.* $NH_2.CS.NH.C_6H_2Me_3$. *Mesityl-thio-urea.* [222°]. Formed by the action of ammonia on the corresponding thio-carbimide (Eisenberg, *B.* 15, 1013). Pearly plates; sol. ether and hot alcohol, insol. water.

Hexa-methyl-di-phenyl thio-urea $C_{19}H_{24}N_2S$ *i.e.* $CS(NH.C_6H_2Me_3)_2$. *Di-mesityl-thio-urea.* Formed by heating mesidine with CS_2 (Eisenberg, *B.* 15, 1013). Formed also by digesting tri-methyl-phenyl thiocarbimide with mesidine in alcoholic solution. White needles. Conc. H_3PO_4 converts it into the thiocarbimide.

Isomeride *v.* DI-ψ-CUMYL-THIO-UREA.

Octo-methyl-di-phenyl-thio-urea $C_{21}H_{28}N_2S$ *i.e.* $SC(NH.C_6HMe_4)_2$. [278°]. Formed by the action of CS_2 on tetra-methyl-phenyl-amine [14°] (Hofmann, *B.* 17, 1916). Four-sided plates (from alcohol); sl. sol. alcohol.

Deca-methyl-di-phenyl-thio-urea $C_{23}H_{32}N_2S$ *i.e.* $SC(NH.C_6Me_5)_2$. [252°]. Formed by the action of CS_2 upon penta-methyl-phenyl-amine (Hofmann, *B.* 18, 1827). White needles; sol. HOAc, v. sl. sol. alcohol.

TRI-METHYL-PHENYL-UREA *v.* ψ-CUMYL-UREA.

Hexa-methyl-di-phenyl-urea $C_{19}H_{24}N_2O$ *i.e.* $OC(NH.C_6H_2Me_3)_2$. *Di-mesityl-urea.* [above 300°]. Formed by the action of mesidine on tri-methyl-phenyl cyanate (Eisenberg, *B.* 15, 1017). Minute prisms; sl. sol. hot alcohol, insol. water.

Hexa-methyl-di-phenyl-urea $OC(NH.C_6H_2Me_3)_2$. *Di-ψ-cumyl-urea.* According to Frentzel (*C. C.* 1888, 1361) this substance melts between 260° and 270° (*cf.* vol. ii. p. 296).

METHYL-PHLOROGLUCINS *v.* PHLOROGLUCIN.

METHYL PHOSPHATES.

Methyl-phosphoric acid $MeO.PO(OH)_2$. Formed by slowly adding methyl alcohol to cooled $POCl_3$ (H. Schiff, *A.* 102, 334).—BaA″2aq: laminæ; much less soluble in boiling water than in warm water.—CaA″ (dried at 100°).

Di-methyl-phosphoric acid $(MeO)_2PO.OH$. Formed by pouring $POCl_3$ into methyl alcohol (Schiff). Acid syrup; sol. alcohol and ether. Its salts are more soluble than those of the preceding acid.—BaA'_2 (dried at 150°): pearly plates, nearly insol. alcohol.—SrA'_2 2aq.—PbA'_2xaq.—CaA'_2 (dried at 100°): very soluble nodules.

Tri-methyl phosphate Me_3PO_4. (197° cor.). S.G. $\frac{0}{}$ 1·238 (Weger, *A.* 221, 89). S.V. 139·5 (Lossen, *A.* 254, 74).

METHYL-PHOSPHINE CH_5P *i.e.* $CH_3.PH_2$. Mol. w. 48. (−14°). V.D. 24·4 (calc. 24). S. (ether) 70 at 0°. Formed, together with di-methyl-phosphine, by heating PH_4I with MeI and ZnO at 150°. When water is added to the product $MePH_3I$ is decomposed, with evolution of $MePH_2$, while Me_2PH_2I remains (Hofmann, *B.* 4, 605). Formed also by heating chloroform with PH_4I and ZnO (Hofmann, *B.* 6, 302). Gas, with powerful odour. May be condensed by 2 atmospheres' pressure at 0°. Fumes in the air, and takes fire when gently warmed. Feeble base, being absorbed by conc. HClAq or conc.

HIAq, producing crystalline salts, which are decomposed by water into $MePH_2$ and the acid. When passed into fuming HNO_3 it yields methane phosphonic acid or 'methyl-phosphinic acid' $MePO(OH)_2$, which forms crystals, v. sol. water, melting at 105°. This acid is not attacked by aqua regia. It yields the salts $MePO_3Ba$, $MePO_3Pb$, and $MePO_3Ag_2$, and the chloride $MePOCl_2$ [32°] (163°).

Salts.—$MePH_2HCl$: four-sided plates, very volatile in the air, being dissociated.—$MePH_2HI$: laminæ.

Di-methyl-phosphine C_2H_7P *i.e.* $(CH_3)_2PH$. Mol. w. 62. (25°). Obtained by the action of caustic soda on its hydro-iodide, which is obtained as above described (Hofmann, *B.* 4, 610). Very volatile liquid which takes fire in the air. May be oxidised to $Me_2PO.OH$, a waxy solid, v. sol. water. This acid melts at 76°, forms crystalline $Me_2PO.OAg$ and is converted by PCl_5 into the chloride Me_2POCl [66°], (204°). This chloride is reconverted by water into the corresponding acid with less energy than $MePOCl_2$ (Hofmann, *B.* 5, 109; 6, 307).

Tri-methyl-phosphine C_3H_9P *i.e.* $P(CH_3)_3$. Mol. w. 76. (41°).

Formation.—1. By the action of MeCl upon calcium phosphide (Thénard, *C. R.* 21, 144; 25, 892).—2. From sodium or zinc phosphide and MeI (Cahours a. Hofmann, *A. Ch.* [3] 41, 631; *Chem. Gaz.* 1855, 11).—3. From PCl_3 and $ZnMe_2$ (Hofmann a. Cahours, *C. R.* 104, 29).—4. From PH_3 and MeI (Drechsel a. Finkelstein, *B.* 4, 354; Hofmann, *B.* 4, 205, 430).—5. By heating CS_2 with PH_4I at 140° (Drechsel, *J. pr.* [2] 10, 180). 6. From phosphorus and MeI (Friedel a. Silva, *Wurtz's Dict.* 2, 938).

Preparation.—By treating PCl_3 with $ZnMe_2$ in an atmosphere of CO_2, decomposing the product with caustic soda, and distilling in a very slow current of hydrogen.

Properties.—Volatile oil with powerful nauseous odour; heavier than water. Forms readily soluble, crystallisable salts. Unites readily with halogens, oxygen, and sulphur. With $ClCH_2CO_2H$ at 100° it yields $PMe_3Cl.CH_2.CO_2H$ which forms the platinochloride $(C_5H_{12}PO_2)_2PtCl_6$ (Meyer, *B.* 4, 734; *C. J.* 24, 1066).

Salts.—$B'_2H_2PtCl_6$: orange-yellow crystalline pp.—B'_2PtCl_2 (Cahours a. Gal, *Z.* 1870, 662). Combines with CS_2 forming pale-red crystals of PMe_3CS_2, which slowly changes, in ethereal solution, into PMe_3S (Hofmann, *A. Suppl.* 1, 59).

Oxide PMe_3O. [138°] (Collie, *C. J.* 53, 637). (215°). Formed by exposing PMe_3 to a slow current of dry air. Deliquescent crystals. Formed also, together with CH_4, by distilling PMe_4OH. Yields a platinochloride $(PMe_3O)_3H_2PtCl_6$ aq crystallising in orange plates or needles.

Sulphide PMe_3S. [105°]. Obtained by gradually adding flowers of sulphur to PMe_3, or by distilling PMe_3 with cinnabar. Not formed from the oxide and H_2S or ammonium sulphide. Four-sided prisms (from concentrated aqueous solution). When warmed with a solution of a silver salt Ag_2S is deposited as a black mirror (Collie).

Selenide PMe_3Se. [84°]. Formed from PMe_3 and selenium. Blackens in the air, depositing selenium.

Methylo-hydroxide $PMe_4.OH$. Formed by treating PMe_4I with moist Ag_2O. Caustic base, split up on distillation into PMe_3O and CH_4.

Methylo-iodide PMe_4I. *Tetra-methyl-phosphonium-iodide:* Formed from PMe_3 and MeI (Hofmann a. Cahours, *A.* 104, 31). Formed also, together with PMe_3, by heating PH_4I (1 mol.) with MeOH (3 mols.) at 180° (Hofmann, *B.* 4, 208). Silvery crystals.

Methylo-chloride PMe_4Cl. From PMe_4OH and HCl. Deliquescent crystals, decomposed by heat into PMe_3HCl and ethylene (Collie, *C. J.* 53, 637).—$(PMe_4Cl)_2PtCl_4$: glistening yellow octahedra, insol. water.—PMe_4AuCl_4: brilliant yellow needles (from boiling water).

Methylo-sulphate ×$(PMe_4)_2SO_4$. Formed from PMe_4I and Ag_2SO_4 (Collie). Thick deliquescent needles. Does not form an alum with $Al_2(SO_4)_3$. Above 300° it decomposes, giving PMe_3O and PMe_3S.

Methylo-carbonate ×$PMe_4O.CO_2H$. Decomposes above 100° into PMe_3O, CO_2, and CH_4 (Collie).

Methylo-acetate ×PMe_4OAc. Decomposed by heat chiefly into PMe_3O and acetone, with traces of PMe_3 and MeOAc.

Benzoate PMe_4OBz. Formed by neutralising a solution of PMe_4OH with HOBz (Collie, *C. J.* 53, 639). Deliquescent crystals, v. sol. water. Decomposes between 250° and 300° almost completely into PMe_3O and acetophenone.

Ethylo-chloride PMe_3EtCl. Obtained from PMe_3EtI (Collie, *C. J.* 53, 718). Decomposes above 300° into PMe_3HCl, PMe_2EtHCl, and ethylene.—$(PMe_3EtCl)_2PtCl_4$: octahedra.

Ethylo iodide PMe_3EtI. *Tri-methyl-ethyl-phosphonium iodide.* From PMe_3 and EtI in ether (Cahours a. Hofmann, *A.* 104, 33). Crystallises from boiling water. Deliquescent; sol. ether.

Isoamylo-iodide $PMe_3C_5H_{11}I$. Deposited slowly from an ethereal solution of PMe_3 and $C_5H_{11}I$ (Hofmann). Needles (from alcohol). Yields $(PMe_3C_5H_{11}Cl)_2PtCl_4$, crystallising from boiling water in splendid needles aggregated in spherules.

Bromo-ethylo-bromide $C_5H_{13}Br_2$ *i.e.* $CH_2Br.CH_2PMe_3Br$. From PMe_3 and a large excess of ethylene bromide in alcoholic solution at 60°. Trimetric prisms; $a:b:c = \cdot568:1:\cdot407$ Hofmann, *Tr.* 1860, 590). With Ag_2O it yields $CH_2(OH).CH_2.PMe_3OH$ whence the platinochloride $(CH_2(OH).CH_2.PMe_3Cl)_2PtCl_4$ may be got.

Ethyleno-di-bromide $(PMe_3Br)_2C_2H_4$. Formed from ethylene bromide and excess of PMe_3 at 100°. Very deliquescent monoclinic crystals, $a:b:c = 1\cdot054:1:1\cdot126$; $\beta = 37°49'$. Yields $C_2H_4(PMe_3Cl)_2PtCl_4$, which crystallises from boiling HClAq in golden-yellow laminæ. Successive treatment with moist Ag_2O and HI forms $C_2H_4(PMe_3I)_2$, crystallising in sparingly soluble needles.

Tri-methyl-tri-ethyl-di-phosphine ethyleno-dibromide $(PMe_3Br)C_2H_4(PEt_3Br)$. Formed from PMe_3 and $CH_2Br.CH_2.PEt_3Br$. Yields a caustic hydroxide and the platinochloride $(PMe_3Cl)C_2H_4(PEt_3Cl)PtCl_4$.

Tetra-methyl-di-phosphine? P_2Me_4 or $(PMe_2)_x$. (250°). Found among the products of the ac-

tion of MeCl on calcium phosphide, or of MeI on sodium phosphide (Thénard; Hofmann a. Cahours, *A.* 104, 4). Liquid, with unpleasant odour, taking fire in the air. Insol. water. Decomposed by HCl into PMe_3, and a yellow powder P_4Me_2(?).

METHYL PHOSPHITE MeH_2PO_3. *Methyl-phosphorous acid.* Formed by gradually adding PCl_3 to methyl alcohol (Schiff, *A.* 103, 164). Acid syrup, resolved by heat into MeOH and phosphorous acid. Its salts are slightly crystalline hygroscopic masses, v. sol. water, sl. sol. alcohol, insol. ether. In aqueous solution they decompose, slowly in the cold, but rapidly on heating, into MeOH and metallic phosphites.— $Ba(MeHPO_3)_2$. — $Ca(MeHPO_3)_2$ 2aq. — $Pb(MeHPO_3)_2$.

Tri-methyl phosphite Me_3PO_3. (185°). S.G. $_{15}$ 1·1785. Formed from PCl_3 and NaOMe (Jachne, *A.* 256, 281). The compound $Me_3PO_3PtCl_2$ is formed by the action of MeOH on PCl_3PtCl_2 (Schützenberger, *Bl.* [2] 18, 101, 157). It crystallises in orange needles and yields $(Me_3PO_3)_2PtCl_2$ and $(Me_3PO_3)_2PtCl_2N_2H_6$.

METHYL-PHTHALIC ACID *v.* Toluene dicarboxylic acid.

Di-methyl-phthalic acid *v.* Xylene dicarboxylic acid.

Tetra-methyl-phthalic acid *v.* Tetra-methyl-benzene dicarboxylic acid.

METHYL-PHTHALIDE $C_9H_8O_2$ *i.e.*

$C_6H_4<\genfrac{}{}{0pt}{}{CHMe}{CO}>O$. (276°). V.D. 74 (obs. and calc.). Formed by reducing acetophenone carboxylic acid with sodium-amalgam and acidifying the resulting $CO_2Na.C_6H_4.CH(OH).CH_3$ (Gabriel a. Michael, *B.* 10, 2205; 20, 2500). Thick oil, solidifying below 0°. Insol. water and cold alkalis, v. sol. alcohol and ether, sl. sol. ligroïn. Boiling alkalis convert it into salts of the acid, which forms a crystalline silver salt $CO_2Ag.C_6H_4.CH(OH).CH_3$.

Di-methyl-phthalide $C_{10}H_{10}O_2$ *i.e.*

$C_6H_4<\genfrac{}{}{0pt}{}{CMe_2}{CO}>O$. [68°]. (160°) at 25 mm.; (271°) at 760 mm. Formed by the action of zinc-dust and MeI on phthalic anhydride at 100° under a slightly increased pressure (Wislicenus, *A.* 248, 56). Crystallises from ether in large crystals which are doubly refracting.

Reactions.—1. Converted by the action of conc. KOHAq into the K salt of o-oxy-iso-propyl benzoic acid.—2. *Sodium amalgam* yields the dihydride $C_6H_4<\genfrac{}{}{0pt}{}{CMe_2}{CH(OH)}>O$ [90°], a yellow amorphous powder, insol. water, sol. alcohol and ether, which reduces Fehling's solution and ammoniacal $AgNO_3$.—3. Reduction with HI yields *o*-iso-propyl-benzoic acid.—4. *Potassium cyanide* at 250° forms o-propenyl-benzoic acid $CH_2{:}CMe.C_6H_4.CO_2H$ [61°].

METHYL-PHTHALIMIDE *v.* *Methylimide* of Phthalic acid.

METHYL-PHTHALIMIDINE C_9H_9NO *i.e.*

$C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{CO}>NMe$. [120°]. (300°).

Formation.—1. By reducing methyl-phthalimide $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>NMe$ with tin and HClAq (Graebe, *A.* 247, 303).—2. By heating a solution of phthalimidine in aqueous KOH with excess of MeI for 6 hours at 100° (Barbier, *C. R.* 107, 918).—3. By heating phthalide with alcoholic methylamine for 12 hours at 220° (B.).

Properties.—Slender needles or plates, v. sol. water, alcohol, and ether. Oxidised by $KMnO_4$ to methyl-phthalimide and, finally, to phthalic acid. Combines with bromine forming $(C_9H_9NO)_2Br_6$, crystallising in needles [150°].

Salts.—Hydrochloride. [120°]. Prisms. B'_2HAuCl_4: yellow prisms, sl. sol. cold water.

a-METHYL-HOMO-*o*-PHTHALONITRILE *v.* *o-Cyano-phenyl-propionitrile.*

METHYLPIASELENOL *v.* *Organic* Selenium compounds.

METHYL-PIAZTHIOLE $C_7H_6N_2S$ *i.e.*

$\left[3{:}\genfrac{}{}{0pt}{}{6}{5}\right]C_6H_3Me<\genfrac{}{}{0pt}{}{N}{N}>S$. [34°]. (234°). Mol. w. (by Raoult's method) 143 (calc. 150). Formed by heating tolylene *o*-diamine with H_2SO_3 at 180° (Hinsberg, *B.* 22, 2900). Yields a periodide when treated with I in HIAq. Br in $CHCl_3$ forms $C_7H_5BrN_2S$ which crystallises in white needles [98°]. A mixture of conc. H_2SO_4 and HNO_3 forms $C_7H_5(NO_2)N_2S$ crystallising in colourless needles [156°].

Salt.—$B'_2H_2PtCl_6$: reddish-yellow crystals, decomposed by water.

METHYL-PIPECOLINE *v.* Di-methyl-pyridine-hexahydride.

METHYL-PIPERIDINE *v.* Methyl-pyridine hexahydride.

METHYL-PROPARGYL-AMINE C_4H_7N *i.e.* $CH_3.NH.C{:}C.CH_3$. Formed by the action of MeI on propargylamine in alcoholic solution (Paal a. Hermann, *B.* 22, 3083). Very volatile yellowish liquid, with ammoniacal odour.—B'HI. [83°]. Groups of long hygroscopic needles.—$B'H_2C_2O_4$. [141°]. Slender white needles, sl. sol. alcohol.

METHYL-PROPIONIC ACID *v.* Butyric acid.

METHYL-PROPYL-ACETAL *v.* Aldehyde.

METHYL-PROPYL-ACETIC ACID *v.* Hexoic acid.

METHYL-PROPYL-ACETOACETIC ETHER *v.* Acetoacetic acid.

METHYL-ISOPROPYL-ACETONE *v.* Methyl isoamyl ketone.

DI-METHYL-PROPYL-ALKINE *v.* Di-methyl-oxypropyl-amine.

DI-METHYL-ISOPROPYL-ALLYL-CARBINOL *v.* Ennenyl alcohol.

TRI-METHYL-PROPYL-AMMONIUM IODIDE NMe_3PrI. *Propylo-iodide* of *trimethylamine.* [190°]. Formed by heating propylamine with alcoholic NMe_3 (Langeli, *G.* 16, 385). Long needles. Yields crystalline NMe_3PrCl and $(NMe_3PrCl)_2PtCl_4$. The hydroxide NMe_3PrOH is decomposed by heat into propylene and NMe_3.

METHYL-PROPYL-ANILINE $C_{10}H_{15}N$ *i.e.* $C_6H_5.NMePr$ (212° uncor.). Liquid. Prepared by the action of methyl iodide upon propyl-aniline (Claus a. Hirzel, *B.* 19, 2785; *cf.* Nölting, *J.* 1883, 702).—B'HCl: very hygroscopic crystals, [106°].

Ethylo-iodide *v.* *Propylo-iodide* Methyl-ethyl-aniline.

METHYL-PROPYL-BENZENE *v.* Cymene.

s-Methyl-di-propyl-benzene $C_{13}H_{20}$ *i.e.* $C_6H_3Me(C_3H_7)_2$[1:3:5]. (243°–248). Formed by

the action of H_2SO_4 on a mixture of acetone and methyl *n*-propyl ketone (Jacobsen, *B.* 8, 1259). Yields uvitic acid on oxidation with dilute HNO_3.

s-**Di-methyl-propyl-benzene** $C_{11}H_{16}$ *i.e.* $C_6H_3Me_2.C_3H_7$ [1:3:5] (206°–210°). Formed by the action of H_2SO_4 (3 vols.) on a mixture of acetone (4 vols.) and methyl propyl ketone (2 vols.) (Jacobsen, *B.* 8, 1259). Oxidised by boiling dilute HNO_3 to mesitylenic acid.

u-**Di-methyl-propyl-benzene** $C_{11}H_{16}$ *i.e.* $C_6H_3Me_2Pr$ [1:4:2]. (206°). Formed from bromo-*p*-xylene, propyl bromide, and sodium (Uhlhorn, *B.* 23, 2350). Liquid, not solidified at −20°. Yields a tri-nitro- derivative [85°], and a tri-bromo- derivative [49°].

Sulphonic acid $C_6H_2Me_2Pr.SO_3H$. Salts.—BaA'_2.—NaA' $1\frac{1}{2}$aq.—
Amide $C_6H_2Me_2Pr.SO_2NH_2$. [125°].—
Anilide $C_6H_2Me_2Pr.SO_2NHPh$. [216°].

u-**Di-methyl-propyl-benzene** $C_6H_3Me_2Pr$[1:3:4]. (208°). Formed from bromo-*m*-xylene, propyl bromide, and Na (Uhlhorn). Liquid, not solid at −20°. Yields a tri-nitro-derivative [110°] and a tri-bromo- derivative [39°]. May be oxidised to (1,3,4)-di-methyl-benzoic acid.

Sulphonic acid $C_6H_2Me_2Pr.SO_3H$. Groups of needles. — Salts. — NaA' $4\frac{1}{2}$aq.— BaA'_2 2aq.—MgA'_2 5aq.—
Amide $C_6H_2Me_2Pr.SO_2NH_2$ [102°].—
Anilide $C_6H_2Me_2Pr.SO_2NHPh$. [c. 182°].

u-**Di-methyl-propyl-benzene** $C_6H_3Me_2Pr$ [1:2:4]. (209°). Formed from bromo-o-xylene, propyl bromide and sodium (Uhlhorn, *B.* 23, 2349). Liquid, not solid at − 20°. Yields on oxidation (1,2,4)-di-methyl-benzoic acid [162°].

Sulphonic acid $C_6H_2Me_2Pr.SO_3H$. Thin needles.—Salts.—BaA'_2 $3\frac{1}{2}$aq.—
Amide $C_6H_2Me_2Pr.SO_2NH_2$. [124°].—
Anilide $C_6H_2Me_2Pr.SO_2NHPh$. [214°].

u-**Di-methyl-isopropyl-benzene** $C_6H_3Me_2Pr$ [1:3:4]. (194°). Formed from bromo-*m*-xylene, isopropyl bromide, and sodium (U.). Liquid. Yields a tri-bromo- derivative [261°] and a tri-nitro- derivative [182°].

Sulphonic acid $C_6H_2Me_2Pr.SO_3H$. Needles.—Salts.—NaA' 4aq.—BaA'_2. —
Amide $C_6H_2Me_2Pr.SO_2NH_2$. [163°].—
Anilide $C_6H_2Me_2Pr.SO_2NHPh$. [207°].

METHYL-PROPYL-BENZOIC ACID $C_{11}H_{14}O_2$ *i.e.* $C_6H_3Me(C_3H_7)CO_2H$. *Carbocymolic acid.* [63°]. Obtained from its nitrile, which is produced by distilling potassium cymene sulphonate with KCy (Paterno a. Fileti, *B.* 8, 442; Paterno a. Spica, *G.* 9, 400).

Amide $C_6H_3Me(C_3H_7).CONH_2$. [139°]. Obtained by boiling the nitrile with alcoholic potash. Needles, sl. sol. cold water.

METHYL-PROPYL-CARBINOL *v.* *Sec*-AMYL ALCOHOL.

Di-methyl-propyl-carbinol *v.* *Tert*-HEXYL ALCOHOL.

Methyl-di-propyl-carbinol *v.* OCTYL ALCOHOL.

METHYL PROPYL CARBONATE $C_5H_{10}O_3$ *i.e.* $CH_3O.CO.OC_3H_7$. (131° cor.). S.G. $\frac{27}{}$ ·978 (Röse, *A.* 205, 230).

METHYL-PROPYL-COUMARIN $C_{13}H_{14}O_2$ *i.e.* $C_6H_2\overset{(1)}{(CH_3)}\overset{(4)}{(C_3H_7)}\left\langle\begin{array}{l}CH{:}CH\ (2)\\ \quad | \\ O-CO\ (3)\end{array}\right.$. [53°]. (220°–230°). Formed by heating a mixture of thymol, malic acid and H_2SO_4 (Pechmann a. Welsh, *B.* 17, 1647). Fine white needles. V. sol. alcohol, ether, benzene, acetic acid, and chloroform, v. sl. sol. water.

METHYL-PROPYLENE-ψ-THIO-UREA $C_5H_{10}N_2S$ *i.e.* $\begin{array}{l}CHMe.S\\ | \\ CH_2.NH\end{array}\!\!\!>C{:}NMe$ or $\begin{array}{l}CHMe.S\\ | \\ CH_2.N\end{array}\!\!\!>C.NHMe$. *Methyl - amido - methyl - thiazole dihydride.* [50°]. Formed by the action of methyl thiocarbimide on β-oxy-propylamine (Hirsch, *B.* 23, 971). Long needles (from ligroïn), v. sol. water. Its aqueous solution is strongly alkaline.—$B'_2H_2PtCl_6$. [143°]. Large dark-red needles (from hot water). — $B'C_6H_2(NO_2)_3OH$. [145°]. Needles. — Compound with methyl thiocarbimide B'MeNCS. [64°]. White columns (from MeOH).

Methyl-propylene-ψ-thio-urea $C_5H_{10}N_2S$ *i.e.* $\begin{array}{l}CHMe.S\\ | \\ CH_2.NMe\end{array}\!\!\!>C{:}NH$. *Imido - di - methyl - thiazole tetrahydride.* Formed from propylene-ψ-thio-urea, MeI, and KOH (Gabriel, *B.* 22, 2989). Converted by bromine water into the acids $NHMe.CH_2.CHMe.SO_3H$ [220°–223°] and $CONH_2.NMe.CH_2.CHMe.SO_3H$. [230°–240°].

METHYL-PROPYL-ETHANE *v.* HEXANE.

METHYL-ISOPROPYL-FLUORENE $C_{17}H_{18}$ *i.e.* $CH_2\left\langle\begin{array}{l}C_6H_4\\ | \\ C_6H_2MePr\ [6{:}5{:}1{:}4]\end{array}\right.$. *Retene-fluorene.* [97°]. Formed by passing the vapour of methyl-isopropyl-di-phenylene ketone (retene ketone) through a red-hot tube (Bamberger a. Hooker, *A.* 229, 142). Formed also by heating this ketone with HIAq and phosphorus in sealed tubes. White plates, v. sol. cold ether, hot alcohol, and HOAc. In the fused state, or in alcoholic solution, it exhibits violet fluorescence. It yields a di-nitro- derivative [245°].

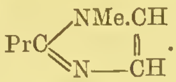
METHYL-ISOPROPYL-FLUORENE ALCOHOL $C_{17}H_{18}O$ *i.e.* $CH(OH)\left\langle\begin{array}{l}C_6H_4\\ | \\ C_6H_2MePr\end{array}\right.$. [134°]. Formed by the reduction of methyl-isopropyl-di-phenylene ketone (Bamberger a. Hooker, *A.* 229, 144). White needles, insol. water, v. sol. alcohol and ether. Readily oxidised back to the ketone. The acetate melts at 71°.

METHYL-PROPYL-GLUTARIC ACID $CO_2H.CHPr.CH_2.CHMe.CO_2H$. [102°]. Formed from sodium propyl-malonic ether and bromo-isobutyric ether, the product being saponified, and the resulting $(CO_2H)_2CHPr.CH_2.CHMe.CO_2H$ [168°] being decomposed by heat (Bischoff, *B.* 23, 1940). White aggregates of crystals (from petroleum-ether).

DI-METHYL-PROPYL-GLYCOLLINE *v.* DI-METHYL-DI-OXY-PROPYL-AMINE.

METHYL-PROPYL-GLYOXALINE $C_7H_{12}N_2$ *i.e.* $CH_3.C\left\langle\begin{array}{l}NPr.CH\\ \quad\ \| \\ N-CH\end{array}\right.$. *Oxal - propyl - ethyline.*

(225°). S.G. ·9641. Formed by the action of propyl-bromide on methyl-glyoxaline (glyoxal-ethyline) (Radziszewski, *B.* 16, 489). Colourless liquid.

Methyl-propyl-glyoxaline 

Oxal-methyl-butyline. (215° at 722 mm.). S.G. $\frac{20}{}$ ·985. From propyl-glyoxaline and MeI (Rieger, *M.* 9, 606). Oil, v. sol. alcohol, ether, and chloroform.—$B'_2H_2PtCl_6$: orange-red prisms.

METHYL-PROPYL-GLYOXAL *v.* METHYL-PROPYL-DIKETONE.

DI-METHYL-PROPYLIDENE DIKETONE $C_7H_{12}O_2$ *i.e.* $(CH_3.CO)_2CHEt$. *Ethyl-acetyl-acetone.* (179°). Prepared by heating the sodium derivative of methylene di-methyl diketone with EtI at 140° (Combes, *A. Ch.* [6] 12, 248; *C. R.* 104, 920). Colourless liquid with pleasant odour, sl. sol. water, miscible with ether, alcohol, and chloroform. Decomposed by potash into CH_3CO_2K and $CH_3.CO.CH_2Et$. Combines with $NaHSO_3$. Sodium yields $(CH_3.CO)_2CNaEt$ which reacts with alkyl iodides.

METHYL PROPYL KETONE $C_5H_{10}O$ *i.e.* $CH_3.CO.C_3H_7$. *Ethyl-acetone.* (102°). S.G. $\frac{15}{15}$ ·8124; $\frac{25}{25}$ ·8044 (Perkin, *C. J.* 45, 479); $\frac{22}{}$ ·805 (F. a. D.). H.F.p. 72,410. H.F.v. 69,400 (Thomsen, *Th.*). M.M. 5·499 at 16·1° (P.).

Formation.—1. By distilling calcic acetate (48 g.) mixed with calcic butyrate (65 g.), and rectifying the product. The yield (10 g.) is small (Semljanitzin, *J. pr.* [2] 23, 263; *cf.* Friedel, *A. Ch.* [4] 16, 366; *A.* 108, 124; Grimm, *A.* 157, 251).—2. By boiling ethyl-acetoacetic ether with potash or baryta (Frankland a. Duppa, *A.* 138, 216).—3. By the action of $ZnMe_2$, followed by water, on butyryl chloride (Butlerow, *Bl.* [2] 5, 17).—4. By the oxidation of *sec-n*-amyl alcohol (Wurtz, *A.* 148, 133; Schorlemmer, *C. J.* 25, 1085; *A.* 161, 269; Wagner a. Saytzeff, *A.* 179, 322).—5. By the action of water and $HgBr_2$ on valerylene (Kutscheroff, *B.* 14, 1542).—6. By the action of KOH on $(CH_3.CO)_2CHEt$ (Combes, *A. Ch.* [6] 12, 248).

Properties.—Liquid, v. sl. sol. water. Combines with hydrogen sodium sulphite, forming $C_5H_{10}(OH)SO_3Na\ \frac{1}{2}aq$ (Grimm). Reduced by means of sodium-amalgam to *sec*-amyl alcohol $CH_3.CH(OH).CH_2Et$ (119° cor.) (Belohoubek, *Sitz. W.* [2] 74, 80) and a pinacone $C_{10}H_{22}O_2$ (225°–230°). Yields acetic and propionic acids on oxidation (Schorlemmer); Wagner obtained butyric acid (*Bl.* [2] 38, 264). PCl_5 forms $CH_3.CCl_2.CH_2Et$, whence alcoholic potash produces $CH{:}C.CH_2Et$, and this is converted by alcoholic potash at 170° into $CH_3.C{:}CEt$ (56°) (Favorsky, *J. R.* 1887. 414). $CH_3.CCl_2.CH_2Et$ is split up on distillation into HCl and C_5H_9Cl (c. 95°). Amyl nitrite and HCl or NaOEt forms the nitroso- derivative $C_3H_7.CO.CH{:}NOH$ [48°–51°], which is also an oxim of propyl-glyoxal. From this oxim may be prepared the compounds $C_3H_7.C(NOH).CH(NOH)$ [168°] and $C_3H_7.C(N_2HPh).CH(N_2HPh)$ [163°] (Claisen a. Manasse, *B.* 22, 528).

Oxim $C_3H_7.C(NOH).CH_3$. Oil. Converted by gaseous HCl in HOAc at 100° into propylamine and acetic acid (Beckmann, *B.* 20, 2580).

Methyl isopropyl ketone $C_5H_{10}O$ *i.e.* $CH_3.CO.CH(CH_3)_2$. *Di-methyl-acetone.* '*Amylene oxide.*' (94°). S.G. $\frac{0}{}$ ·822; $\frac{18}{}$ ·805 (Winogradoff); $\frac{13}{}$ ·810 (F. a. D.). C.E. (0°–18°) ·00118.

Formation.—1. By the action of baryta-water on di-methyl-aceto-acetic ether (Frankland a. Duppa, *Pr.* 14, 463; *A.* 138, 332).—2. By the dry distillation of a mixture of calcium isobutyrate and calcium acetate (Münch, *B.* 7, 1370; *A.* 180, 327).—3. By the action of tin and HClAq on di-nitro-heptoic acid, which is one of the products of the action of nitric acid on camphor (Kachler, *A.* 191, 162).—4. From amylene glycol $(CH_3)_2C(OH).CH(OH).CH_3$ by dehydration with P_2O_5 (Flavitzky, *B.* 10, 2240).—5. From $(CH_3)_2CH.CH(OH).CH_2(OH)$ by dehydration with $ZnCl_2$ or P_2O_5 (F.).—6. From $(CH_3)_2C(OH).CH(OH).CH_3$, by heating with dilute HCl at 100°, and treating the product with potash (Bauer, *C. R.* 51, 55; A. 115, 91; Eltekoff, *J. R.* 14, 358).—7. By shaking $(CH_3)_2CH.C{:}CH$ with diluted H_2SO_4 (S.G. 1·64) (Flavitzky a. Kryloff, *J. R.* 10, 347).—8. By oxidising Me.CH(OH).Pr by CrO_3 (Winogradoff, *A.* 191, 133).—9. By heating $(CH_3)_2CBr.CHBr.CH_3$ with water and PbO at 150° (Eltekoff, *J. R.* 10, 215), or by digesting it with water alone (Niederist, *A.* 196, 360; Nägeli, *B.* 16, 2983).—10. By heating Me.CH(OH).Pr with excess of dilute (1 p.c.) H_2SO_4 at 100° (Kondakoff, *J. R.* 17, 300).

Properties.—Liquid. Gives the iodoform reaction with iodine and potash. Forms a crystalline compound with $NaHSO_3$. On oxidation it yields acetone and acetic acid, and finally CO_2 and acetic acid.

Oxim $CH_3.C(NOH).CHMe_2$. (158°). From the ketone and hydroxylamine (Nägeli, *B.* 16, 2984). Formed also by heating the oxim of dimethyl-acetoacetic acid above 97° (Wallach, *A.* 248, 178).

Reference.—CHLORO-METHYL ISOPROPYL KETONE.

Methyl propyl diketone $C_6H_{10}O_2$ *i.e.* $CH_3.CO.CO.CH_2.CH_2.CH_3$. *Acetyl-butyryl.* (128°). S.G. $\frac{19}{4}$ ·9343. Obtained by boiling its monooxim with dilute H_2SO_4 (Von Pechmann, *B.* 21, 2140). Yellow oil, with irritating odour like quinone.

Mono-oxim $CH_3.CO.C(NOH).C_3H_7$. *Isonitroso-propyl-acetone.* [49·5°]. Formed by the action of nitrous acid on propyl-acetoacetic ether (Treadwell, *B.* 14, 2159). Large plates. With phenyl cyanate it reacts with formation of $CH_3.CO.CPr{:}NO.CO.NHPh$ [93°] (Goldschmidt, *B.* 22, 3108), whence hydroxylamine yields $CH_3.C(NOH).CPr{:}NO.CO.NHPh$ [129°–131°].

Di-oxim $CH_3.C(NOH).C(NOH).C_3H_7$. *Methyl-propyl-glyoxim.* [168°]. Formed by the action of hydroxylamine hydrochloride in aqueous-alcoholic solution on isonitroso-propyl-acetone (Schramm, *B.* 16, 2185). Small needles. With phenyl cyanate it reacts with formation of CMe(NO.CO.NHPh).CPr(NO.CO.NHPh), crystallising in pearly plates [164°–170°] (Goldschmidt a. Strauss, *B.* 22, 3108).

Oxim-phenyl-hydrazide $C_{12}H_{17}N_3O$ *i.e.* $CMe(N_2HPh).CPr(NOH)$. [130·5°]. Formed by the action of phenyl-hydrazine acetate on the mono-oxim (Otte a. Pechmann, *B.* 22, 2121). Needles, sl. sol. dilute NaOHAq. Gives a violet colour with H_2SO_4 and $FeCl_3$.

(α)-*Phenyl-hydrazide* $C_{12}H_{16}N_2O$ *i.e.* Me.C(N_2HPh).COPr. [114°]. Formed by the action of phenyl hydrazine on the diketone (O. a. P.). Insol. water and ligroïn, v. sol. alcohol and ether. With conc. H_2SO_4 and FeCl it gives a red colour.

(β)-*Phenyl-hydrazide* $C_{12}H_{16}N_2O$ *i.e.* Me.CO.C(N_2HPh).Pr. [109°]. Formed from propyl-acetoacetic acid by the action of diazobenzene chloride in presence of NaOAc (Japp a. Klingemann, *A.* 247, 220). Colourless needles (from benzene and ligroïn).

Di-phenyl-di-hydrazide $C_{18}H_{22}N_4$ *i.e.* Me.C(N_2HPh).C(N_2HPh).Pr. [136·5°]. Formed as a yellow pp. when excess of phenyl-hydrazine acetate is added to the ketone, its phenyl-hydrazide, or its oxim-phenyl-hydrazide (Otte a. Pechmann, *B.* 22, 2121). Yellow needles (from benzene), more easily soluble than its homologues with fewer atoms of carbon in the molecule.

Methyl isopropyl diketone $C_6H_{10}O_2$ *i.e.* CH_3.CO.CO.CH$(CH_3)_2$. *Acetyl-isobutyryl.* (116°). Formed by boiling its oxim with dilute H_2SO_4 (Von Pechmann, *B.* 21, 2140; 22, 2122). Yellow liquid, with irritating odour, sl. sol. water.

Oxim CH_3.CO.C(NOH).$CHMe_2$. *Isonitroso-methyl-isobutyl-ketone.* [75°]. Formed by the action of nitrous acid on isopropyl-acetoacetic ether (Westenberger, *B.* 16, 2991). White plates, sol. alcohol, ether, alkalis, and hot water.

METHYL-PROPYL-KETONE CARBOXYLIC ACID *v. Ethyl*-ACETOACETIC ACID.

Methyl-propyl-ketone tricarboxylic acid CH_3.CO.CH(CH_2.CO_2H).CH$(CO_2H)_2$. *α-Carboxy-β-acetyl-glutaric acid.* [121°–124°]. The tri-ethyl ether is formed by the action of chloro- or bromo-lævulic (acetyl-propionic) ether upon sodio-malonic ether. Colourless crystalline solid. At 160° it splits off CO_2, giving acetoglutaric acid. The neutral NH_4 salt gives pps. with $AgNO_3$, $BaCl_2$, and $Pb(OAc)_2$. The zinc salt is a very soluble amorphous solid.

Tri-ethyl ether A‴Et_3: (285°–295°); oil (Conrad a. Guthzeit, *B.* 19, 43).

METHYL - ISOPROPYL - KETONE - CARBOXYLIC ALDEHYDE. *Di-oxim* $C_6H_{11}N_2O_2$ *i.e.* CH_3.C(NOH).CH_2CMe.CH:NOH. [90°]. Formed from di-methyl-pyrrole and hydroxylamine (Ciamician, *B.* 23, 1788). Small needles or prisms, v. sol. alcohol, and water, sl. sol. ether. Reduces Fehling's solution. Sodium reduces it in alcoholic solution to di-methyl-tetra-methylene-diamine.

METHYL-PROPYL-DI-KETOXIM *v. Oxim* of METHYL-PROPYL-DIKETONE.

METHYL-ISOPROPYL-MALONIC ACID $C_7H_{12}O_4$ *i.e.* CO_2H.CMePr.CO_2H. [124°]. Formed by saponifying its ether (Van Romburgh, *R. T. C.* 5, 236). Crystallises from benzene. Split up at 150°–200° into CO_2 and a hexoic acid.

Salts.—CaA'_2. V. sol. water.—AgA′: white pp.

Ethyl ether Et_2A″. (221°). S.G. $\frac{15}{}$ ·990. Formed from sodio-malonic ether, MeI, and PrI. Colourless liquid with agreeable odour.

METHYL PROPYL OXIDE $C_4H_{10}O$ *i.e.* CH_3.O.Pr. (38·9°). S.G. $\frac{0}{0}$ ·7471. S.V. 105·1. C.E. (0° to 10°) ·00146 (Dobriner, *A.* 243, 2; *cf.* Chancel, *A.* 151, 305).

METHYL-PROPYL-PHENOL *v.* CARVACROL, CYMENOL, and THYMOL.

Tetrahydride v. BORNEOL and CINEOL.

DI-METHYL-PROPYLPHENYL-AMINE $C_6H_4(C_3H_7)$.NMe_2. *Di-methyl-phenpropyl-amine.* (230° uncor.). Formed by the action of sodium on a mixture of propyl bromide and di-methyl-*p*-bromo-aniline (Claus a. Howitz, *B.* 17, 1327). Colourless oil.

Methylo-iodide B′MeI: [168°]; plates.

METHYL - ISOPROPYL - PHENYL CARBAMINE *v. Iso*-CYMYL CARBAMINE.

METHYL-PROPYL-PHENYLENE-DIAMINE $C_6H_2Me(C_3H_7)(NH_2)_2$. Formed by reducing the di-oxim of thymoquinone with tin and HCl (Liebermann, *B.* 18, 3193). Oxidised by CrO_3 or $FeCl_3$ to thymoquinone.—B″H_2Cl_2: needles.

METHYL-ISOPROPYL-DIPHENYLENE KETONE $C_{17}H_{16}O$ *i.e.* $CO\Big\langle\begin{array}{l}C_6H_4\\ |\\ C_6H_2Me(C_3H_7)\end{array}$. *Retene-ketone.* [90°]. Formed by oxidising retene-glycolic acid $C_{10}H_{16}$.C(OH).CO_2H (Bamberger a. Hooker, *A.* 229, 136). Formed also from retene-quinone by the action of alkaline $KMnO_4$ or by passing it over red-hot $Ba(OH)_2$ or PbO (Ekstrand, *B.* 17, 692). Yellow prismatic needles or rectangular trimetric plates (by spontaneous evaporation), v. sol. ligroïn, benzene, chloroform, alcohol, and HOAc. Volatile with steam and with vapour of alcohol. Does not react with hydroxylamine or with $NaHSO_3$. Reacts with phenyl-hydrazine. Reduced by sodium-amalgam to methyl-isopropyl-fluorene alcohol (*q. v.*), and by red-hot zinc-dust to methyl-isopropyl-fluorene.

METHYL - ISOPROPYL - PHENYL - ETHYL-GUANIDINE *v. Iso*-CYMYL-ETHYL-GUANIDINE.

METHYL - PROPYL - PHENYL - GLYOXYLIC ACID $C_{12}H_{14}O_3$ *i.e.* [2:5:1] C_6H_3MePr.CO.CO_2H. Formed by oxidising the ketone C_6H_3MePr.CO.CH_3 with cold aqueous $KMnO_4$ (Claus, *B.* 19, 233). Thick oil, easily decomposing into CO_2 and C_6H_3MePr.CHO. Dilute nitric acid yields $C_6H_3Me(CO_2H)_2$.

METHYL-PROPYL-PHENYL METHYL KETONE $C_{12}H_{16}O$ *i.e.* C_6H_3MePr.CO.CH_3. (248°). Formed from cymene, AcCl, and $AlCl_3$ (Claus a. Cropp, *B.* 19, 232).

METHYL - ISOPROPYL - PHENYL - THIO-ETHYL-UREA *v. Iso*-CYMYL-ETHYL-THIO-UREA.

DI - METHYL - DI-ISOPROPYL-DI-PHENYL-THIO-UREA *v. Di-iso*-CYMYL-THIO-UREA.

METHYL - ISOPROPYL - PHENYL - UREA *v. Iso*-CYMYL-UREA.

METHYL - ISOPROPYL - PHENYL - URETHANE *v. Iso*-CYMYL-CARBAMIC ETHER.

METHYL-ISOPROPYL-PHOSPHINE $C_4H_{11}P$ *i.e.* CH_3.PH.C_3H_7. (79°). Obtained by heating isopropyl-phosphine with MeI at 100° (Hofmann, *B.* 6, 299).

DI-METHYL-DI-PROPYL-PYRAZINE $C_{12}H_{20}N_2$ *i.e.* $N\Big\langle\begin{array}{l}CMe.CPr\\ CPr{:}CMe\end{array}\Big\rangle N$. *Di-propyl-ketine.* (233°–245°). Prepared by the reduction of the oxim of methyl propyl diketone (nitroso-methyl-butyl-ketone) with tin and HCl (Treadwell, *B.* 14, 1461, 2160; Oeconomides, *B.* 19, 2526). Oil, with narcotic odour, turning brown in the air.—$B'_2H_2PtCl_6$: red octahedra,

sl. sol. water.—$B'AgNO_3$aq: crystals, insol. cold water.

METHYL-PROPYL-PYRIDINES. Parvoline. The base obtained by the action of P_2O_5 on a mixture of propionic aldehyde and acetamide (Hesekiel, *B.* 18, 3097) has been shown by Dürkopf a. Göttsch (*B.* 23, 685) to yield pyridine tricarboxylic acid on oxidation, and must therefore be di-methyl-ethyl-pyridine (*q. v.*). Parvolines, which must be C_5HMe_4N, $C_5H_3Me(C_3H_7)N$, $C_5H_2Me_2EtN$, or $C_5H_3Et_2N$, occur in crude paraffin oil (Williams, *C. J.* 7, 97), in coal-tar (Thenius, *J.* 1861, 502), in the product of the distillation of cinchonine with KOH (Oechsner de Coninck, *Bl.* [2] 34, 214), and in putrid flesh (Gautier, *Bl.* 48, 11).

Di-methyl-propyl-pyridine $C_{10}H_{15}N$ *i.e.* $C_5H_2NMe_2Pr$ (1:3:5). *n-Propyl-lutidine. Coridine.* (c. 195°) at 718 mm. Formed by distilling potassium di-methyl-propyl-pyridine dicarboxylate with lime (Jæckle, *A.* 246, 37). Colourless liquid; sl. sol. water, v. sol. alcohol and ether. Its hydrochloride is crystalline.—$B'_2H_2PtCl_6$. [185°].

Isomeride *v.* CORIDINE.

ν-Methyl-isopropyl-pyridine hexahydride $C_9H_{19}N$ *i.e.* $CH_2<\begin{smallmatrix}CH_2.CH_2\\CH_2.CHPr\end{smallmatrix}>NMe$. (167°). S.G. $\frac{0}{0}$ ·8593. Formed by adding the calculated quantity of MeI to a solution of isopropyl-pyridine hexahydride in MeOH, evaporating and distilling the residue with potash (Ladenburg, *A.* 247, 77). Oil, smelling like coniine.—$B'HAuCl_4$. [131°]. Plates, sl. sol. water.—$B'_2H_2PtCl_6$. [100°]. Plates, v. sol. water and alcohol, insol. ether.—Picrate $B'C_6H_2(NO_2)_3OH$. [149°].

Di-methyl-propyl-pyridine hexahydride $C_{10}H_{21}N$ *i.e.* $CHPr<\begin{smallmatrix}CH_2.CHMe\\CH_2.CHMe\end{smallmatrix}>NH$. *Propyl-lupetidine.* (c. [180°]) at 718 mm. Obtained by reducing di-methyl-propyl-pyridine in alcoholic solution with sodium (Jaeckle, *A.* 246, 46). Colourless oil. Gives a brownish pp. with $FeCl_3$, and a yellowish pp. with $MnSO_4$.—$B'_2H_2PtCl_6$. [197°]. Orange stellate needles.

DI-METHYL-PROPYL-PYRIDINE DICARBOXYLIC ACID $C_{12}H_{15}NO_4$ *i.e.* $CPr<\begin{smallmatrix}C(CO_2H).CMe\\C(CO_2H):CMe\end{smallmatrix}>N$. [247°]. Formed by saponifying its ether, which is obtained by oxidation, with nitrous gas, from the product of the action of ammonia on butyric aldehyde mixed with acetoacetic ether (Jaeckle, *A.* 246, 36). Colourless prisms (containing aq). When anhydrous it melts at 247°, but at 212° when hydrated. V. e. sol. hot, m. sol. cold, water. Yields di-methyl-propyl-pyridine when distilled with lime.

Ethyl ether Et_2A''. (308°) at 715 mm. Light-yellow oil. Saponified by boiling first with aqueous, and then with alcoholic, potash.—$(C_{16}H_{23}NO_4)_2H_2PtCl_6$. [187°]. Orange prisms.

Dihydride of the ethyl ether $CHPr<\begin{smallmatrix}C(CO_2Et):CMe\\C(CO_2Et):CMe\end{smallmatrix}>NH$. [118°]. Formed by condensation of butyric aldehyde with acetoacetic ether and ammonia (Jaeckle, *A.* 246, 34). Yellowish-white prisms; v. sol. alcohol and ether, insol. water.

Di-methyl-isopropyl-pyridine dicarboxylic ether. *Dihydride* $CHPr<\begin{smallmatrix}C(CO_2Et):CMe\\C(CO_2Et):CMe\end{smallmatrix}>NH$. [97°]. Formed by the action of alcoholic ammonia on a mixture of isobutyric aldehyde and acetoacetic ether (Engelmann, *A.* 231, 47). Long prisms (from 90 p.c. alcohol). Oxidised by nitrous acid, in presence of alcohol, to di-methyl-pyridine dicarboxylic ether $C_5HMe_2N(CO_2Et)_2$.

METHYL-DI-ISOPROPYL-QUINOLINE DIHYDRIDE $C_{16}H_{23}N$. (299°). Formed by heating di-iso-propyl-indole with MeI and MeOH (Dennstedt, *B.* 21, 3437). Oil.—$B'_2H_2PtCl_6$. [177°].

METHYL PROPYL-STYRIL KETONE $C_{13}H_{16}O$ *i.e.* $C_6H_4(C_3H_7).CH:CH.CO.CH_3$. *Cuminal-acetone.* (181° at 23 mm.). Formed by the action of dilute (10 p.c.) NaOHAq upon a mixture of cuminic aldehyde (20 g.), acetone (20 g.), water (300 g.), and alcohol (170 g.) (Claisen a. Ponder, *A.* 223, 147). Yellow oil.

METHYL ISOPROPYL SULPHIDE $C_4H_{10}S$ *i.e.* MeSPr. (93°–95°). V.D. 45·02. Formed by dissolving sodium in an ethereal solution of isopropyl mercaptan, and slowly adding MeI to the product (Obermeyer, *B.* 20, 2923).

METHYL PROPYL DITHIOCARBONATE $MePrCS_2O$. *Methyl propyl xanthate.* S.G. $\frac{4}{4}$ 1·084 (Nasini a. Scala, *G.* 17, 66).

s-**METHYL-PROPYL-THIO-UREA** $C_5H_{12}N_2S$ *i.e.* $CH_3.NH.CS.NHC_3H_7$. [79°]. Prepared from methyl-thiocarbimide and propylamine, or from propyl thiocarbimide and methylamine (Otto Hecht, *B.* 23, 284). Transparent glassy plates (from very dilute alcohol); sl. sol. cold water, m. sol. hot water, v. sol. alcohol and wood-spirit, extremely sol. acetone and chloroform, v. sol. ether, benzene, and CS_2, v. sl. sol. warm light petroleum.

DI-METHYL-PYRAZINE $C_6H_8N_2$ *i.e.* $N<\begin{smallmatrix}CMe.CH\\CH:CMe\end{smallmatrix}>N$. *Ketine. Di-methyl-aldine* (Meyer, *B.* 21, 19). (170°–180°). Formed by reduction of nitroso-acetone with tin and HCl (Treadwell a. Steiger, *B.* 15, 1059, 1055; Oeconomides, *B.* 19, 2526; Wolff, *B.* 20, 433). Formed also by heating its dicarboxylic acid. Oil, with alkaloidal odour.—$B''H_2PtCl_6$: golden plates, sol. hot water.

Tetra-methyl-pyrazine $C_8H_{12}N_2$ *i.e.* $N<\begin{smallmatrix}CMe.CMe\\CMe:CMe\end{smallmatrix}>N$. *Methyl-ketine. Di-methyl-ketine. Tetra-methyl-aldine.* [86°]. (190°). Formed by reducing with tin and HCl the oxim of di-methyl-diketone (methyl nitroso-ethyl ketone) $CH_3.CO.C(NOH).CH_3$ (Gutknecht, *B.* 13, 1116; Treadwell, *B.* 14, 1469; Braun a. V. Meyer, 21, 1947). An intermediate base appears to be C_4H_9N (Braun, *B.* 22, 556). Tetra-methyl-pyrazine is also formed, together with CO_2 and other products, by heating $CH_3.CO.CHBr.CH_2.CO_2H$ or $CH_3.CO.CH(OH).CH_2.CO_2H$ with conc. NH_3Aq (Wolff, *B.* 20, 427). Glistening prisms (anhydrous) or long white needles (containing 3aq). Very volatile. Melts at 74°–77° when hydrated, but at 86° when anhydrous. Strong characteristic smell. V. sol. alcohol and ether. By alkaline $KMnO_4$ it is oxidised to pyrazine-tetra-carboxylic acid $C_4N_2(CO_2H)_4$.

Salts.—$B''HCl$ 2aq: easily soluble, [91° anhy.]. $B''_2H_2Cl_2PtCl_4$: red glistening needles.—$B''H_2Cl_2PtCl_4$ 4aq: orange-red needles.

Methylo-iodide B″MeI: [216°] anhy. Yellow needles (containing 2aq); v. sol. water and alcohol, insol. ether.

Methylo-chloride B″MeCl: [c. 105°]; needles.—$B''MeClHClPtCl_4$ aq: orange-red pyramids (from hot water).

DI-METHYL-PYRAZINE DICARBOXYLIC ACID $C_8H_8N_2O_4$ *i.e.* $N\lessdot\begin{smallmatrix}CMe.C(CO_2H)\\C(CO_2H):CMe\end{smallmatrix}\gtrdot N$. [201°]. Prepared by saponification of its ether, which is formed by reducing nitroso-acetoacetic ether with stannous chloride (Wleügel, *B.* 15, 1050). Formed also by oxidising di-methyl-di-ethyl-pyrazine by aqueous $KMnO_4$, and by condensation of imido-oximido-butyric ether $CH_3.C(NH).C(NOH).CO_2Et$ by warm $ZnCl_2$ (Oeconomides, *B.* 19, 2524).

Properties.—Colourless crystals (containing 2aq), melting at 201° when anhydrous. V. sol. alcohol and acetone, m. sol. hot water and toluene, nearly insol. ether, benzene, and ligroïn. Decomposes when heated above 200° into CO_2 and di-methyl-pyrazine.

Salts.—BaA″3aq: glistening crystals.—*K_2A'': slender felted needles. Gives amorphous pps. with $FeCl_3$ and $CuSO_4$.—Ag_2A'': yellowish-white pp.

Ethyl ether Et_2A''. [86°]. (316° cor.). Long colourless needles, sol. alcohol.

METHYL-PYRAZOLONE *v.* OXY-METHYL-PYRAZOLE.

(α)-**METHYL-PYRIDINE** C_6H_7N *i.e.* $N\lessdot\begin{smallmatrix}CMe.CH\\CH:CH\end{smallmatrix}\gtrdot CH$. (α)-*Picoline.* Mol. w. 93. (129°) (L.); (133·4° cor.) (Thorpe, *C. J.* 37, 223). S.G. $\frac{0}{4}$ ·9656 (L.); ·9616 (T.). C.E. (0°–10°) ·000975; (0°–100°) ·0010968 (T.). S.V. 111·5.

Occurrence.—In bone-oil (Anderson, *A.* 60, 86; Weidel, *B.* 12, 2008), where it is mixed with a little (β)-picoline and di-methyl-pyridine (Ladenburg, *B.* 18, 49). It is also the chief constituent of coal-tar-picoline (Goldschmidt a. Constam, *B.* 16, 2976).

Formation.—1. By heating pyridine (α)-carboxylic acid with fuming HIAq at 260°, or by treating the acid with zinc and HOAc (Seyfferth, *J. pr.* [2] 34, 244).—2. By the action of aldehyde on aldehyde-ammonia (Dürkopf a. Schlaugk, *B.* 21, 297).—3. By heating pyridine methylo-iodide in sealed tubes at 300° (Ladenburg, *A.* 247, 7; *C. R.* 103, 692).

Preparation.—Crude pyridine (50 g. boiling between 128° and 134°) is dissolved in HClAq (170 g. of 11 p.c.), and a hot solution of $HgCl_2$ (312 g.) in water ($4\frac{1}{2}$ litres) is poured in. The double salt crystallises out, and, after recrystallisation, is decomposed by aqueous NaOH (Ladenburg, *A.* 247, 6).

Properties.—Liquid, inactive to light, miscible with water and alcohol. Picoline lessens the heart's action, and acts on the nervous system somewhat like nicotine (Oechsner, *Bl.* [2] 38, 547).

Reactions.—1. Yields pyridine (α)-carboxylic (picolinic) acid on oxidation (Weidel).—2. When heated with sodium it yields di-methyl-dipyridyl. 3. *Methylal* and $ZnCl_2$ yield $CH_2(C_6H_6N)_2$.—4. *Chloral* forms $C_5NH_4.CH_2.CH(OH).CCl_3$ [87°], the hydrochloride of which $C_8H_8NOCl_3HCl$ melts at 202°. Alcoholic potash converts it into pyridyl-acrylic acid (Einhorn a. Liebrecht, *B.* 20, 1592).—5. *Paraldehyde* at 260° forms allyl-pyridine $C_5NH_4.C_3H_5$ (190°), S.G. $\frac{0}{}$ ·9595 (Ladenburg, *A.* 247, 26). Its aurochloride melts at 136°, its platinochloride at 186°. Allyl-pyridine is reduced in alcoholic solution by sodium to coniïne.—6. *Furfuraldehyde* and a little $ZnCl_2$ at 170° yields $C_5H_4N.CH:CH.C_4H_3O$ [53°] (Merck, *B.* 21, 2709), *v.* FURFURYL-VINYL-PYRIDINE. In alcoholic solution it is reduced by sodium to the hexahydride of furfuryl-ethyl-pyridine (*q.v.*). 7. *Glycolic chlorhydrin* at 140° forms a compound $C_8H_{11}NO$, which yields the salts $B'_2H_2PtCl_6$ [200°] and $B'HAuCl_4$ [100°] (Alexander, *B.* 23, 2714).

Salts.—$B'_2H_2PtCl_6$ aq. [178°]. Monoclinic tables or prisms, sl. sol. water.—$B'_2H_2PtCl_6$ 2aq (Weidel). — $B'_2H_2PtCl_6$. [195°]. Monoclinic plates; $a:b:c$ = ·6636:1:·9078; β = 72° 46′ (Stöhr, *J. pr.* [2] 42, 420).—$B'HAuCl_4$. [168°]. Needles, sl. sol. water.—$B'HHg_2Cl_5$. [154°]. Prisms (from dilute HClAq), v. sl. sol. cold, v. sol. hot, water.—B'_2ZnCl_2 (at 120°). Crystals (from alcohol) (Lachovitch a. Bandrowsky, *M.* 9, 517).

Picrate $B'C_6H_2(NO_2)_3OH$. [165°]. M. sol. water (Lange, *B.* 18, 3436).

(α)-**Methyl-pyridine tetrahydride** $C_6H_{11}N$ *i.e.* $NH\lessdot\begin{smallmatrix}CMe:CH\\CH_2.CH_2\end{smallmatrix}\gtrdot CH_2$. Formed by the action of alcoholic NH_3 upon methyl ω-bromo-butyl-ketone, probably by elimination of water from the intermediate $CH_3.CO.CH_2.CH_2.CH_2.CH_2.NH_2$ (Lipp, *B.* 19, 2843).

(α)-**Methyl-pyridine hexahydride** $C_6H_{13}N$ *i.e.* $NH\lessdot\begin{smallmatrix}CHMe.CH_2\\CH_2\ \ .CH_2\end{smallmatrix}\gtrdot CH_2$. (α)-*Methyl-piperidine.* (α)-*Pipecoline.* (119°). S.G. $\frac{0}{0}$ ·8600. Obtained by reducing (α)-methyl-pyridine in alcoholic solution with sodium (Ladenburg a. Roth, *B.* 18, 47; *A.* 247, 62; *C. R.* 103, 747). Colourless liquid, smelling like piperidine, v. sol. water, alcohol, and ether. Separated by KOH from its aqueous solution. Inactive, but if a crystal of hydrogen coniïne tartrate be added to a conc. solution of the acid tartrate, crystals of the acid tartrate of dextrorotatory (α)-methyl-pyridine hexahydride separate, while the salt of the lævo-rotatory isomeride remains as an oil. The rotation of the dextro-(α)-methyl-piperidine is $[\alpha]_D$ = 21°44′, while that of the lævo- base is (probably) equal and opposite.

Reactions.—1. Treatment with Br and NaOHAq yields (α)-pipecoleïn $C_6H_{11}N$, an oily base (126°), S.G. $\frac{0}{}$ ·880 (Ladenburg, *B.* 20, 1645). Its acetyl derivative boils at about 230°.—2. Combines with sulphide of carbon, forming methyl-piperidine methyl-piperyl-di-thio-carbamate $C_6H_{12}N.CS.SC_6H_{14}N$, [119°], v. e. sol. water and alcohol.

Salts.—B′HCl. [189°]. Colourless needles, v. sol. water. Not deliquescent.—B′HBr. [182°]. Silky matted needles, m. sol. water.—The platinochloride is v. sol. water.—The mercurichloride forms sparingly soluble plates.

(β)-**Methyl-pyridine** C_6H_7N *i.e.* $N\lessdot\begin{smallmatrix}CH.CMe\\CH:CH\end{smallmatrix}\gtrdot CH$. *m-Picoline.* (β)-*Picoline* (144° cor.). S.G. $\frac{0}{4}$ ·9771 (L.); ·9765 (B.).

Occurrence.—In bone-oil (Weidel, *B.* 12, 2008) and in coal-tar (Mohler, *B.* 21, 1009).

Formation.—1. By distillation of acroleïn-ammonia (Baeyer, *A.* 155, 283; *cf.* Claus, *A.*

Suppl. 2, 134; 130, 185; 158, 222).—2. By heating $CH_2Br.CHBr.CH_2Br$ with alcoholic ammonia at 250° (Baeyer).—3. By distilling strychnine with lime (Stoehr, *B.* 20, 2728; Löbisch a. Malfatti, *M.* 9, 632).—4. By heating acetamide (10 g.) with glycerin (32 g.) and P_2O_5 (26 g.) (Zanoni, *J.* 1882, 498; Hesekiel, *B.* 18, 3091).—5. Together with homologues, by distilling glycerin with $(NH_4)_2SO_4$ and a little H_2SO_4 (Storch, *B.* 19, 2458).—6. One of the bases got by distilling brucine with lime (Behrend, *J. pr.* [2] 42, 415).—7. Together with tri-methylene-imine (66°–70°) by distilling tri-methylene-diamine hydrochloride (Ladenburg a. Sieber, *B.* 23, 2729).

Purification.—By digesting in hydrochloric acid solution with $NaNO_2$ on a water-bath, followed by crystallisation of its mercury double salt (Bachér, *B.* 21, 293).

Properties.—Liquid. When prepared from strychnine it boils at 149°, and the base so obtained (called (β')-methyl-pyridine) is less soluble in water than the variety boiling at 144°, and forms a platinochloride melting at 258° instead of 241° (Ladenburg, *B.* 23, 2688). Optically inactive (Landolt, *B.* 19, 157). Less soluble in water than (α)-picoline. The absorption spectrum has been studied by Hartley (*C. J.* 41, 45). Oxidised by a 2 p.c. solution of $KMnO_4$ to pyridine (β)-carboxylic (nicotinic) acid.

Salts.—$B'_2H_2PtCl_6$ aq. Monoclinic prisms, v. sol. hot water. Melts, when anhydrous, at 191° (L.) or 195° (Stoehr). On heating at 120° for some time it gives off HCl, leaving B'_2HPtCl_5 [214°]. A boiling aqueous solution deposits B'_2PtCl_4, while B'_2HPtCl_5 crystallises from the filtrate—$B'HAuCl_4$. [184°]. Needles (from hot water), v. sol. alcohol.—$B'HHg_2Cl_5$. [143°]. Needles (from water), plates or needles (from HClAq) or prisms (on slow crystallisation); v. sl. sol. water, more sol. HClAq.—B'_2HgCl_2: white pp.—$B'_2H_2ZnCl_4$. [158°]. Pearly needles, v. sol. hot water.—Picrate $B'C_6H_2(NO_2)_3OH$. [145°]. Needles or plates, m. sol. water and alcohol.

(β)-Methyl-pyridine hexahydride $C_6H_{13}N$ *i.e.* $NH\!<\!\begin{smallmatrix}CH_2.CHMe\\CH_2.CH_2\end{smallmatrix}\!>\!CH_2$. ($\beta$)-*Methyl-piperidine.* ($\beta$)-*Pipecoline.* ($\beta$)-*Picoline hexahydride.* (125°). S.G. $\frac{0}{0}$ ·8684. V.D. (H=1) 98·14. Obtained by reducing (β)-picoline in alcoholic solution with sodium (Ladenburg, *A.* 247, 67; Stoehr, *B.* 20, 2732; Hesekiel, *B.* 18, 910). Colourless liquid, smelling like piperidine, v. sol. water. When heated with MeI it forms $C_6H_{12}NMe_2I$ [192°]. The hydrochloride of (β)-methyl-pyridine hexahydride is not ppd. by $HgCl_2$.

Salts.—B'HCl. Colourless needles, v. e. sol. water and alcohol.—B'HI. [131°]. Colourless, non-deliquescent needles.—$B'_2H_2PtCl_6$. [192°]. Orange-yellow prisms, m. sol. water.—$B'HAuCl_4$. [131°]. M. sol. water.—$B'_2H_2CdI_4$ aq. White plates, melting at 145° when anhydrous. $B'_2H_4FeCy_6$ 2aq: yellow monoclinic prisms, less soluble than the ferrocyanides of homologous bases. Decomposed by water at 75°.—Picrate $B'C_6H_2(NO_2)_3OH$. [138°]. Yellow pp., m. sol. water.

(γ)-Methyl-pyridine C_6H_7N *i.e.* $N\!<\!\begin{smallmatrix}CH.CH\\CH:CH\end{smallmatrix}\!>\!CMe$. *p-Picoline.* ($\gamma$)-*Picoline.* (143·5° cor.). S.G. $\frac{0}{0}$ ·9742.

Occurrence.—In coal tar, from which it may be obtained by preparing its platinochloride from the so-called lutidine (Schulze, *B.* 20, 413; Ladenburg, *B.* 21, 285; *A.* 247, 11).

Formation.—1. By heating di-chloro-pyridine (γ)-carboxylic acid with conc. HIAq and P at 175° (Behrmann a. Hofmann, *B.* 17, 2696).—2. In small quantity by heating pyridine methylo-iodide in sealed tubes at 300°, distilling the product with KOH, converting the fraction (142°–146°) into platinochloride, and decomposing the Pt salt by H_2S (L.).—3. By distilling sparteïne with lime (Ahrens, *B.* 21, 828).

Properties.—Oil, smelling like (α)-methyl-pyridine, v. sol. water, alcohol, and ether. Oxidised by dilute $KMnO_4$ to pyridine (γ)-carboxylic (isonicotinic) acid. [307°].

Salts.—$B'_2H_2PtCl_6$. [231°]. Four-sided plates, sl. sol. cold water.—$B'HAuCl_4$. [205°]. Prisms, v. sl. sol. water.—$B'HHg_2Cl_5$. [129°]. Needles, v. sol. hot, sl. sol. cold, water.—Picrate $B'C_6H_2(NO_2)_3OH$. [167°]. Tufts of needles, sl. sol. cold water.

(γ)-Methyl-pyridine dihydride C_6H_9N *i.e.* $NH\!<\!\begin{smallmatrix}CH:CH\\CH:CH\end{smallmatrix}\!>\!CHMe$. Formed from ethyl-pyrrole and HClAq at 130° (Dennstedt a. Zimmermann, *B.* 19, 2197).—$B'_2H_2PtCl_6$; red needles, v. sol. water.

(γ)-Methyl-pyridine hexahydride $C_6H_{13}N$ *i.e.* $NH\!<\!\begin{smallmatrix}CH_2.CH_2\\CH_2.CH_2\end{smallmatrix}\!>\!CHMe$. ($\gamma$)-*Pipecoline.* (126·5°–129° cor.). S.G. $\frac{0}{0}$ ·8674. Obtained by reducing (γ)-methyl-pyridine in alcoholic solution by sodium (Ladenburg, *B.* 21, 288; *A.* 247, 69). Colourless hygroscopic liquid which fumes in the air, and smells like piperidine. V. sol. water.

Salts.—B'HCl: v. e. sol. water.—$B'_2H_2PtCl_6$. [203°]. Prisms, m. sol. water.—$^{\times}B'HAuCl_4$. [127°]. Yellow needles, sl. sol. water.—$^{\times}B'_2H_2CdI_4$. [135°].—Bismutho-iodide: characteristic red plates. The picrate and mercury double chloride are crystalline.

ν-Methyl-pyridine dihydride C_6H_9N *i.e.* $NMe\!<\!\begin{smallmatrix}CH:CH\\CH:CH\end{smallmatrix}\!>\!CH_2$ (?). (129°). Obtained by distilling pyridine methylo-iodide with KOH (2 pts.) and a little water (Hofmann, *B.* 14, 1498). Very pungent oil, almost insol. water. Absorbs oxygen from the air. Combines with bromine, with iodine, and with sulphur. Combines with CS_2 and with mercaptan. Conc. HClAq at 180° decomposes it, giving off methylamine.

ν-Methyl-pyridine hexahydride $C_6H_{13}N$ *i.e.* $NMe\!<\!\begin{smallmatrix}CH_2.CH_2\\CH_2.CH_2\end{smallmatrix}\!>\!CH_2$. *Methyl-piperidine.* (105°) (L.). Formed by adding potash to the product of spontaneous union of piperidine with MeI (Cahours, *A. Ch.* [3] 38, 76). Formed also by heating piperidine hydrochloride (10 g.) with MeOH (7·5 g.) for 4 hours at 300°, excess of alcohol being distilled off, and the dry residue distilled with aqueous potash (Ladenburg, *A.* 247, 56). Liquid.—B'HCl. Needles.—$B'_2H_2PtCl_6$. Orange crystals, v. sol. water.

Methylo-iodide B'MeI. Crystalline; m. sol. hot alcohol. When heated with solid KOH it yields oily 'di-methyl-piperidine' (118°), a strongly alkaline base, which is decomposed by gaseous HCl into methyl chloride and methyl-

piperidine. 'Di-methyl-piperidine' forms the salts $C_7H_{15}NHCl$ and $C_7H_{15}NHAuCl_4$. It combines with halogens, forming crystalline $C_7H_{15}NI_2$, $C_7H_{15}NICl$ (which yields $C_7H_{15}NIClAuCl_3$), and $C_7H_{15}NBr_2$. The latter is converted by moist Ag_2O into crystalline $C_7H_{14}NBr$, whence further treatment with moist Ag_2O produces $C_7H_{14}NOH$ which is split up on distillation into H_2O and 'di-methyl-piperideïne.' Ladenburg suggests the formula $CH_2{:}CH.CH_2.CH_2.CH_2.NMe_2$ for 'di-methyl-piperidine,' and Merling (*B.* 19, 2628) suggests $CH_2<\begin{matrix}CHBr.CH_2\\CH_2.CH_2\end{matrix}>NMe_2Br$ for the compound $C_7H_{15}NBr_2$. This dibromide is accompanied by an oily isomeride which may possibly be $CH_2Br.CHBr.CH_2.CH_2.CH_2.NMe_2$, which changes into the other variety on heating its alcoholic solution. The di-iodide $C_7H_{15}NI_2$ is converted, on treatment with Ag_2O into 'di-methyl-piperideïne' $C_7H_{13}N$, a liquid (137°–140°) which forms the salts $(C_7H_{13}N)_2H_2PtCl_6$ and $(C_7H_{13}N)HAuCl_4$, and a methylo-iodide $C_7H_{13}NMeI$. 'Di-methyl-piperidine' combines with MeI forming crystalline $C_7H_{15}NMeI$ [200°] whence moist Ag_2O forms strongly alkaline $C_7H_{15}NMeOH$ which is split up by heat into pirylene C_5H_8, water, NMe_3, MeOH, and di-methyl-piperidine. Di-methyl-piperidine also combines with methylene iodide forming $C_7H_{15}NCH_2I_2$ (Ladenburg, *B.* 14, 1347). Ladenburg suggests for di-methyl-piperideïne the formula $CH\Big\langle\begin{matrix}CH.CH_2\\ |\\ CH_2.CH.NMe_2\end{matrix}$.

Methyl pyridine from Bone-oil. The following salts described by Ramsay (*P. M.* Oct. 1876 and 1877; July 1878) were prepared from a methyl-pyridine obtained from Dippel's oil, which was probably (α)-methyl-pyridine mixed with a little (β)-methyl-pyridine. — ×B'HCl. [160°]. White deliquescent crystals.—B'HBr. [187°]. Deliquescent. Absorbs bromine forming $B'HBr_3$, golden-yellow needles, sl. sol. water.—$B'Br_2$. Needles.—×B'HI. Decomposed by heat, yielding $B'HI_3$ which crystallises in brown needles [79°].—B'ICl: yellow tables.—$B'HgCl_2$.—$B'_2H_2PtCl_6$ (at 100°). Converted by water at 170° into yellow flocculent B'_2PtCl_4 and $B'PtCl_4$, a yellowish-green insoluble powder.—Platinocyanide $B'_2H_2PtCy_6 4aq$: yellow crystals. The crude bone-oil picoline forms the following combinations with alkyl salts.—B'MeCl: deliquescent needles (from alcohol).—$(B'MeCl)_2PtCl_4$: small cubes.—B'MeI. [227°]. Long white deliquescent needles (from alcohol).—$B'MeI_3$. [129°]. Bluish-black feathery plates, insol. water and CS_2, sol. alcohol and ether.—$B'MeNO_3$: transparent prisms.—$(B'C_3H_5Cl)_2PtCl_4$.—$B'_2C_2H_4Br_2$. [276°]. Small prisms. The same picoline forms with acetyl chloride deliquescent brown crystals of B'AcCl. According to Gardner (*B.* 23, 1589) crude picoline forms with acetic and formic acids the salts $(C_6H_7N)_2(HOAc)_3$ (c. 148°) and $C_6H_7N(CO_2H_2)_3$ (156°–159°) which distil unchanged.

Di-methyl-di-pyridine $(C_6H_7N)_2$. *Dipicoline. Parapicoline.* (310°–320°). S.G. 1·12. H.F.p. 8084 (Ramsay; that for picoline being 3753). Formed by boiling bone-oil picoline (6 pts.) with sodium (1 pt.) for two days (Anderson, *A.* 105, 344). Pale-yellow oil, miscible with alcohol and ether. Bromine-water gives a pp. of $C_{12}H_{13}BrN_2H_2Br_2$.—$C_{12}H_{14}N_2H_2PtCl_6$: pale-yellow powder. Its aurochloride is decomposed by boiling water (O. de Coninck, *Bl.* [2] 45, 131).

Methylo-iodide $C_{12}H_{14}N_2(MeI)_2$. Yellow powder, v. sol. water, almost insol. alcohol and ether. Yields $C_{12}H_{14}N_2Me_2PtCl_6$ and $C_{12}H_{14}N_2Me_2I_8$.

(αα)-Di-methyl pyridine C_7H_9N *i.e.* $N<\begin{matrix}CMe.CH\\CMe{:}CH\end{matrix}>CH$. *(αα)-Lutidine. oo-Lutidine.* Mol. w. 107. (142° cor.) (L.); 145° (E.). S.G. $\frac{0}{0}$ ·942.

Occurrence.—In coal-tar, being obtained by extracting with H_2SO_4, ppg. by alkali, and separating from the isomeride (157°) by fractionating (Lunge a. Rosenberg, *B.* 20, 127; Ladenburg a. Roth, *A.* 247, 28). It occurs also in bone-oil, and may be obtained from the fraction (135°–145°) (Roth, *B.* 19, 786).

Formation.—1. By the action of cinnamic aldehyde and alcoholic NH_3 on acetoacetic ether, the resulting dihydride of styryl-di-methyl-pyridine dicarboxylic ether being saponified, oxidised by $KMnO_4$, and the di-methyl-pyridine tricarboxylic acid so produced distilled with lime in a current of hydrogen (Epstein, *A.* 231, 18).—2. By distilling its dicarboxylic acid with lime (Engelmann, *A.* 231, 54).—3. By distilling oxy-di-methyl-pyridine (lutidone) with zinc-dust (Conrad a. Epstein, *B.* 20, 162).

Preparation.—Crude picoline (139°–142°) from bone-oil is dissolved in excess of HClAq and a hot solution of $HgCl_2$ is added. The double salt which is ppd. is recrystallised and decomposed by aqueous NaOH. The base is finally separated by solid KOH (Ladenburg, *A.* 247, 30).

Properties.—Liquid, smelling and tasting like pyridine, sol. cold water, the base separating again on warming. Its aqueous solution ppts. solutions of $ZnSO_4$, $CdSO_4$, $FeSO_4$, and $FeCl_3$. With $CuSO_4$ it gives a pale-blue pp. not turned black by heating. With $AgNO_3$ it gives minute needles of B'_2AgNO_3. Dilute $KMnO_4$ oxidises it to pyridine dicarboxylic acid [227°].

Salts.—×B'HCl. Deliquescent needles.—$B'_2H_2PtCl_6$. [208°]. Orange-red monoclinic plates; $a{:}b{:}c$ = ·892:1: ·660; β = 81° 55'. V. sol. hot, m. sol. cold, water, insol. alcohol.—$B'HAuCl_4$. [124°]. Yellow needles (from very dilute HCl).—$B'HHgCl_3$. [186°]. Thin plates (from acidulated water).—$B'HHg_2Cl_5$ (Mohler, *B.* 21, 1008).—$B'_2H_2Cr_2O_7$. [92°]. Orange prisms.—$B'(NH_3)H_2Cr_2O_7$. [c. 160°].—Picrate [159°]. Yellow needles or thin plates.

(αα)-Di-methyl-pyridine hexahydride $C_7H_{15}N$ *i.e.* $NH<\begin{matrix}CHMe.CH_2\\CHMe.CH_2\end{matrix}>CH_2$. (127°–130°). S.G. $\frac{0}{0}$ ·8492. Formed by reducing the corresponding di-methyl-pyridine in alcoholic solution with sodium (Ladenburg, *A.* 247, 87; *B.* 18, 54). Colourless liquid, miscible with water, alcohol, and ether.—B'HCl: non-deliquescent needles, m. sol. water.—B'HBr. Needles, v. sol. water.—$B'_2H_2PtCl_6$: [212°]; orange-red crystals.

(αγ)-Dimethyl-pyridine C_7H_9N *i.e.* $N<\begin{matrix}CMe.CH\\CH{:}CH\end{matrix}>CMe$. *Lutidine.* (157°). S.G. $\frac{0}{4}$ ·9493. S. 20.

Occurrence.—In coal-tar oil, being extracted with other bases by H_2SO_4 (Ladenburg a. Roth, *B.* 18, 913; Lunge a. Rosenberg, *B.* 20, 131); Ladenburg, 21, 286).

Formation.—1. By distilling oxy-di-methyl-pyridine $CMe{<}{CH.CO \atop CH:CMe}{>}NH$ with zinc-dust (Hantzsch, *B.* 17, 2908).—2. By distilling its tri-carboxylic acid with lime (Hantzsch, *A.* 215, 56).—3. By distilling with lime the acid $N{<}{CMe.C(CO_2H) \atop CH:CH}{>}CMe$ the ether of which is obtained by condensation of an equal number of molecules of acetoacetic ether, acetic aldehyde, and acetic aldehyde-ammonia (Michael, *B.* 18, 2020).

Preparation.—The fraction of coal-tar bases boiling between 155° and 160° is dissolved in dilute HClAq, conc. HClAq is then added, followed by a hot concentrated solution of $HgCl_2$. The double salt which then crystallises out is decomposed by distilling with NaOHAq (Ladenburg, *A.* 247, 35).

Properties.—Liquid, smelling like pyridine, dissolving in 5 pts. of cold water, less soluble in hot water. Miscible with alcohol and ether. Easily volatile with steam. Oxidised by $KMnO_4$ to pyridine dicarboxylic (lutidinic) acid [235°]. Reacts with benzoic aldehyde and $ZnCl_2$ forming styryl-methyl-pyridine (Bachér, *B.* 21, 3071).

Salts.—$B'HHg_2Cl_5\frac{1}{2}aq$. Needles. Melts at 132° when anhydrous. Mohler (*B.* 21, 1008) obtained from coal-tar lutidine in acid solution a salt $B'HHgCl_3$.—$B'_2H_2PtCl_6$. [220°]. Plates or prisms.—$B'HAuCl_4$: amorphous pp., changing to prisms.—$^{\times}B'HCl$: slender needles.—$^{\times}B'HBr$. Needles.—Picrate. [179°]. Needles, l. sol. cold water.

($\alpha\gamma$)-Di-methyl-pyridine hexahydride $NH{<}{CHMe.CH_2 \atop CH_2.CH_2}{>}CHMe$. ($\alpha\gamma$)-*Di-methyl-piperidine.* (141°). S.G. $\frac{0}{}$ ·8615. Obtained by reducing the corresponding di-methyl-pyridine in alcoholic solution with sodium (Ladenburg, *A.* 247, 88). Colourless strongly alkaline liquid, smelling like piperidine. Fumes with HCl. M. sol. water, v. e. sol. alcohol and ether.

Salts.—B'HCl. [235°]. Long colourless needles, v. sol. water.—B'HBr. [142°]. Short needles, v. e. sol. water.—$B'_2H_2PtCl_6$: groups of yellow needles.

($\beta\beta$)-Di-methyl-pyridine C_7H_9N *i.e.* $N{<}{CH.CMe \atop CH:CMe}{>}CH$. (170°). S.G. $\frac{0}{4}$ ·9614. Obtained by heating with lime the di-methyl-pyridine carboxylic acid formed by oxidation of the ($\beta\beta\alpha$)-di-methyl-ethyl-pyridine produced by heating propionic aldehyde-ammonia with propionic aldehyde (Dürkopf a. Göttsch, *B.* 23, 1113). Transparent, strongly refracting liquid, with a pleasant odour characteristic of (β)-alkyl-pyridines; m. sol. cold water, sl. sol. hot water. Yields on oxidation a pyridine dicarboxylic acid [315°].

Salts.—$B'_2H_2PtCl_6$. [256°]. Dark-red needles and plates, sl. sol. water.—$B'HAuCl_4$. [149°]. Yellow needles, sl. sol. water.—Mercury double chloride. [176°]. Long needles, sl. sol. cold water.

($\alpha\beta'$)-Di-methyl-pyridine $N{<}{CMe.CH \atop CH:CMe}{>}CH$. (162°–166°). Occurs in coal-tar (Lunge a. Rosenberg, *B.* 20, 134). Yields isocinchomeronic (pyridine dicarboxylic) acid on oxidation.

($\alpha\nu$)-Di-methyl-pyridine tetrahydride? $C_7H_{13}N$ *i.e.* $NMe{<}{CHMe.CH_2 \atop CH=CH}{>}CH_2$. Formed, together with MeCl, hydrocarbons, methylamine, NH_3, and other bases, by heating anhydro-ecgonine with conc. HClAq (Einhorn, *B.* 22, 1362). Oil. When heated with conc. HClAq at 280° it yields a mixture of bases which appear to yield methyl-pyridine when distilled over zinc-dust.—$B'HAuCl_4$. [212°]. Small needles, m. sol. water.—$B'C_6H_2(NO_2)_3OH$. Long needles, v. sl. sol. hot water.—$^{\times}B'HCl$: very hygroscopic.

Di-methyl-pyridine of bone oil (156°–159°) is a mixture of ($\alpha\gamma$)-di-methyl-pyridine, ($\alpha\beta'$)-di-methyl-pyridine, (β)-ethyl-pyridine, and (γ)-ethyl-pyridine. The existence of these bases is shown by the production of the corresponding pyridine di- and mono- carboxylic acids on oxidation by $KMnO_4$ (Weidel a. Herzig, *M.* 1, 1; Weidel a. Pick, *M.* 5, 658; *cf.* Anderson, *A.* 80, 5). Bone oil also contains ($\alpha\alpha$)-di-methyl-pyridine (*v. supra*). Greville Williams (*C. J.* 7, 97; *Pr.* 13, 311) obtained a lutidine from coal-tar; this has since been shown to contain ($\alpha\alpha$), ($\alpha\gamma$), and ($\alpha\beta$) di-methyl-pyridines (*v. supra*). Oechsner de Coninck (*Bl.* [2] 41, 249) found (γ)-ethyl-pyridine (154°) in coal tar. Lutidines have also been obtained by distilling the bituminous shale of Dorsetshire (Williams) and peat (Church a. Owen, *P. M.* [4] 20, 110). Among the products obtained by distilling cinchonine with KOH Oechsner de Coninck (*C. R.* 91, 296) obtained a lutidine (165°), V.D. 3·8 (calc. 3·7); S.G. $\frac{0}{}$ ·959, which formed a deliquescent crystalline hydrochloride and a platinochloride $B'_2H_2PtCl_6$ crystallising in orange-red needles, converted by boiling water into B'_2PtCl_4 crystallising in yellow needles. When brucine is distilled with KOH it yields a lutidine (166°) whence $B'_2H_2PtCl_6$ [180°] and B'_2PtCl_4 [205°] (Oechsner de Coninck, *C. R.* 95, 298; 96, 437). Lutidine aurochloride $B'HAuCl_4$ is decomposed on boiling with water, yielding first thin red plates of $B'HAuCl_4B'_2AuCl_3$, and then a red crystalline pp. B'_2AuCl_3 (O. de Coninck, *Bl.* [2] 34, 634).

Di-methyl-pyridine dihydride $C_7H_{11}N$. (199°). V.D. 3·3. Occurs in cod-liver oil (Gautier a. Mourgues, *C. R.* 107, 111; *Bl.* [3] 2, 213). Colourless strongly alkaline and caustic oil; absorbs CO_2 from the air. Poisonous. Its salts taste bitter. Oxidised by boiling aqueous $KMnO_4$ to methyl-pyridine carboxylic acid and a little pyridine carboxylic acid.

Salts.—$^{\times}B'HCl$: confused needles, v. sol. water.—$^{\times}B'HNO_3$. Reduces $AgNO_3$.— $B'_2H_2SO_4$. Groups of deliquescent needles.—$B'_2H_2PtCl_6$. Lozenge-shaped plates, loses HCl on boiling with water.

Methylo-iodide B'MeI. Colourless needles, sol. water and alcohol. Yields a tri-methyl-pyridine dihydride on treatment with potash.

Di-methyl-pyridine hexahydride. *Methylo-iodide* $C_7H_{15}NMeI$. [192°]. Formed by heating (β)-pyridine hexahydride with MeI and MeOH at 100° (Hesekiel, *B.* 18, 3099; *A.* 247, 69). Needles (from acetone). Not decomposed by aqueous KOH. Yields $(C_7H_{15}NMeCl)_2PtCl_4$, an orange crystalline pp. turned black at 234°.

(s)-Tri-methyl-pyridine $C_8H_{11}N$ *i.e.* $N{<}\begin{matrix}CMe.CH\\CMe{:}CH\end{matrix}{>}CMe$. *(γ)-Collidine.* (172° cor.) (H.; M.); (168°) (D.). S.G. $\frac{15}{}$ ·917 (H.); ·922 (M.); $\frac{}{4}$ ·9312 (D.). Occurs in coal-tar, from which it may be obtained by fractional distillation followed by ppn. of the bases by K_4FeCy_6 (Mohler, *B.* 21, 1011). Formed by heating with quicklime the potassium salt of its dicarboxylic acid, which is obtained by the action of nitrous acid on its dihydride produced from acetoacetic ether and aldehyde-ammonia (Hantzsch, *A.* 215, 32). Formed also by heating acetone with NH_4Cl for 3 days at 265°, CH_4 being evolved (Riehm, *A.* 238, 16), and by heating acetone with aldehyde-ammonia for 10 hours at 200° (Dürkopf, *B.* 21, 2713).

Properties.—Liquid which turns brown in the air. More than 3 times as soluble in water as aldehyde-collidine. Less soluble in hot than in cold water. It differs also from aldehyde-collidine in giving a pp. with $AgNO_3$, an orange crystalline pp. with CrO_3, and an aurochloride that melts under water. It is oxidised by $KMnO_4$ to $N{<}\begin{matrix}C(CH_3)\ .CH\\C(CO_2H){:}CH\end{matrix}{>}CMe$ and uvitonic acid. Bromine added to its solution in CS_2 forms unstable orange crystals of $C_8H_{11}NBr_2$ (Pfeiffer, *B.* 20, 1344).

S a l t s.—B'HCl. Slender, non-deliquescent needles.—$B'_2H_2PtCl_6$: yellow crystalline pp.—$B'HAuCl_4$. [113°] (H.); [115°] (M.); [106°] (D.). Needles (from hot water).—$B'HHg_2Cl_5$. [155°]. — B'HI. — ×$B'HNO_3$ [above 300°]. — $B'_2H_2Cr_2O_7$. Yellow prisms, decomposing at 190°.—×$B'_2H_2SO_4$. [203°].—P i c r a t e. [156°] (M.). Silky yellow needles, sl. sol. water, v. sol. alcohol.

Reference.—Di-bromo-tri-methyl-pyridine.

Tri-methyl-pyridine dihydride $C_8H_{13}N$. *Dihydro-collidine.* (175°–180°). Formed by heating its dicarboxylic ether (obtained from aldehyde-ammonia and acetoacetic ether) with dilute HClAq at 130° (Hantzsch, *A.* 215, 44). Pungent oil with alkaloidal smell. Alkaline to litmus, v. sol. cold water. Precipitates the hydroxides of Mg, Zn, and Fe from solutions of their salts.—$B'_2H_2PtCl_6$. Minute needles which blacken at 200°.—B'HI.

P o l y m e r i d e $C_{16}H_{26}N_2$. *Tetrahydrodicollidine.* (255°–260°). Formed at the same time as the preceding. — $C_{16}H_{26}N_2H_2PtCl_6$. — $C_{16}H_{26}N_2HI$.

s-Tri-methyl-pyridine hexahydride $C_8H_{17}N$ *i.e.* $NH{<}\begin{matrix}CHMe.CH_2\\CHMe.CH_2\end{matrix}{>}CHMe$. *Copellidine.* (146°). S.G. $\frac{}{4}$ ·8475. Formed by reducing *s*-tri-methyl-pyridine in alcoholic solution with sodium (Jaeckle, *A.* 246, 43). Formed also, together with *s*-tri-methyl-pyridine, by heating acetone with aldehyde-ammonia at 200° (Dürkopf, *B.* 21, 2715). Liquid, smelling like piperidine, sl. sol. water, miscible with alcohol and ether. Unlike *s*-tri-methyl-pyridine it gives a brownish-black pp. with $Hg_2(NO_3)_2$. Gives no pps. with $HgCl_2$ or picric acid.

S a l t s.—B'HCl. Needles or prisms, v. e. sol. water and alcohol.—B'HBr.—$B'_2H_2PtCl_6$. [205°] (J.); [244°] (D.).

Isomerides of tri-methyl-pyridine *v.* Methyl-ethyl-pyridine, where (α)- and (β)- collidines, aldehyde-collidine and other isomerides are described.

A collidine dihydride $C_8H_{13}N$, (210°), S.G. $\frac{0}{}$ 1·029, is contained in putrid horseflesh and putrid beef, and forms a crystalline hydrochloride and platinochloride (Gautier, *Bl.* [2] 48, 12).

Tetra-methyl-pyridine dihydride $C_9H_{15}N$ *i.e.* $NH{<}\begin{matrix}CMe{:}CMe\\CH_2.CMe\end{matrix}{>}CMe$. *Dihydroparvoline.* (159°). Formed by heating potassium pyrrole carboxylate with MeI and MeOH at 120° (Ciamician a. Anderlini, *B.* 21, 2862). Basic liquid.—$B'HAuCl_4$. [110°]. Yellow needles.

Tetra-methyl-pyridine hexahydride $C_9H_{19}N$ *i.e.* $NH{<}\begin{matrix}CHMe.CHMe\\CH_2\ \ .CHMe\end{matrix}{>}CHMe$. *Parpevoline* (151°). Obtained by reducing the preceding in alcoholic solution with sodium (C. a. A.). Liquid, smelling like pyridine. Does not turn brown in air.—$B'HAuCl_4$. [119°]. Yellow needles.

M e t h y l o - i o d i d e B'MeI. [262°]. Prisms, v. sol. water, insol. ether.

A parvoline $C_9H_{13}N$ (c. 200°) is present among the products of the putrefaction of horseflesh (Gautier, *Bl.* [2] 48, 11). It is an oil which resinifies in the air, and forms a flesh-coloured platinochloride.

A parvoline $C_9H_{13}N$ (188°) occurs among the bases obtained by distilling cinchonine with KOH (O. de Coninck, *C. R.* 91, 296).

Penta-methyl-pyridine dihydride $C_{10}H_{17}N$ *i.e.* $NMe{<}\begin{matrix}CMe{:}CMe\\CH_2.CMe\end{matrix}{>}CMe$. (189°); (46° at 7 mm.). Prepared by heating *ν*-methyl-pyrrole with MeI, K_2CO_3, and methyl alcohol at 140° (Ciamician a. Anderlini, *Rend. Accad. Linc.* [4] 203; *B.* 21, 2863; 22, 658). Formed also by heating tetra-methyl-pyridine dihydride with MeI (Anderlini, *B.* 22, 2507). Oil, with strong alkaline reaction.—$B'HAuCl_4$. [100°]. Yellow needles. Reacts energetically with MeI, forming an oily product, whence successive treatment with AgCl and $AuCl_3$ yields $C_{12}H_{21}NHAuCl_4$, which crystallises in thin golden-yellow needles [100°].

METHYL-PYRIDINE CARBOXYLIC ACID $C_7H_7NO_2$ *i.e.* $N{<}\begin{matrix}CMe.CH\\CH\ :CH\end{matrix}{>}C.CO_2H$. *Picoline carboxylic acid.* Formed by heating methyl-pyridine dicarboxylic (uvitonic) acid at 275° (Böttinger, *B.* 14, 67; 17, 92). Trimetric crystals (containing aq), sol. hot, sl. sol. cold, water and alcohol, nearly insol. ether. Sublimes without melting. Forms salts both with acids and bases. Yields on oxidation with $KMnO_4$ pyridine dicarboxylic (lutidinic) acid.

S a l t s.—HA'HCl: prisms. — BaA'_2 11aq: very soluble needles.—CaA'_2 aq: very soluble four-sided colourless prisms.—CuA'_2 aq: blue pp.—×AgA': white pp.

Methyl-pyridine carboxylic acid $C_7H_7NO_2$ *i.e.* $N{<}\begin{matrix}CH.C(CO_2H)\\CH{:}CH\ \text{———}\end{matrix}{>}CMe$. *Homonicotinic acid. Methyl-carbopyridic acid.* [212°]. Obtained by heating methyl-pyridine dicarboxylic (methyl-quinolinic) acid at 170°, or by warming it with HOAc (Hoogewerff a. Van Dorp, *R. T. C.* 2, 21). Formed also by the slow oxidation of (β)-collidine by $KMnO_4$ (O. de Coninck, *A. Ch.* [5] 27, 493; *Bl.* [2] 43, 107). Needles, v. sol. hot

water. Oxidised by $KMnO_4$ to pyridine dicarboxylic (cinchomeronic) acid.

Salts.—KA′: small plates.—CuA'_2: small blue crystals.—AgA′: needles.—HA′HCl: small prisms. — $(HA')_2H_2PtCl_6$: orange prisms. — $HA'HAuCl_4$: yellow needles.

(α)-Methyl-pyridine (β)-carboxylic acid $C_7H_7NO_2$ *i.e.* $N\begin{smallmatrix}\diagup CMe.CH \diagdown \\ \diagdown CH:C\diagup CO_2H\end{smallmatrix}CH$. [207°]. Formed by oxidising (α)-methyl-(β′)-ethyl-pyridine (aldehyde-collidine) with a 2 p.c. solution of $KMnO_4$, allowing the mixture to stand for 48 hours, and then heating to 60°. The filtrate from MnO_2 is neutralised by H_2SO_4 and evaporated, the residue is extracted with alcohol and the acid purified by means of its silver salt (Dürkopf, *B.* 18, 3432; Ladenburg, *A.* 247, 43). Prisms, v. e. sol. water and alcohol. On distillation with lime it yields (α)-methyl-pyridine (128°). $KMnO_4$ oxidises it to pyridine dicarboxylic (isocinchomeronic) acid.

Salts.—$(HA')_2H_2PtCl_6$. [240°]. Aggregates of needles, v. sol. water, insol. ether-alcohol.—$(CuA'_2)_2Cu(OAc)_2$. Crystalline powder, formed by boiling a solution of the acid with cupric acetate. The silver salt is amorphous. The aurochloride forms yellow needles [c. 202°].

Methyl pyridine carboxylic acid $C_7H_7NO_2$ *i.e.* $N\begin{smallmatrix}\diagup C(CO_2H).CH \diagdown \\ \diagdown CH\ :\ CH \diagup\end{smallmatrix}CMe$ (?). [c. 260°]. Formed in small quantity, together with pyridine (αγ)-di-carboxylic acid, by oxidising (αγ)-di-methyl-pyridine with $KMnO_4$ (Bachér, *B.* 21, 3080). Plates (from alcohol), v. e. sol. water. It is possibly identical with the isomeride described by Böttinger (*v. supra*).

(β)-Methyl-pyridine (β′)-carboxylic acid $N\begin{smallmatrix}\diagup CH.CMe \diagdown \\ \diagdown CH:C(CO_2H) \diagup\end{smallmatrix}CH$. [216°]. Formed by heating (β)-methyl-pyridine (αβ′)-dicarboxylic acid with HOAc and Ac_2O at 225° (Dürkopf a. Göttsch, *B.* 23, 1113). White mass, m. sol. water. Its aqueous solution is not coloured by $FeSO_4$.

Methyl-pyridine dicarboxylic acid $C_8H_7NO_4$ *i.e.* $N\begin{smallmatrix}\diagup CMe —— CH \diagdown \\ \diagdown C(CO_2H):CH \diagup\end{smallmatrix}C.CO_2H$. *Uvitonic acid.* [274°]. Formed by the action of ammonia on pyruvic acid (Böttinger, *A.* 188, 330; 208, 138; *B.* 13, 2032; 16, 35; 17, 144). Formed also by oxidising *s*-tri-methyl-pyridine, or di-methyl-ethyl-pyridine, $N\begin{smallmatrix}\diagup CMe.CH \diagdown \\ \diagdown CMe:CH \diagup\end{smallmatrix}CEt$, with $KMnO_4$ (Altar, *A.* 237, 191; Dürkopf, *B.* 21, 2717). Minute six-sided trimetric plates (Friedländer, *J.* 1882, 367), v. sl. sol. cold, sl. sol. hot, water, m. sol. NH_3Aq and HClAq, v. sol. aniline, phenol, HOAc, and glycerin, sl. sol. isoamyl alcohol and chloroform, insol. benzene and CS_2. Gives a violet-red colour with $FeSO_4$. It is a powerful antiseptic. Yields (α)-methyl-pyridine on distillation with lime. Split up by heat into CO_2 and $N\begin{smallmatrix}\diagup CMe.CH \diagdown \\ \diagdown CH:CH \diagup\end{smallmatrix}C.CO_2H$. Alkaline $KMnO_4$ oxidises it to pyridine tricarboxylic acid. Bromine-water forms bromoform, CO_2, and formic acid.

Salts.—$(NH_4)HA''$: powder.—CaA″ 6aq: amorphous.—CaA″ 4aq: prisms.—BaA″ 2aq: slender needles.—CuA″ 4aq.—$Cu_3(OH)_2A_2''$ 9aq: ×PbA″: dense pp.—Ag_2A''aq: gelatinous pp.

Methyl-pyridine di-carboxylic acid $C_8H_7NO_4$ *i.e.* $N\begin{smallmatrix}\diagup C(CO_2H):C(CO_2H) \diagdown \\ \diagdown CH ———— CH \diagup\end{smallmatrix}CMe$. *Methyl-quinolinic acid.* [c. 183°]. S. ·84 at 10°. Formed by the oxidation of (*Py.* 1)-methyl-quinoline (lepidine) (1 pt.) by $KMnO_4$ ($7\frac{1}{2}$ pts.) (Königs, *B.* 12, 983; 14, 103; Hoogewerff a. Van Dorp, *R. T. C.* 2, 15; *B.* 13, 1639; 14, 645). Tables or prisms, sol. hot, sl. sol. cold, water, sl. sol. alcohol, ether, and benzene. Decomposes on fusion into CO_2 and methyl-pyridine carboxylic acid [210°], which on further oxidation yields cinchomeronic acid. $KMnO_4$ oxidises it to pyridine (α)-tricarboxylic acid. The aqueous solution of the acid gives pps. with the acetates of Pb, Ba, and Cu, and a yellow colour with $FeSO_4$.

Salts.—KHA″ 2aq: needles.—KHA″ 3aq.—Ag_2A''aq: crystalline powder.

Methyl-pyridine dicarboxylic acid $C_8H_7NO_4$ *i.e.* $N\begin{smallmatrix}\diagup CMe.C(CO_2H) \diagdown \\ \diagdown CH:C(CO_2H) \diagup\end{smallmatrix}CH$. *Methyl-dinicotinic acid.* [245°–250°]. Formed from methyl-pyridine tricarboxylic acid $N\begin{smallmatrix}\diagup CMe —— C(CO_2H) \diagdown \\ \diagdown C(CO_2H):C(CO_2H) \diagup\end{smallmatrix}CH$ by heating at 150° (Weber, *A.* 241, 9). Spherical groups of needles (containing aq), sl. sol. cold water. $KMnO_4$ oxidises it to a pyridine tricarboxylic acid.—HA′HCl aq: transparent efflorescent crystals.—PbA″ 2aq: crystalline pp.

Methyl-pyridine dicarboxylic acid

$N\begin{smallmatrix}\diagup CH ——— CMe \diagdown \\ \diagdown C(CO_2H):C(CO_2H) \diagup\end{smallmatrix}CH$ or

$N\begin{smallmatrix}\diagup C(CO_2H).CMe \diagdown \\ \diagdown CH:C(CO_2H) \diagup\end{smallmatrix}CH$. [223°].

Obtained by oxidising the di-methyl-ethyl-pyridine, which is formed by the action of NH_3 on propionic aldehyde (Dürkopf a. Göttsch, *B.* 23, 688, 1110), and by the action of paraldehyde on propionic aldehyde-ammonia (Dürkopf a. Schlaugk, *B.* 21, 834). White powder (from hot water). The K, Ag, and Cu salts are sl. sol. water.

Methyl-pyridine hexahydride dicarboxylic acid $C_8H_{13}NO_4$ *i.e.* $NH\begin{smallmatrix}\diagup CH_2 —— CH_2.CH_2 \\ \diagdown CMe(CO_2H).CH.CO_2H\end{smallmatrix}$. [127°]. *Cincholeuponic acid.* A product of the oxidation of cinchonine by chromic acid mixture (Skraup, *M.* 9, 786). Prisms (containing aq); v. e. sol. water, insol. alcohol and ether. Ac_2O at 125° forms an amorphous acetyl derivative $C_8H_{12}AcNO_4$. Distillation of the lead salt over zinc-dust yields a small quantity of pyridine.

Salts.—PbA″: powder, v. e. sol. water.—$H_2A''HCl$. [194°]. Trimetric crystals. $[\alpha]_D =$ 34·4° at 18·7°.

Nitrosamine $C_8H_{12}(NO)NO_4$. [163°]. Trimetric crystals, sl. sol. cold water, m. sol. alcohol. Warm conc. HClAq reproduces $C_8H_{13}NO_4$ and nitrous acid.—BaA″ (at 115°). Deliquescent amorphous powder, in sol. alcohol.

In the preparation of cincholeuponic acid a base called cincholeupone $C_9H_{17}NO_2$ is also formed. It yields cincholeuponic acid on oxidation with chromic acid mixture, and ethyl-pyridine on distillation over red-hot zinc-dust. It forms the salts $(C_9H_{17}NO_2)HCl$ [200°], $B'_2H_2PtCl_6$ $3\frac{1}{2}$aq and $B'HAuCl_4$ [203°], an acetyl

derivative $C_8H_{16}AcNO_2$ [121°], and a nitrosamine $C_9H_{16}(NO)NO_2$ [84°].

Methyl-pyridine tricarboxylic acid $C_9H_7NO_6$ *i.e.* $N\left<\begin{array}{l}CMe\text{——}C(CO_2H)\\C(CO_2H):C(CO_2H)\end{array}\right>CH$. [226°]. Formed by oxidising $N\left<\begin{array}{l}CMe.C(CO_2H)\\CMe:C(CO_2H)\end{array}\right>CH$ with $KMnO_4$ (Weber, *A.* 241, 6). Spherical aggregates (containing aq). At 150° it slowly gives off CO_2, yielding methyl-pyridine dicarboxylic acid [245°–250°].—$KH_5A'''_2$ 6aq: spherical aggregates.—AgH_2A''' 2aq: needles (from hot water).

Methyl-pyridine tricarboxylic acid $N\left<\begin{array}{l}C(CO_2H).C(CO_2H)\\CH\text{===}C(CO_2H)\end{array}\right>CMe$. *Methyl-carbodinicotinic acid.* Formed by the oxidation of ($\alpha\gamma$)-di-methyl-pyridine dicarboxylic acid by $KMnO_4$ (Weber, *A.* 241, 25). Needles (containing aq) or prisms (containing 2aq). Less soluble in water than the preceding acid. Turns yellow at 205°, and completely decomposes at 260°. $FeSO_4$ colours its solutions deep red. The calcium salt yields (γ)-methyl-pyridine on distillation.

Methyl-pyridine tricarboxylic acid $N\left<\begin{array}{l}C(CO_2H).C(CO_2H)\\C(CO_2H)\text{=}CH\end{array}\right>CMe$. *Picoline tricarboxylic acid.* [238°]. Formed by the oxidation of flavenol (1 mol.) with $KMnO_4$ (9 mols.) (Fischer a. Täuber, *B.* 17, 2926). Formed also by oxidising potassium tri-methyl-pyridine carboxylate with aqueous $KMnO_4$ (Michael, *A.* 225, 140). Slender needles (from water). Does not combine with acids. On further oxidation with $KMnO_4$ it yields pyridine tetra-carboxylic acid [227°]. $FeSO_4$ colours its solution brownish-red.

S a l t s.—BaA'': amorphous pp.—Ag_2A''.

Methyl-pyridine tetracarboxylic acid $C_{10}H_7NO_8$ *i.e.* $N\left<\begin{array}{l}C(CO_2H).C(CO_2H)\\C(CO_2H):C(CO_2H)\end{array}\right>CMe$. [199°]. Obtained by boiling potassium tri-methyl-pyridine dicarboxylate with a solution of $KMnO_4$ (Hantzsch, *A.* 215, 57). Small prisms (from water); v. e. sol. water, m. sol. alcohol, sl. sol. ether. Gives (γ)-picoline on distillation with lime. Its neutral salts crystallise with difficulty. Neutral solutions give pps. with salts of Pb and Ag, mercurous salts, and $Ba(OAc)_2$, but no pps. with dilute $BaCl_2$ or with salts of Mg, Zn, Mn, Ni, Co, and Cu, and mercuric salts.—$K_2H_2A^{iv}$ 4aq: large trimetric tables, v. sol. hot water, with acid reaction.—KH_3A^{iv} 2aq.—Ca_2A^{iv} 4aq; ppd. by adding NH_3 and $CaCl_2$.—Mg_2A^{iv} 6aq.

Di-methyl-pyridine carboxylic acid $C_8H_9NO_2$ *i.e.* $N\left<\begin{array}{l}CMe:C(CO_2H)\\CH\text{————}CH\end{array}\right>CMe$. *Lutidine carboxylic acid.* Obtained by saponifying with alcoholic potash its ether, which is formed by adding acetic aldehyde (50 pts.) to a mixture of aceto-acetic ether (130 pts.) and aldehyde-ammonia (61 pts.); the reaction, which sets in at once, being completed by heating to 100° (Michael, *B.* 18, 2020). Transparent prisms (containing 2 aq); v. sol. water and alcohol. Gives ($\alpha\gamma$)-lutidine on distillation with lime. On oxidation with $KMnO_4$ it yields pyridine dicarboxylic (carbocinchomeronic) acid.

S a l t s.—$HA'HCl$. [166°]. Large prisms or thick tables. — $(HA')_2H_2PtCl_6$ 2aq. [216°]. Reddish-yellow prisms.

Ethyl ether EtA'. (216° uncor.). Yellowish oil, not volatile with steam.—$(EtA)_2H_2PtCl_6$. [191°]. Thin yellow pointed prisms; v. sl. sol. water and strong alcohol.

Di-methyl-pyridine carboxylic acid $N\left<\begin{array}{l}CMe\text{——}CH\\C(CO_2H):CH\end{array}\right>CMe$. *Di-methyl-picolinic acid.* [153°]. Formed by oxidising s-tri-methyl-pyridine with $KMnO_4$ (Altar, *A.* 237, 183). Small crystals; v. e. sol. water and alcohol, m. sol. ether. Yields ($\alpha\gamma$)-di-methyl-pyridine on distillation with lime. Its metallic salts are v. sol. water.—$B'HCl$ aq: minute white needles, v. e. sol. water. — $B'_2H_2PtCl_6$ 4EtOH. [221°]. Prisms.

Di-methyl-pyridine carboxylic acid $N\left<\begin{array}{l}CMe\text{———}CH\\CMe:C(CO_2H)\end{array}\right>CH$. *Di-methyl-nicotinic acid.* [160°]. Prepared by distilling the mono-ethylic ether of di-methyl-pyridine dicarboxylic acid $N\left<\begin{array}{l}CMe.C(CO_2H)\\CMe:C(CO_2H)\end{array}\right>CH$ (Weiss, *B.* 19, 1308). Needles (containing ½aq); v. e. sol. water. Oxidised by $KMnO_4$ to the corresponding pyridine tricarboxylic acid.—AgA'.—$HA'HCl$: small prisms.—$(HA')_2H_2PtCl_6$ 2aq: orange needles.

Di-methyl-pyridine carboxylic acid $N\left<\begin{array}{l}CH\text{———}CMe\\C(CO_2H):CMe\end{array}\right>CH$. [151°]. Formed by oxidising the parvoline obtained from propionic aldehyde and NH_3 (Dürkopf a. Göttsch, *B.* 23, 687; 1110).—$(HA')_2H_2PtCl_6EtOH$. V. sol. water, sl. sol. alcohol. Decomposes at 260°.

Di-methyl-pyridine carboxylic acid $C_5H_2Me_2N.CO_2H$. Formed by saponifying, by alcoholic potash, its ethyl ether, which is produced from acetoacetic ether (30 g.) by heating with formic aldehyde (5 g.) and $ZnCl_2$ (30 g.) for 12 hours at 100° (Canzoneri a. Spica, *G.* 14, 449). Silky needles; v. e. sol. water.—$HA'HCl$ aq. [220°]. Transparent rhombohedra (from water).—$(HA')_2H_2PtCl_6$: red crystals.

Ethyl ether EtA'. (260°). Oil.

Di-methyl-pyridine dicarboxylic acid $C_9H_9NO_4$ *i.e.* $N\left<\begin{array}{l}CMe.C(CO_2H)\\CH:C(CO_2H)\end{array}\right>CMe$. ($\alpha\gamma$)-*Di-methyl-di-nicotinic acid.* [258°]. Obtained by heating ($\alpha\gamma$)-di-methyl-pyridine tricarboxylic acid at 175° (Weber, *A.* 241, 20). Formed also by oxidation of the corresponding tetra-methyl-pyridine (Dürkopf a. Göttsch, *B.* 23, 1112). Needles (containing 2 aq (W.) or anhydrous (D. a. G.). Its solution is not coloured by $FeSO_4$.—PbA'': gelatinous pp., becoming crystalline on boiling.—$H_2A''HCl$ aq: slender needles, decomposed by water.—$(H_2A'')_2H_2PtCl_6$: orange tables, melting above 300°.

Di-methyl-pyridine dicarboxylic acid

$$N\left<\begin{array}{l}CMe\text{————}CH\\C(CO_2H):C(CO_2H)\end{array}\right>CMe \text{ or}$$

$$N\left<\begin{array}{l}CMe.C(CO_2H)\\C(CO_2H):CH\end{array}\right>CMe. \quad [245°].$$

Formed by oxidising s-tri-methyl-pyridine carboxylic acid in neutral solution with $KMnO_4$ (Michael, *A.* 225, 137). Prisms (from water).—CaA''.—MgA'' 3aq.—$(H_2A''HCl)_2PtCl_6$ 6aq.

Di-methyl-pyridine dicarboxylic acid $N\left<\begin{array}{l}CMe.C(CO_2H)\\CMe:C(CO_2H)\end{array}\right>CH$. *Lutidine dicarboxylic acid.* Formed by saponifying with alcoholic potash its ether, which is produced by passing nitrous acid gas into di-methyl-isopropyl-dicarb-

oxylic ether in alcohol (Engelmann, *A.* 231, 50). Its ether is also one of the products of the action of acetoacetic ether on hexamethylene tetramine at 170° (Griess, *B.* 21, 2740). The same ether appears to be formed by oxidising with nitrous acid gas the product obtained by the action of phenyl-acetic aldehyde on aceto-acetic ether and ammonia (Jeanrenaud, *B.* 21, 1784). Slender needles (containing $\frac{1}{2}$aq). Melts at a very high temperature. V. sl. sol. cold water, alcohol, and ether. $KMnO_4$ oxidises it to pyridine tetra-carboxylic acid. On distillation it yields CO_2 and di-methyl-pyridine carboxylic acid. Distillation over CaO yields ($\alpha\alpha$)-di-methyl-pyridine.

Salts.—BaA″ 2 aq.—PbA″ 2aq: amorphous pp. changing to stout prisms.—$H_2A''HCl$ 2aq: prisms.

Mono-ethyl-ether EtHA″. [131°]. Obtained by decomposing the di-ethyl ether (1 mol.) with alcoholic KOH (1 mol.) (Weiss, *B.* 19, 1308). Needles (from water). Its neutral solution is ppd. by salts of Ag, Hg, and Cu.—EtHA″HCl 2aq. [90°]. Needles (from water).

Diethyl ether Et_2A''. [72°]. (302°). Long white needles.—$Et_2A''HAuCl_4$: v. e. sol. alcohol.

Di-methyl-pyridine dicarboxylic ether dihydride $C_5H_3NMe_2(CO_2Et)_2$. [170°]. Formed by heating acetoacetic ether (20 g.) with $ZnCl_2$ (20 g.) and hexamethylene tetramine (4 g.) at 100° (Griess a. Harrow, *B.* 21, 2740). Four-sided plates or needles, almost insol. water, sl. sol. cold alcohol and ether, v. sol. chloroform. By treatment with nitrous acid, or even by solution in hot dilute HCl, it is oxidised to $C_5HNMe_2(CO_2Et)_2$.

Di-methyl-pyridine tricarboxylic acid

$C_{10}H_9NO_6$ *i.e.* $N{<}{\begin{matrix}CMe\text{——}C(CO_2H)\\C(CO_2H){:}C(CO_2H)\end{matrix}}{>}CMe$. *Lutidine tricarboxylic acid. Dimethylcarbodinicotinic* acid. [212°]. Formed by oxidation of potassium tri-methyl-pyridine dicarboxylate with $KMnO_4$ in a solution kept neutral by CO_2 (Hantzsch, *A.* 215, 52; Weber, *A.* 241, 20). Crystallises from water in hard crusts composed of rhombohedra (containing 2aq). Split up by heat into CO_2 and ($\alpha\gamma$)-di-methyl-pyridine dicarboxylic acid. Yields ($\alpha\gamma$)-di-methyl-pyridine on distillation with lime. Its neutral solutions give no pps. with salts of Cu, Ag, or Pb, nor with $FeCl_3$, but with $Hg(NO_3)_2$ a pp. soluble in hot water.

Salts. — KH_2A''' 2aq. — $Ba_3A'''_2$ 8 (?) aq: minute needles.—$Mg_3A'''_2$ 10aq.—$Ca_3A'''_2$ 8aq.—Ag_3A'''.

Di-methyl-pyridine tricarboxylic acid

$N{<}{\begin{matrix}CMe.C(CO_2H)\\CMe{:}C(CO_2H)\end{matrix}}{>}C.CO_2H$. S. ·178 at 8°. Formed by oxidising potassium styryl-di-methyl-pyridine dicarboxylate with cold aqueous $KMnO_4$ (Epstein, *A.* 231, 11). Crystallises from water in prisms (containing aq); almost insol. water, alcohol, ether, benzene, and chloroform. Turns brown at about 220° but decomposes without melting. Gives ($\alpha\alpha$)-di-methyl-pyridine on distillation with lime. A solution of its ammonium salt gives pps. with $CaCl_2$, $CdSO_4$, $Hg_2(NO_3)_2$, $AgNO_3$, $SnCl_2$, $Pb(OAc)_2$, and $Bi(NO_3)_3$, but not with $BaCl_2$, $MgSO_4$, $MnSO_4$, and alum, nor, in the cold, with $ZnSO_4$ or $CuSO_4$. $FeCl_3$ gives a reddish colour.

Salts. $H_3A'''HCl$: needles, decomposed by water and by alcohol. — $Pb_3A'''_2$ 6aq. — $Cu(NH_4)A'''$ 4aq.—Ag_3A''' 3aq.

Tri-methyl-pyridine carboxylic acid

$C_9H_{11}NO_2$ *i.e.* $N{<}{\begin{matrix}CMe.C(CO_2H)\\CMe\text{==}CH\end{matrix}}{>}CMe$. *Collidine carboxylic acid.* [155°]. Obtained by saponifying with alcoholic potash its ethyl ether, which is obtained by passing nitrous acid into its dihydride (Hantzsch, *A.* 215, 42) and by heating the mono-ethyl ether of tri-methyl-pyridine dicarboxylic acid (Michael, *A.* 225, 131). Crystallises from water in short needles or cubes (containing 2aq). Melts at 110° when hydrated, or 155° when anhydrous. On oxidation with $KMnO_4$ it yields di-methyl-pyridine dicarboxylic acid, methyl-pyridine tricarboxylic acid, and pyridine tetracarboxylic acid.

Salts. — KA′: needles (from alcohol). — CaA'_2 aq. — HA′HCl: needles or prisms. — $(HA')_2H_2PtCl_6$ aq.

Ethyl ether EtA′. (256°). S.G. $\frac{15}{}$ 1·0315. Liquid, v. sol. ether, alcohol, benzene, and chloroform, insol. water, sol. dilute acids.—$(EtA')_2H_2PtCl_6$. [193°]. Prisms (from alcohol). —EtA′MeI. [128°]. Needles, v. sol. water and alcohol, insol. ether. With Ag_2O it yields crystalline $C_{10}H_{13}NO_2$ 3aq, whence $C_{10}H_{13}NO_2HCl$ aq (Hantzsch, *B.* 19, 35).

Tri-methyl-pyridine dihydride carboxylic ether $C_5H_3NMe_3.CO_2Et$. Formed by warming $C_5H_2NMe_3(CO_2Et)_2$ with HClAq (of 25 p.c.) at 100° (Hantzsch, *A.* 215, 40). Feebly basic oil.—$(HA')_2H_2PtCl_6$: minute needles.

Tri-methyl-pyridine dicarboxylic acid

$C_{10}H_{11}NO_4$ *i.e.* $N{<}{\begin{matrix}CMe.C(CO_2H)\\CMe{:}C(CO_2H)\end{matrix}}{>}CMe$.

Formed by saponifying with alcoholic potash its ether, which is obtained by the action of nitrous acid gas and alcohol upon its dihydride, which is itself produced by the action of aldehyde-ammonia on aceto-acetic ether (Hantzsch, *A.* 215, 26). Fluffy mass of needles (from hot water), melting above 300°, v. sl. sol. cold, v. sol. hot, water, v. sl. sol. alcohol and ether. Oxidised by $KMnO_4$ to di-methyl-pyridine tricarboxylic acid, methyl-pyridine tetra-carboxylic acid, and pyridine pentacarboxylic acid. Decomposed by heat into CO_2 and tri-methyl-pyridine carboxylic acid. Bromine acting on an aqueous solution of the K salt yields di-bromo-*s*-tri-methyl-pyridine. The salts which it forms with alkalis and alkaline earths are very soluble, crystallise badly, have an alkaline reaction, and split up on heating into *s*-tri-methyl-pyridine and carbonates. $FeCl_3$ gives an intense red colour to a solution of the K salt.—K_2A''.—CaA″aq: needles. — BaA″3aq. — MgA″ 2aq.—$(CuA'')_2CuO$ 11aq. — Ag_2A''. — $H_2A''HCl$ 2aq. — $(H_2A'')_2H_2PtCl_6$.

Di-methyl ether Me_2A''. [82°]. (286°). Formed by oxidation of its dihydride by nitrous acid (Hantzsch, *B.* 16, 1947). White needles, v. sol. water.—$Me_2A''HCl$ 2aq: long glistening prisms melting, when anhydrous, at 142°.—$(Me_2A'')_2H_2PtCl_6$. [200°]. Orange spangles.—$Me_2A''HAuCl_4$. [105°]. Slender light-yellow needles.—$Me_2A''HNO_3$. [140°]. Prisms.

Mono-ethyl ether EtHA″ 2aq. Formed from the neutral ether by boiling with the calculated quantity of potash dissolved in alcohol. Needles in radial groups (from alcohol), v. sol.

water, v. sl. sol. ether. Melts, when anhydrous, at 157°. — HEtA''HCl. [178°]. Cubes. — $(EtHA'')_2H_2PtCl_6$ 2aq: prisms (from cold water). Melts, when anhydrous, at 219°.—$BaEt_2A''_2$ 3aq. — $BaEt_2A''_2$ aq. — $CaEt_2A''_2$ 3aq: needles. — $CuEt_2A''_2$. — $CdEt_2A''_2$ 4aq. — $ZnEt_2A''_2$ 5aq. — $AgHEt_2A''_2$ aq: monoclinic prisms.

Di-ethyl ether Et_2A''. (308°–310°). S.G. $\frac{15}{}$ 1·087. Formed from its dihydride (*v. infra*) by treatment with HNO_3 or, better, by alcohol and nitrous acid gas (Hantzsch, *A.* 215, 21). Bright-yellow viscid oil with faint odour and burning taste. Not volatile with steam. It has no action on litmus. It does not ppt. metallic salts. With $HgCl_2$ it gives, only after a time, silky needles of a double compound. It dissolves in dilute acids.—$Et_2A''HCl$: very hygroscopic. — $(Et_2A'')_2H_2PtCl_6$: rose-coloured tables. [184°].—$Et_2A''HNO_3$: needles. [92°]. $Et_2A''HI$. [170°–173°]. Dark plates, which dissolve with rotation in cold water.—$Et_2A''HI_3$: violet pyramids.

Methylo-iodide of the diethyl ether $Et_2A''MeI$. [140°]. Formed by heating the ether with MeI and MeOH at 120°. Crystalline mass, more soluble in water or alcohol than $Et_2A''HI$. It is ppd. unaltered from its aqueous solution by NaOH. Its aqueous solution is acid to litmus. It is not affected by fuming HCl at 150° or by alcoholic NH_3 at 150°. Concentrated aqueous KOH forms methyl-di-carbo-collidylium dehydride $C_{11}H_{13}NO_4$. This substance crystallises in needles, [92°], v. e. sol. alcohol, v. sl. sol. cold water, and distils without decomposition at a temperature far above 360°. It has neither acid nor basic properties. When heated with H_2SO_4 at 150°–180° it yields CO_2, HOAc, and methyl-pseudo-lutidostyril $C_8H_{11}NO$. When 'methyl-dicarbo-collidylium dehydride' is heated in a current of HCl it loses CO_2 and forms methyl-carbo-collidylium dehydride $C_{10}H_{13}NO_2$. This is also an indifferent body; it crystallises in needles [103°], v. sol. water, and boils above 340°. On heating with H_2SO_4 it evolves acetic acid and gives methyl-pseudo-lutidostyril (Hantzsch, *B.* 17, 1022).

Methylo-chloride of the *diethyl ether* $Et_2A''MeCl$. Formed by treating $Et_2A''MeI$ with AgCl (Hantzsch, *B.* 17, 1019). Crystals. Yields $(Et_2A'')_2Me_2PtCl_6$ which crystallises in thick yellow prisms.

Tri-methyl-pyridine dihydride dicarboxylic acid $C_{10}H_{13}NO_4$ *i.e.* $NH{<}\begin{matrix}CMe{:}C(CO_2H)\\CMe{:}C(CO_2H)\end{matrix}{>}CHMe$.

Methyl ether Me_2A''. [156°]. Formed by the action of methyl acetoacetate on aldehyde-ammonia (Hantzsch, *B.* 16, 1946). When heated with HCl it exchanges CO_2Me for H and yields the methyl ether of the monocarboxylic acid. On oxidation with nitrous acid it gives $C_5Me_3(CO_2Me)_2N$.

Di-ethyl ether Et_2A''. [131°]. Formed by heating aceto-acetic ether (52 g.) with aldehyde-ammonia (13·5 g.) (Hantzsch, *A.* 215, 8).

Properties.—Compact colourless tables with many facets (from alcohol), with bright-blue fluorescence. V. sl. sol. boiling water, sl. sol. cold alcohol, ether and CS_2, m. sol. benzene, v. sol. boiling alcohol, v. e. sol. chloroform. Boils above 315° with decomposition.

Reactions.—1. Boiling conc. KOHAq has no action.—2. Alcoholic NH_3 at 150° has no action. 3. Alcoholic potash slowly decomposes it, forming NH_3 and K_2CO_3.—4. Boiling dilute *acids* do not dissolve it; it forms no platinochloride.—5. Conc. H_2SO_4 dissolves it, but on pouring into water it is reppd. unchanged.—6. Warm conc. HCl completely destroys it, forming CO_2, EtCl, NH_3, aldehyde, and acetone.—7. HCl passed into an ethereal solution removes the H_2 (Hantzsch, *A.* 215, 37), and forms other products.—8. Aqueous HCl (25 p.c.) at 100° forms hydro-tri-methyl-pyridine mono-carboxylic ether.—9. Dilute HCl at 130° forms ethyl chloride, CO_2, and tri-methyl-pyridine dihydride. Another product is an oil composed of a ketone $C_8H_{12}O$ (208°–209°), V.D. 4·20, which combines with $NaHSO_3$, and with bromine, and with hydroxylamine yields crystals [76°].—10. *Nitrous acid* removes H_2, leaving tri-methyl-pyridine dicarboxylic ether.—11. *Bromine* dissolved in CS_2 forms a dibromide of di-bromo-tri-methyl-pyridine dihydride carboxylic ether $NC_8H_7Br_2(CO_2Et)_2H_2Br_2$ [88°]. This is extremely soluble in boiling alcohol, and crystallises as yellow twin-crystals. Fuming HNO_3 converts it into the di-bromide of di-bromo-tri-methyl-pyridine di-carboxylic ether [102°].—12. *Chloride* forms the di-chloride of penta-chloro-tri-methyl-pyridine dicarboxylic ether, crystallising as woolly needles [150°].

Tetra-methyl-pyridine dihydride carboxylic ether $C_{15}H_{23}NO_4$ *i.e.* $NMe{<}\begin{matrix}CMe{:}C(CO_2Et)\\CMe{:}C(CO_2Et)\end{matrix}{>}CHMe$. [86°]. Formed by the action of paraldehyde and H_2SO_4 on methyl-amido-oxy-butyric ether (Kuckert, *B.* 18, 620); and, in small quantity, by the action of methylamine on a mixture of acetoacetic ether and aldehyde (Hantzsch, *B.* 18, 2580). Crystals, with blue fluorescence.

METHYL-PYRIDINE-HYDRIDES *v.* METHYL-PYRIDINE.

DI-METHYL-DIPYRIDYL $C_{12}H_{12}N_2$ *i.e.* $NC_5H_3Me.C_5H_3MeN$. *Dipicolyl.* [84°]. (295°–298°). Obtained by treating (α)-picoline with sodium at 80°–90°, exposing the product to air, and fractionally distilling (Ahrens, *B.* 21, 2930; Heuser, *J. pr.* [2] 42, 430). Very deliquescent yellowish needles. With water it forms a compound (containing 4aq) melting at 38°. When oxidised by potassium permanganate it yields $NC_5H_3Me.C_5H_3N.CO_2H$ [193°], which on heating by itself or with HOAc yields methyl-dipyridyl [94°].—$B''H_2Cl_2$. Hygroscopic plates (from alcohol). Picrate $B''2C_6H_2(NO_2)_3OH$. [240°].—$B''H_2Cl_26HgCl_2$. [220°]. — $B''H_2PtCl_6$: small plates; v. sl. sol. water, v. sol. HClAq. Discolours at 235°, but only partially decomposed at 275°. — $B''2HAuCl_4$: nodules (from conc. HClAq) decomposes at 200° (A.); [210°] (H.).—The tin double salt melts at 180°.

Di-methyl-dipyridyl dodecahydride $C_{12}H_{24}N_2$ *i.e.* $MeNC_5H_9.C_5H_9NMe$. *Di-methyl-dipiperidyl.* (230°–235°). Formed, together with tri-methyl-dipyridyl dodecahydride, by treating the product of the action of MeI upon dipyridyl dodecahydride (dipiperidyl) with Ag_2O (Liebrecht, *B.* 19, 2595). Liquid, miscible with water, but separating on addition of NaOH.—$B''H_2Cl_2(HgCl_2)_2$:

flocculent pp., sol. hot water.—$B''H_2PtCl_6$: small dark-red crystals.

Tri-methyl-dipyridyl dodecahydride $C_{13}H_{26}N_2$ *i.e.* $NMe.C_5H_9.C_5H_8Me.NMe$. (205°–212°). Formed as above. Yellowish oil; insol. water.—$B''H_2PtCl_6$: yellowish-red crystals; v. e. sol. water.

TRI-METHYL-PYRIDYLENE DIHYDRIDE DI-METHYL DIKETONE $C_{12}H_{17}NO_2$ *i.e.* $N\left\langle\begin{matrix}CMe.CH(CO.CH_3)\\CHMe.C(CO.CH_3)\end{matrix}\right\rangle CMe$. [153°]. (250° *in vacuo*). Formed by heating methylene di-methyl diketone (2 mols.) with aldehyde-ammonia (1 mol.) on the water-bath (Combes, *Bl.* [2] 51, 15). Hexagonal prisms (from alcohol); insol. water.

METHYL-PYRIDYL-ACETYLENE TETRA-HYDRIDE $C_5H_7NMe.C{:}CH$. Formed by boiling the hydrobromide of anhydro-ecgonine dibromide with aqueous K_2CO_3 (Eichengrün a. Einhorn, *B.* 23, 2879). Oil.—$B'HAuCl_4$. [179°].

DI-METHYL-DI-PYRIDYL-PROPANE DO-DECAHYDRIDE $C_{15}H_{30}N_2$ *i.e.* $(C_5H_9NMe.CH_2)_2CH_2$. *Methylo-iodide* $B''Me_2I_2$. Obtained by heating $(C_5H_{10}N.CH_2)_2CH_2$ with MeI (Ladenburg, *B.* 21, 3102). White non-hygroscopic crystals; v. sol. hot water. The aurochloride $B''(HAuCl_4)_2$ [171°] obtained from the methylo-iodide; crystallises from water in needles.

(*Py.* 1:5) - **DI - METHYL - PYRIDYL** - (*Py.* 3)- **QUINOLINE** $C_{16}H_{14}N_2$ *i.e.* $C_5NH_2Me_2.C_6H_3\left\langle\begin{matrix}CH:CH\\ | \\ N:CH\end{matrix}\right.$. *Lutidyl - quinoline.* [109°]. Colourless glistening crystals. Formed by heating *m*-amido-phenyl-di-methyl-pyridine $C_5NH_2(CH_3)_2.C_6H_4.NH_2$ with glycerine, nitro-benzene, and H_2SO_4. The chloride and nitrate form white needles; the platino-chloride small orange needles; the auro-chloride long golden-yellow needles [215°] (Lepetit, *B.* 20, 2399; *G.* 17, 473).

METHYL - PYROCATECHIN $C_7H_8O_2$ *i.e.* $C_6H_3Me(OH)_2$ [1:3:4]. Formed by heating creosol $C_6H_3Me(OMe)(OH)$ [1:3:4] with HIAq (H. Müller, *C. N.* 10, 269). Formed also by the dry distillation of di-oxy-toluic ((*a*)-homo-protocatechuic) acid (Tiemann a. Nagai, *B.* 10, 210), and from $C_6H_3Me(NO_2)(OH)$ [1:3:4] by displacement of NO_2 by OH (Nevile a. Winther, *B.* 15, 2983). Liquid, which may be distilled; v. e. sol. water, alcohol, and ether. Reduces Fehling's solution and ammoniacal $AgNO_3$ in the cold. $FeCl_3$ gives a green colouration, turned reddish-violet by ammonia.

Mono-methyl ether $C_6H_3Me(OH)(OMe)$ [1:3:4]. *Isocreosol.* (c. 185°). Prepared from $C_6H_3Me(NH_2)(OMe)$ [1:3:4] by the diazo-reaction (Limpach, *B.* 22, 350). Yellow liquid; v. sol. alcohol and ether, sl. sol. water. Volatile with steam.

Mono-methyl ether $C_6H_3Me(OMe)(OH)$ [1:3:4] *v.* CREOSOL.

Isomerides *v. Methyl ethers* of PYROCATECHIN.

TETRA-METHYL-PYROCOLL $C_{14}H_{14}N_2O_2$ *i.e.* $NC_4HMe_2\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_4HMe_2N$. [272·5°]. Formed, together with ($a\beta'$)-di-methyl-pyrrole, by heating ($a\beta'$)-di-methyl-pyrrole-($a'\beta$)-dicarboxylic anhydride at 350° (Magnanini, *B.* 21, 2877; 22, 2502). Trimetric yellow needles (by sublimation); insol. water, v. sol. chloroform. Its molecular weight was determined by Raoult's method. Boiling alcoholic KOH gives

$NC_4H_2Me_2.CO.NC_4HMe_2.CO_2K$.

METHYL - PYROGALLOL $C_7H_8O_3$ *i.e.* $C_6H_2(CH_3)(OH)_3$. [129°]. Prepared by heating the dimethyl ether with HCl to 150°. Sublimes in small needles. Sl. sol. benzene.

Dimethyl ether $C_6H_2(CH_3)(OH)(OMe)_2$. [36°]. (265°). Crystalline. Occurs together with the dimethyl ether of pyrogallol in beech-wood tar-oil, from which it can be isolated by means of its benzoyl compound [118°] (Hofmann, *B.* 12, 1371). With bromine it yields $C_6Br_2(CH_3)(OH)(OMe)_2$ [126°]. If a mixture of the sodium salts of the dimethyl ethers of pyro-gallol and methyl-pyrogallol is oxidised by heating in the air or with C_2Cl_6 eupittonic acid (pit-takal) is formed.

METHYL-PYROMUCIC ACID $C_6H_6O_3$ *i.e.* $C_4H_2MeO.CO_2H$. [108°]. Formed by the oxidation of methyl-furfuraldehyde (Hill, *B.* 22, 608) and by the action of conc. KOHAq upon that aldehyde (Bieler a. Tollens, A. 258, 125). Needles; more soluble than pyromucic acid in water, benzene, and chloroform. With isatin and H_2SO_4 it gives a deep-green colour on warming. $FeCl_3$ gives a brown pp.

Reaction.—Bromine (2 mols.) added to its aqueous solution gives off CO_2 and forms an acid $C_5H_6O_3$ (?acetylacrylic), which crystallises in broad flat needles [123°], S. 6·7 (in the cold). This acid is v. sol. alcohol, ether, and hot water; it forms an addition-product [108°] with bromine, a silver salt $AgC_5H_5O_3$, crystallising in slender needles, and a phenyl-hydrazide [157°] apparently identical with that of acetyl-acrylic acid (Hill a. Hendrixson, *B.* 23, 452; *cf.* Bender, *B.* 21, 2494; Decker, *B.* 21, 2937).

Salt.—$AgC_6H_5O_3$: slender needles (from hot water); sl. sol. hot water.

DI-METHYL-PYRONE *v. Anhydride* of DI-METHYLENE DI-METHYL DIKETONE.

Di-methyl-pyrone carboxylic acid *v.* DE-HYDRACETIC ACID.

Di-methyl-pyrone dicarboxylic acid *v. Anhydride* of DI-METHYLENE DI-METHYL TRIKETONE.

ν-METHYL-PYRROLE C_5H_7N *i.e.* $NMe\left\langle\begin{matrix}CH:CH\\CH:CH\end{matrix}\right\rangle$. *Methyl-pyrroline.* (113°). (B.); (114° i.V.) (C. a. D.). S.G. $\frac{10}{}$ ·9203 (B.). Formed by the dry distillation of methylamine mucate (C. A. Bell, *B.* 10, 1866). Formed also by treating potassium pyrrole with MeI (Ciamician a. Dennstedt, *B.* 17, 2951). Liquid. Resolved by heating with KOH into pyrrole and MeOH. When ν-methyl-pyrrole (3 g.) is heated with MeOH (5 g.), MeI (7 g.), and K_2CO_3 (3 g.) for 10 hours at 140° there is formed a tri-methyl-pyrrol (150°–165°) and penta-methyl-pyridine dihydride $C_5H_2Me_4NMe$ (Ciamician a. Anderlini, *B.* 22, 656). Methyl-pyrrole acts on alloxan in warm aqueous solution forming $C_9H_9N_3O_4$ *i.e.* $NH_2.CO.NH.CO.CO.CO.C_4H_3NMe$, which crystallises in white plates; sol. hot water, sl. sol. alcohol and cold water (Ciamician a. Silber, *B.* 19, 1710).

ν-**Methyl - pyrrole dihydride** C_4H_6NMe. *Methyl-pyrroline.* (80°). Formed by reduction of ν-methyl-pyrrole with zinc-dust and HOAc (Ciamician a. Magnaghi, *B.* 18, 725). Colour-

less, strongly alkaline liquid, miscible with water. Tertiary base. Its hydrochloride forms colourless crystals.—$B'_2H_2PtCl_6$: trimetric crystals, v. e. sol. water (Le Valle, *G.* 15, 490).

Methylo-iodide $C_4H_6NMe_2I$. [286°]. Obtained by the action of MeI on the above or on pyrrole dihydride (Ciamician, *B.* 16, 1541; *G.* 15, 492). Pearly plates. Yields the platinochloride $(C_4H_6NMe_2Cl)_2PtCl_6$ *x*aq.

Methyl-pyrrole tetrahydride $C_5H_{11}N$ *i.e.* $NMe<\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}>$. *Methyl-pyrrolidine.* (82°). Formed by heating the dihydride with fuming HIAq and amorphous phosphorus at 250° (Ciamician a. Magnaghi, *G.* 15, 493). Liquid, miscible with water.

Methylo-iodide $C_4H_8NMe_2I$. Formed by the action of MeI on methyl-pyrrole tetrahydride or on pyrrole tetrahydride. Deliquescent needles, v. e. sol. alcohol, insol. ether and NaOHAq. Ag_2O yields $C_4H_8NMe_2OH$, which is decomposed by distillation into MeOH and C_4H_8NMe. Distillation of the iodide with solid KOH yields C_4H_7MeNMe [89°–92°].

(α)-Methyl-pyrrole C_5H_7N *i.e.* $C_4H_3Me.NH$. (α)-*Homopyrrole.* (148°). Occurs, together with the (β)-isomeride, in bone-oil. The fraction 140°–150° is boiled with KOH, and the potassium derivatives that separate are washed with ether, decomposed by water, and fractionally distilled (Ciamician, Dennstedt, a. Zimmermann, *B.* 19, 173, 2200; 22, 1918; Weidel a. Ciamician, *B.* 13, 77). The isomerides may also be separated by conversion into their carboxylic acids, separation of these by means of their lead salts, and dry distillation of their calcium salts (Ciamician, *B.* 14, 1053).

Properties.—Liquid, smelling like chloroform. Turns brown in air. Resinified by HCl, but more slowly than pyrrole; gives a white pp. with $HgCl_2$. Forms a potassium compound C_4H_3MeNK, which combines with CO_2 at 200°, forming (α)-methyl-pyrrole carboxylic acid. The potassium compound reacts with chloroform, yielding chloro-methyl-pyridine. Potash-fusion yields pyrrole (α)-carboxylic acid. Oxidising agents form HOAc, ammonia, and CO_2. HCl passed into its ethereal solution ppts. di-methyl-di-pyrrole hydrochloride $(C_5H_7N)_2HCl$, whence cold dilute H_2SO_4 forms di-methyl-indole (c. 275°), of which the picrate melts at 156° (Dennstedt, *B.* 21, 3439). On heating with phthalic anhydride and HOAc at 240° there is formed a yellow compound $C_{13}H_9NO_2$ [157°], which appears to be the anhydride of an acid, which may be obtained from it by boiling with dilute KOHAq, acidifying, and extracting with ether. This acid forms colourless crystals, and melts at 170°–172° (Ciamician a. Zimmermann, *B.* 19, 2203).

(β)-Methyl-pyrrole C_4H_3MeNH. (143°). Occurs in bone-oil (*v. supra*). Liquid. Resembles the (α)-isomeride in its reactions. Potash-fusion yields pyrrole (β)-carboxylic acid. CO_2 acting on its potassium compound forms (β)-methyl-pyrrole carboxylic acid. HCl passed into its ethereal solution forms the hydrochloride of (β)-dimethyl-dipyrrole $(C_5H_7N)_2HCl$; and when dilute H_2SO_4 is allowed to act for 24 hours on this hydrochloride there is formed a di-methyl-indole of which the picrate melts at 149° (Dennstedt, *B.* 21, 3439). On heating (β)-methyl-pyrrole (5 g.) dissolved in HOAc (3 vols.) with phthalic anhydride (10 g.) for 5 hours at 200° there is formed a compound $C_{13}H_9NO_2$ [215°], which may be purified by crystallisation from alcohol and sublimation, and obtained as lemon-yellow needles, insol. water (Ciamician a. Dennstedt, *B.* 17, 2957; 19, 2201). Dilute KOH converts the compound $C_{13}H_9NO_2$ into an acid $C_{13}H_{11}NO_3$, which forms colourless crystals (from ether), and melts at 159°.

Acetyl derivative of methyl-pyrrole C_4H_3MeNAc. (197°). Formed, together with methyl-pyrryl methyl ketone, by boiling methyl-pyrrole with NaOAc and Ac_2O (Ciamician a. Silber, *B.* 19, 1409). Liquid. Volatile with steam, almost insol. water. Easily saponified by alkalis.

Methyl-pyrrole-tetra-hydride $C_5H_{11}N$ *i.e.* $\begin{matrix}CH_2.CHMe\\|\\CH_2.CH_2\end{matrix}>NH$. *Methyl-pyrrolidine.* (97° at 737 mm. i.V.). Formed by reduction of oxy-methyl-pyrrole-di-hydride (from γ-amido-valeric acid) in boiling amyl-alcohol with metallic sodium (Tafel, *B.* 20, 250). Colourless mobile liquid. Very volatile at the ordinary temperature. Boiling MeI and MeOH form crystalline $C_5H_{10}MeNMeI$.

Salts (Tafel a. Neugebauer, *B.* 22, 1865).—B'HCl. [210°–220°]. Colourless prisms.—$B'_2H_2PtCl_6$ aq: golden needles (from hot water).—$B'H_2AuCl_5$. [140°–144°]. Golden crystals, v. sol. water and alcohol.—$B'_2H_2C_2O_4$. [165°–168°]. Small needles.

Nitrosamine $C_5H_{10}(NO)N$. Yellow oil.

Methyl-pyrrole tetrahydride $NH<\begin{matrix}CH_2.CHMe\\CH_2.CH_2\end{matrix}>$. (104°). S.G. $\frac{0}{4}$ ·8654. This base is formed by the dry distillation of the hydrochloride of methyl-tetramethylene-diamine $NH_2.CH_2.CH_2.CHMe.CH_2.NH_2$ (Oldach, *B.* 20, 1657). Liquid, fuming in the air, and smelling like piperidine.

Salts.—Hydrochloride: very deliquescent.—$B'_2H_2PtCl_6$. [194°]. Long prisms.—$B'HAuCl_4$. [170°]. Minute tables, v. sol. water. $B'_3HI(BiI_3)_2$.—$B'C_6H_2(NO_2)_3OH$. [105°].

Nitrosamine $C_5H_{10}(NO)N$. (224°).

Di-methyl-pyrrole C_6H_9N *i.e.* $HN<\begin{matrix}CMe:CH\\CMe:CH\end{matrix}>$. (165°). Occurs in bone-oil (Weidel a. Ciamician, *B.* 13, 78).

Formation.—1. By the action of alcoholic potash at 150°–160° on its dicarboxylic ether, which is formed by reduction of a mixture of acetoacetic and isonitroso-acetoacetic ethers with zinc-dust and acetic acid (Knorr, *B.* 17, 1638).—2. By heating its mono- (or di-) carboxylic acid, obtained from di-acetyl-succinic ether (Knorr, *B.* 18, 1565).—3. By heating acetonyl-acetone $CH_3.CO.CH_2.CH_2.CO.CH_3$ with a slight excess of alcoholic NH_3 for an hour at 150° (Paal, *B.* 18, 2254).

Properties.—Colourless liquid with unpleasant odour, almost insol. water, v. e. sol. alcohol and ether. Very volatile with steam. Gives a white pp. with $HgCl_2$. Slowly resinified by HCl. Its vapour colours pine-wood moistened with HCl red. Bromine-water gives a white pp. $FeCl_3$ gives a brownish-red colouration. H_2SO_4 added to its acetic acid solution mixed with phenanthraquinone gives a deep-brownish red colour. H_2SO_4 and isatin give a green colour, changing on warming to brownish-red. Phenyl glyoxylic

acid and sulphuric acid also give a brownish-red colour. Hydroxylamine acting on its alcoholic solution forms the di-oxim of acetonyl-acetone $CH_3.C(NOH).CH_2.CH_2.C(NOH).CH_3$ [136·5°] (Ciamician a. Zanetti, *B.* 22, 3177).

Acetyl derivative C_4H_3MeNAc. Liquid, not solidified at −20°; v. sl. sol. water. Saponified by potash. Does not reduce $AgNO_3$ in very dilute ammoniacal alcoholic solution.

Di-methyl-pyrrole tetrahydride $C_6H_{13}N$ *i.e.* $NH\left<\begin{array}{l}CHMe.CH_2\\CHMe.CH_2\end{array}\right>$. (107° i.V.). Formed by distilling the hydrochloride of hexylene-diamine $NH_2.CHMe.CH_2.CH_2.CHMe.NH_2$ obtained by reducing the phenyl-hydrazide of acetonyl-acetone (Tafel, *B.* 22, 1854; Tafel a. Neugebauer, *B.* 23, 1547). Colourless oil, smelling like piperidine, miscible with water, alcohol, and ether. Its hydrochloride crystallises in needles [188°–190°].—$B'_2H_2C_2O_4$: small needles (from alcohol).—$B'_2H_2PtCl_6$: golden prisms.

Nitrosamine $C_4H_6Me_2N.NO$. (135° at 60 mm.). Yellow oil, lighter than water; sl. sol. cold water, v. sol. ether and alcohol. Conc. H_2SO_4 dissolves it without becoming coloured, but on warming the liquid becomes yellow and gives off gas. The nitrosamine may be reduced to an oily hydrazine, which on oxidation with HgO yields the tetrazone $C_{12}H_{24}N_4$ [43°].

Di-methyl-pyrrole C_6H_9N *i.e.* $NH\left<\begin{array}{l}CMe{:}CH\\CH\ {:}CMe\end{array}\right>$. (171° cor.). Formed by distilling its carboxylic acid (Knorr, *A.* 236, 326). Liquid, with blue fluorescence and characteristic sweet odour, sl. sol. water, v. sol. alcohol, ether, and benzene. Its aqueous solution becomes red on warming with $FeCl_3$.

Di-methyl-pyrrole tetrahydride $C_4H_7Me.NMe$. (89°–92°). Formed by distilling the methylo-iodide of methyl-pyrrole tetrahydride with KOH (Ciamician a. Magnaghi, *G.* 15, 485). Liquid, miscible with water. Its hydrochloride is deliquescent.

Methylo-iodide $C_4H_7MeNMe_2I$. Small needles (from alcohol); v. e. sol. water. Ppd. from its aqueous solution by addition of KOH. On distillation with KOH it yields trimethylamine and butinene C_4H_6.

Tri-methyl-pyrrole $C_7H_{11}N$. (180°–195°). Occurs in bone-oil (fraction 180°–205°); from which it is isolated by conversion into the potassium compound (Ciamician a. Dennstedt, *B.* 14, 1340). Colourless oil. Sol. acids, sl. sol. water. Turns brown in air. Its vapour turns pine-wood moistened by HCl red. Reduces $PtCl_4$. Gives a white pp. with $HgCl_2$. Potassium acts on it very slowly with production of the solid compound $C_7H_{10}NK$. Conc. HClAq at 120° forms ammonia and a di-methyl-pyridine dihydride $C_7H_{11}N$.

Tri-methyl-pyrrole $C_7H_{11}N$. (150°–165°). Prepared by heating methyl-pyrrole (3 g.) dissolved in MeOH (5 g.) with MeI (7 g.) and K_2CO_3 (3 g.) for 10 hours at 140°. The product is acidified and distilled with steam (Ciamician a. Anderlini, *B.* 22, 656).

Tri-methyl-pyrrole $C_7H_{11}N$ *i.e.* $NMe\left<\begin{array}{l}CMe{:}CH\\ \quad\ \ |\\CMe{:}CH\end{array}\right.$. (173° cor.). Formed by heating its dicarboxylic acid at 260° (Knorr, *A.* 236, 304). Liquid, volatile with steam; v. sol. alcohol and ether. Boiling aqueous $FeCl_3$ gives an intense red colour.

Tri-methyl-pyrrole tetra-hydride $C_7H_{15}N$ *i.e.* $NMe\left<\begin{array}{l}CHMe.CH_2\\ \qquad\quad\ |\\CHMe.CH_2\end{array}\right.$. (116°) at 750 mm. Formed by the action of MeI on $NH\left<\begin{array}{l}CHMe.CH_2\\CHMe.CH_2\end{array}\right>$ (Tafel a. Neugebauer, *B.* 23, 1549). Liquid, sl. sol. water.—B'HCl: glittering white prisms.—$B'_2H_2PtCl_6$: yellow oil, sl. sol. alcohol.

Methylo-iodide B'MeI. [256°]. Colourless prisms, v. sol. water, sl. sol. warm alcohol.

A tri-methyl-pyrrole tetrahydride $NH\left<\begin{array}{l}CH_2.CHMe\\ \qquad\ \ |\\CMe_2.CH_2\end{array}\right.$ appears to be formed by distilling oxy-tri-methyl-pyrrole dihydride with zinc-dust (Weil, *A.* 232, 213).

METHYL-PYRROLE-DISAZO- COMPOUNDS *v.* *Dis*-AZO- COMPOUNDS.

(α)-METHYL-PYRROLE CARBOXYLIC ACID $C_6H_7NO_2$ *i.e.* $C_4H_3MeN.CO_2H$. (α)-*Homo-pyrroline carboxylic acid. Carbohomopyrrolic acid.* [169·5°]. When crude potassium methyl-pyrrole is heated in a current of CO_2 at 190° there is formed a mixture of the potassium salts of (α)- and (β)-methyl-pyrrole carboxylic acids. These acids may be separated by lead acetate, which ppts. the (β)- acid only (Ciamician, *G.* 11, 230; *B.* 14, 1056). Colourless scales, sol. water. Yields (α)-methyl-pyrrole on distillation with lime.

(β)-Methyl-pyrrole carboxylic acid $C_6H_7NO_2$ *i.e.* $C_5H_3MeN.CO_2H$. [142·4°]. Obtained as above, forms a minutely crystalline mass. Its Ca salt yields (β)-methyl-pyrrole on distillation with lime.

Methyl-pyrrole carboxylic acid $C_6H_7NO_2$ *i.e.* $C_5H_3MeN.CO_2H$. [135°]. Formed by heating its methylamide with alcoholic potash at 120° (Chichester A. Bell, *B.* 10, 1861; 11, 1810).

Methylamide $C_5H_3MeN.CO.NHMe$. [90°]. Formed, together with methyl-pyrrole, by heating methylamine mucate in a paraffin bath (Bell). Scales or prisms; sol. water, volatile with steam.

Di-methyl-pyrrole carboxylic acid $C_7H_9NO_2$ *i.e.* $NH\left<\begin{array}{l}CMe{=\!=}CH\\C(CO_2H){:}CMe\end{array}\right>$. [137°]. Formed by the prolonged action of boiling aqueous KOH on tetra-methyl-pyrroyl-pyrrole carboxylic acid or on tetramethylpyrocoll, which is itself obtained by heating di-methyl-pyrrole dicarboxylic acid (Magnanini, *B.* 22, 38; *Rend. Accad. Linc.* [4] 4, 475). Crystals, v. sl. sol. cold water, dissolves in warm water with partial decomposition into CO_2 and di-methyl-pyrrole. Decomposes on fusion. Boiling Ac_2O converts it into tetra-methyl-pyrocoll and di-methyl-pyrryl methyl ketone. A solution of its ammonium salt gives with lead acetate a white pp., sol. excess, with cupric acetate a green crystalline pp., and with $FeCl_3$ a dark-red pulverulent pp.

Di-methyl-pyrrole carboxyl derivative $C_{14}H_{16}N_2O_3$ *i.e.* $\left.\begin{array}{l}CH.CMe\\ \|\\CMe.NH\end{array}\right>C.CO.N\left<\begin{array}{l}CMe{=\!=}CMe\\ \qquad\qquad\ |\\C(CO_2H){:}CH\end{array}\right.$. *Tetra-methyl-pyrroyl-pyrrole carboxylic acid.* Formed by boiling tetra-methyl-pyrocoll with alcoholic

potash, diluting with water, and ppg. with acetic acid (Magnanini, *B.* 22, 35; *Rend. Accad. Linc.* [4] 4, 468). At 145° it gives off CO_2 and leaves a residue which may be crystallised from alcohol. Boiling aqueous potash forms di-methyl-pyrrole carboxylic acid. On warming solutions of the salts a pp. of tetra-methyl-pyrocoll is formed. The lead and silver salts are white pps., the ferric salt a red pp., and the cupric salt a green pp.—BaA'_2. Tables.

Methyl ether MeA'. [163°]. Formed from the silver salt and MeI. Monoclinic tables; $a:b:c = \cdot701:1:\cdot443$; $\beta = 80° 59'$. Insol. water, sl. sol. benzene, v. sol. $CHCl_3$. Yields MeOH and tetramethylpyrocoll on fusion.

Di-methyl-pyrrole carboxylic acid $C_7H_9NO_2$ *i.e.* $NH\left\langle\begin{matrix}CMe:C(CO_2H)\\ CH{=}{=}{=}CMe\end{matrix}\right\rangle$. [183°]. Obtained from its ether, which is produced by heating the mono-ethyl ether of di-methyl-pyrrole dicarboxylic acid $NH\left\langle\begin{matrix}CMe:C(CO_2Et)\\ C(CO_2H):CMe\end{matrix}\right\rangle$ (Knorr, *A.* 236, 325). Crystalline flocculi. Split up on melting into CO_2 and di-methyl-pyrrole. Boiling Ac_2O forms di-methyl-pyrryl methyl ketone $CH_3.CO.C_4H_2NMe_2$ [122°].

Ethyl ether EtA'. [76°]. (291° cor.). Crystalline mass, v. sol. alcohol and ether.

Anilide $C_4H_2Me_2N.CONHPh$. [80°]. Formed by heating the mono-anilide of di-methyl-pyrrole dicarboxylic acid.

Di-methyl-pyrrole carboxylic acid $C_7H_9NO_2$ *i.e.* $NH\left\langle\begin{matrix}CMe:CH\\ |\\ CMe:C.CO_2H\end{matrix}\right.$. Obtained by saponifying with aqueous NaOH its ether, which is formed by heating the mono-ethyl ether of di-methyl-pyrrole dicarboxylic acid $NH\left\langle\begin{matrix}CMe:C.CO_2H\\ |\\ CMe:C.CO_2Et\end{matrix}\right.$ (Knorr, *B.* 18, 1564). Slender needles. Split up at 210–213° into CO_2 and the corresponding di-methyl-pyrrole.

Salts.—PbA'_2: microcrystalline pp.—AgA': white pp.

Ethyl ether EtA'. [118°]. (290° at 731 mm.). Formed as above, and also by slowly adding conc. NH_3Aq to a mixture of molecular proportions of chloro-acetone and acetoacetic ether. Flat prisms, volatile with steam. Sol. alcohol and ether, insol. water.

Di-methyl-pyrrole dicarboxylic acid $C_8H_9NO_4$ *i.e.* $NH\left\langle\begin{matrix}CMe:C(CO_2H)\\ C(CO_2H):CMe\end{matrix}\right\rangle$.

Preparation.—$NaNO_2$ (2 pts.) in conc. aqueous solution is added to acetoacetic ether (7 pts.) dissolved in HOAc. Zinc-dust (25 pts.) is added to the well-cooled product. On adding water the di-ethyl ether is deposited in needles, and this is saponified by boiling NaOHAq (Knorr, *A.* 236, 317; *B.* 17, 1638).

Properties.—Crystalline flakes, v. sol. water and alcohol, less sol. ether. Rapidly turns red in air. Decomposes completely at 260° into CO_2 and di-methyl-pyrrole, without melting. It reduces boiling ammoniacal $AgNO_3$. It forms normal and acid salts which are mostly amorphous.

Mono-ethyl ether HEtA'' *i.e.* $NH\left\langle\begin{matrix}CMe:C(CO_2Et)\\ C(CO_2H):CMe\end{matrix}\right\rangle$. [202°]. Formed by boiling the di-ethyl ether with alcoholic potash. Needles (from alcohol), sl. sol. cold alcohol, insol. water. Split up on fusion into CO_2 and di-methyl-pyrrole carboxylic ether. Its lead and silver salts are white amorphous pps. When heated with Ac_2O in a sealed tube at 200° it it yields $NH\left\langle\begin{matrix}CMe:C(CO_2Et)\\ CAc:CMe\end{matrix}\right\rangle$ [143°], and this ether gives on saponification a crystalline acid [150°–158°], which on dry distillation is split up into CO_2 and di-methyl-pyrryl methyl ketone [123°] (Magnanini, *B.* 21, 2865).

Di-ethyl ether $C_{12}H_{17}NO_4$ or Et_2A''. [135°]. Formed as above. White matted needles, insol. water, acids, and alkalis, sol. alcohol and ether. Split up by heat into CO_2 and di-methyl-pyrrole. Alcoholic potash forms a pp. of $C_{12}H_{16}KNO_4$.

Mono-anilide $C_{14}H_{14}N_2O_3$ *i.e.* $NH\left\langle\begin{matrix}CMe:C(CONHPh)\\ C(CO_2H):CMe\end{matrix}\right\rangle$. Formed by boiling its ethyl ether (*v. infra*) with alcoholic potash. Slender needles which soften at 180° and decompose at 198° into CO_2 and the anilide of di-methyl-pyrrole carboxylic acid. Boiling dilute H_2SO_4 decomposes it in the same way.

Ethyl ether of the mono-anilide $C_{14}H_{13}N_2O_3Et$. [216°]. Formed by the action of zinc-dust on a mixture of equivalent quantities of acetoacetic anilide and nitroso-acetoacetic ether dissolved in HOAc (Knorr, *A.* 236, 327). Crystals, sol. hot alcohol and HOAc. Yields di-methyl-pyrrole on warming with conc. H_2SO_4.

Ethyl ether of the isomeric mono-anilide $C_{14}H_{13}N_2O_3Et$ *i.e.* $NH\left\langle\begin{matrix}CMe:C(CO_2Et)\\ C(CONHPh):CMe\end{matrix}\right\rangle$. [180°]. Formed by the action of zinc-dust on a mixture of equivalent quantities of acetoacetic ether and nitroso-acetoacetic anilide dissolved in HOAc (Knorr). Needles (from alcohol). Yields di-methyl-pyrrole on warming with H_2SO_4.

Di-anilide $NH\left\langle\begin{matrix}CMe:C(CONHPh)\\ C(CONHPh):CMe\end{matrix}\right\rangle$. [255°]. Formed by the action of zinc-dust on a mixture of equivalent quantities of acetoacetic anilide and nitroso-acetoacetic anilide (Knorr). Needles (from alcohol). Yields di-methyl-pyrrole on warming with H_2SO_4.

Anhydride $C_8H_7NO_3$ *i.e.* $\begin{matrix}N\left\langle\begin{matrix}CMe:C(CO_2H)\\ C{=}{=}{=}CMe\end{matrix}\right\rangle\\ |\;/\\ CO\end{matrix}$. Formed by boiling di-methyl-pyrrole dicarboxylic acid with Ac_2O (Magnanini, *B.* 21, 2876). Powder, almost completely insol. water, alcohol, and ether. Turns brown at 300° and at a higher temperature it splits up into di-methyl-pyrrole and tetra-methyl-pyrocoll.—MgA'_2: needles, m. sol. water. —AgA': yellow amorphous sediment.

Ethyl ether of the anhydride $C_8H_6EtNO_3$. [270°]. Formed by boiling di-methyl-pyrrole dicarboxylic ether with Ac_2O. White, sparingly soluble needles.

Di-methyl-pyrrole dicarboxylic acid $NH\left\langle\begin{matrix}CMe:C.CO_2H\\ |\\ CMe:C.CO_2H\end{matrix}\right.$. [250°]. Formed by dissolving di-acetyl-succinic ether in aqueous NH_3, and saponifying the resulting ether with alcoholic potash (Knorr, *B.* 18, 302, 1558). Needles

(from alcohol). Decomposes at its melting-point into CO_2 and ($\alpha\alpha'$)-di-methyl-pyrrole.—BaA'': small needles.—CuA'' 3aq: slender green needles.—$_x$Ag$_2$A'': microcrystalline powder.

Mono-ethyl ether HEtA''. [227°]. Slender crystals. Evolves CO_2 at its melting-point, giving di-methyl-pyrrole carboxylic acid. It has acid properties, and its Cu, Co, and Ni salts form white felted needles.

Di-ethyl ether Et$_2$A''. [99°]. Colourless crystals, sol. alcohol, $CHCl_3$, and HOAc, sl. sol. ether, nearly insol. water. Has weak basic and acid properties.—$(C_{12}H_{17}NO_4HCl)_2PtCl_4$. Orange-red crystals.—$C_{12}H_{16}KNO_4$: slender felted needles.

Tri-methyl-pyrrole dicarboxylic acid

$C_9H_{11}NO_4$ *i.e.* $NMe\left<\begin{matrix}CMe{:}C.CO_2H\\ |\\ CMe{:}C.CO_2H\end{matrix}\right.$. Obtained by saponifying with alcoholic potash its di-ethyl ether which is produced by boiling di-aceto-succinic ether with methylamine in glacial acetic acid solution (Knorr, *B.* 18, 303; *A.* 236, 304). Slender needles, insol. water, sl. sol. ether, sol. alcohol. Split up at 260° into CO_2 and tri-methyl-pyrrole.—KHA''.—NH$_4$HA''.—BaA''.—CoA''.

Ethyl ether Et$_2$A''. [72°].

Tri-methyl-pyrrole dicarboxylic acid

$C_9H_{11}NO_4$ *i.e.* $NH\left<\begin{matrix}CMe{:}C.CH_2.CO_2H\\ |\\ CMe{:}C.CO_2H\end{matrix}\right.$. *Di-methyl-pyrrole carboxy-acetic acid.* [196°]. Formed by saponification by aqueous NaOHAq from its ether which is obtained by boiling $\alpha\beta$-di-acetyl-glutaric ether with a solution of NH_3 in HOAc (Knorr, *B.* 19, 48). Slender prisms. Imparts a red colouration to acidified pine wood.

Di-ethyl ether Et$_2$A''. [110°]. Glistening plates, v. sol. alcohol and ether, insol. water.

Tri-methyl-pyrrole tricarboxylic acid

$C_{10}H_{11}NO_6$ *i.e.* $CO_2H.CH_2.N\left<\begin{matrix}CMe{:}C.CO_2H\\ |\\ CMe{:}C.CO_2H\end{matrix}\right.$. *Di-methyl-pyrrole-dicarboxy-acetic acid.* Obtained by saponifying its ether which is produced by boiling di-acetyl-succinic ether with glycocoll and HOAc (Knorr, *A.* 236, 315). Crystalline pp., decomposed at 214° giving off CO_2.—K$_3$A'''.—Ag$_2$HA''': crystalline pp.

Di-ethyl ether Et$_2$HA'''. [169°]. Formed as above. Plates, insol. water, v. sol. alcohol, ether, and alkalis.—Pb(Et$_2$A''')$_2$: prisms.

METHYL-PYRROLIDINE *v.* METHYL-PYRROLE TETRAHYDRIDE.

METHYL-PYRROLINE *v.* METHYL-PYRROLE and its *Dihydride.*

TETRA - METHYL - PYRROYL - PYRROLE CARBOXYLIC ACID *v.* DI-METHYL-PYRROLE CARBOXYLIC ACID.

DI-METHYL-PYRRYL-BENZOIC ACID *v.* PHENYL-DI-METHYL-PYRROLE CARBOXYLIC ACID.

METHYL-PYRRYLENE-DIBENZOIC ACID *v.* DI-PHENYL-METHYL-PYRROLE DICARBOXYLIC ACID.

ν-METHYL-PYRRYLENE DI-METHYL DI-KETONE $C_4H_2NMe(CO.Me)_2$. *ν-Methyl-di-acetyl-pyrrole.* [134°]. Formed by heating ν-methyl-pyrrole with acetic anhydride for 8 hrs. at 250°. Colourless needles. V. sol. alcohol, ether chloroform, benzene, and hot water (Ciamician a. Silber, *B.* 20, 1368; *G.* 17, 134).

METHYL-PYRRYL-GLYOXYLIC ACID

$C_7H_7NO_3$ *i.e.* $NMe\left<\begin{matrix}CH{:}CH\\ C(CO.CO_2H)\end{matrix}\right>CH$. [142°]. Formed by boiling methyl-pyrryl methyl ketone with dilute alkaline $KMnO_4$ (De Varda, *B.* 21, 2871; *Rend. Accad. Linc.* [4] 4, 755, 758). Light-yellow needles (from benzene). Bromine added to its solution in glacial acetic acid forms $C_4HBr_2MeN.CO.CO_2H$ crystallising in yellow prisms [160°], oxidised by fuming HNO_3 to the methylimide of di-bromo-maleïc acid.—AgA': white pp.

METHYL PYRRYL KETONE *v.* PYRRYL METHYL KETONE.

METHYL-PYRRYL METHYL KETONE

C_7H_9NO *i.e.* $NH\left<\begin{matrix}CMe{:}CH\\ C(CO.CH_3)\end{matrix}\right>CH$. [86°]. (240°). Formed by the action of Ac_2O and NaOAc upon methyl-pyrrole from bone-oil (Ciamician a. Silber, *B.* 19, 1408; 20, 2604; *G.* 16, 352; 17, 269). Small white needles (from water); v. sol. alcohol, ether, and benzene. Not decomposed by boiling alkalis. Yields a methyl-pyrryl-glyoxylic acid on oxidation. Bromine in CS_2 gives $C_7H_7Br_2NO$ crystallising in needles [162°], which is oxidised by HNO_3 to di-bromo-maleïc imide at −18°. Ammoniacal $AgNO_3$ gives with the ketone a white pp. of $C_4H_2MeAcNAg$.

ν-METHYL - PYRRYL METHYL KETONE $CH_3.CO.C_4H_3NMe$. *Pseudo-acetyl-methyl-pyrrole.* (201°). Prepared by boiling ν-methyl-pyrrole (10 g.) with Ac_2O (70 g.) and NaOAc (12 g.) for 12 hours (Weidel a. Ciamician, *B.* 13, 76; Ciamician a. Dennstedt, *B.* 17, 2952; De Varda, *B.* 21, 2872). Colourless liquid, sl. sol. water. Not hydrolysed by boiling KOHAq. Reduces warm ammoniacal $AgNO_3$, forming a silver mirror.

Di-methyl-pyrryl methyl ketone $C_8H_{11}NO$ *i.e.* $NH\left<\begin{matrix}CMe{:}CH\\ C(CO.CH_3)\end{matrix}\right>CMe$. [123°]. Obtained by distillation of its carboxylic acid (Magnanini, *Rend. Accad. Linc.* [4] 4, 832; *B.* 21, 2867). Monoclinic crystals, $a{:}b{:}c = {\cdot}402{:}1{:}{\cdot}857$; $\beta = 78°\ 16'$. At 100° it sublimes in needles. M. sol. hot water, v. sol. alcohol, benzene, and HOAc, sl. sol. petroleum. Not affected by boiling conc. KOHAq. Yields a phenyl-hydrazide.

Di-methyl-pyrryl methyl ketone

$NH\left<\begin{matrix}CMe{:}C(CO.CH_3)\\ |\\ CMe{:}CH\end{matrix}\right.$. [85°]. A product of the action of Ac_2O on the corresponding di-methyl-pyrrole (Dennstedt a. Zimmermann, *B.* 19, 2195). Crystals. Reduces $AgNO_3$ in very dilute alcoholic solution.

DI-METHYL-PYRRYL METHYL KETONE CARBOXYLIC ACID $C_9H_{11}NO_3$ *i.e.* $NH\left<\begin{matrix}CMe{:}C(CO_2H)\\ C(CO.CH_3){:}CMe\end{matrix}\right>$. [152°–158°]. Formed by saponification of its ethyl ether, which is prepared by heating the mono-ethyl ether of di-methyl-pyrrole dicarboxylic acid (1 pt.) with Ac_2O (5 pts.) at 205° in sealed tubes (Magnanini, *Rend. Accad. Linc.* [4] 4, 830; *B.* 21, 2865). Needles (from HOAc), almost insol. water and cold alcohol, v. sl. sol. ether, $CHCl_3$, and benzene. Completely decomposed on fusion into CO_2 and di-methyl-pyrryl methyl ketone. When heated with isatin and conc. H_2SO_4 it gives a green

colour. A solution of its ammonium salt gives pps. with lead, copper, ferric, cobalt, and mercuric salts.

Ethyl ether EtA'. [143°]. Slender needles, v. sol. hot water, alcohol, and ether.

DI-METHYL-o-PYRRYL-PHENOL $C_{12}H_{13}NO$ *i.e.* [2:1] $C_6H_4(OH).N\langle{}^{CMe:CH}_{CMe:CH}\rangle$. *Oxy-phenyl-di-methyl-pyrrole.* [95°]. Formed by warming acetonyl-acetone with *o*-amido-phenol in alcoholic solution (Paal, *B.* 19, 558). White plates (from alcohol), turning red in air; sl. sol. water, v. sol. alcohol and ether. Dissolves in alkalis, and is reppd. as needles by CO_2.—NaA': crystalline.—The picrate crystallises in reddish-brown plates.

(α)-**METHYL-PYRRYL STYRYL KETONE** $C_4NH_3(CH_3).CO.CH:CH.C_6H_5$. [193°]. Formed by boiling (α)-methyl-pyrryl methyl ketone and benzoic aldehyde with dilute caustic potash (Dennstedt a. Lehne, *B.* 22, 1918). Sulphur-yellow needles (from alcohol).

(β)-**Methyl-pyrryl styryl ketone** $C_{14}H_{13}NO$ *i.e.* $C_4NH_3(CH_3).CO.CH:CH.C_6H_5$. [156°–157°]. Formed from (β)-methyl-pyrryl methyl ketone, benzoic aldehyde, and dilute caustic potash (D. a. L.). Small light-yellow plates, v. sol. alcohol.

(αβ')-**Dimethyl-pyrryl styryl ketone** $\langle{}^{CH:CMe}_{CMe:N}\rangle C.CO.CH:CH.C_6H_5$. [188°]. Formed from (αβ')-di-methyl-pyrryl methyl ketone, benzoic aldehyde, and KOHAq. Yellow shining plates (from alcohol) (Dennstedt, *B.* 22, 1921).

(αβ) (?)-**Di-methyl-pyrryl styryl ketone** $C_4NH_2(CH_3)_2.CO.CH:CH.C_6H_5$. [166°]. Formed like the preceding. Small yellow plates or needles (from boiling alcohol) (Dennstedt, *B.* 22, 1926).

METHYL-PYRUVIC ACID *v.* ETHYL-GLYOXYLIC ACID. Its nitrile is described as PROPIONYL CYANIDE.

Tri-methyl-pyruvic acid $C_6H_{10}O_3$ *i.e.* $CMe_3.CO.CO_2H$. [88°]. (185°). Formed, together with a little $CMe_3.CO_2H$, by oxidising pinacolin with warm alkaline $KMnO_4$ (Glucksmann, *M.* 10, 770). Small colourless prisms (from ether), sl. sol. cold water, v. sol. hot water, m. sol. ether. Volatile with steam. Gives a silver mirror with ammoniacal $AgNO_3$. May be reduced to $CMe_3.CH(OH).CO_2H$ and oxidised to $CMe_3.CO_2H$.

Salts.—NaA'.—CaA'_2 3aq.—AgA'.

Phenyl-hydrazide $C_{12}H_{16}N_2O_2$. [158°]. Long needles.

METHYL-QUINALDINE *v.* DI-METHYL-QUINOLINE.

METHYL-QUINALDINIUM HYDRATE *v.* *Methylo-hydrate* of (*Py.* 3)-METHYL-QUINOLINE.

METHYL-QUINAZOLINE DIHYDRIDE $C_9H_{10}N_2$ *i.e.* $C_6H_4\langle{}^{CH_2.NH}_{N\,:\,CMe}$. Formed by distilling the acetyl derivative of o-amido-benzylamine (Gabriel a. Jansen, *B.* 23, 2812). Colourless tenacious liquid, sol. water. Its solution has a bitter taste and alkaline reaction.—B'HCl: prisms, v. sol. water.—$B'_2H_2PtCl_6$.—Chromate: reddish-yellow needles.—Picrate. [200°]. Long needles.

DI-METHYL-QUINOGEN *v.* DI-METHYL DIKETONE, *Reaction* 6.

METHYL-QUININE *v.* QUININE.

METHYL-(*pseudo*)-QUINISATIN $C_{10}H_7NO_3$ *i.e.* $C_6H_4\langle{}^{CO\,.\,CO}_{NMe.CO}$ | (?). [c. 120°–122°]. Formed by oxidation of (*Py.* 1:2)-di-oxy-(*Py.* 4)-methyl-(*Py.* 3)-pseudo-oxy-quinoline $C_6H_4\langle{}^{C(OH).C(OH)}_{NMe\,.\,CO}$ | with Fe_2Cl_6. V. sol. ordinary solvents. Dissolves in alkalis with a yellow colour (Friedlander a. Müller, *B.* 20, 2015).

METHYL-QUINIZARIN *v.* DI-OXY-METHYL-ANTHRAQUINONE.

METHYL-QUINOLINIC ACID *v.* METHYL-PYRIDINE DICARBOXYLIC ACID.

(*Py.* 1)-**METHYL-QUINOLINE** $C_{10}H_9N$ *i.e.* $C_6H_4\langle{}^{CMe:CH}_{N=CH}\rangle$. *Lepidine. Cincholepidine.* Mol. w. 143. (265° i.V.) (K.); (263° i.V.) (D.). S.G. $\frac{0}{}$ 1·0995; $\frac{20}{}$ 1·0862 (K.).

Formation. — 1. Obtained, together with quinoline, by distilling cinchonine with aqueous KOH (Greville Williams, *Pr. E.* [3] 21, 377).—2. By distilling the hydrochloride of quinoline tetrahydride (*Py.* 1)-carboxylic acid (tetrahydro-cinchonic acid) with zinc-dust (Weidel, *M.* 3, 75).—3. Formic aldehyde or methylal is mixed with acetone, the mixture is saturated with HCl, and heated with a solution of aniline in conc. HCl. The bases are separated from the product by potash and fractionally distilled; the equations being: $CH_2O + CH_3.CO.CH_3 = H_2O + CH_2:CH.CO.CH_3$; and the following $CH_2:CH.CO.CH_3 + C_6H_5NH_2 = C_{10}H_9N + H_2O + H_2$ (Beyer, *J. pr.* [2] 32, 127).—4. By heating oxy-(*Py.* 1)-methyl-quinoline with zinc-dust (Knorr, *A.* 236, 94).—4. By heating cinchene with HOAc at 200° (Koenigs, *B*, 23, 2677).

Preparation.—1. The fraction 250°–260° of the distillate from cinchonine and KOHAq is converted into acid sulphate; the acid sulphate of (*Py.* 1)-methyl-quinoline being insoluble in alcohol, whilst the acid sulphate of quinoline is soluble (Hoogewerff a. Van Dorp, *R. T. C.* 2, 1). 2. Obtained in pure state by the action of KOH upon cinchonine in presence of superheated steam (Krakau, *Bl.* [2] 45, 248).

Properties. — Oil, solidifying when cooled below 0°; sl. sol. water, miscible with alcohol, ether, benzene, and ligroïn. Smells like quinoline. Turns brown in air and light. According to Oechsner de Coninck (*Bl.* [2] 38, 546), two lepidines (258°) and (268°) are obtained by distilling cinchonine or brucine, and the base of higher boiling-point alone solidifies in a freezing mixture.

Reactions.—1. *Oxidation* with $KMnO_4$ in alkaline solution gives methyl-pyridine dicarboxylic acid and, finally, pyridine tricarboxylic acid (Hoogewerff a. Van Dorp, *B.* 13, 1639). Oxidation by $K_2Cr_2O_7$ and H_2SO_4 yields quinoline (*Py.* 1)-carboxylic (cinchonic) acid.—2. By adding *sodium-amalgam* to lepidine C. Greville Williams (*C. N.* 37, 85) obtained a base which formed a red crystalline nitrate $C_{20}H_{18}N_2HNO_3$. 3. When heated with an equivalent quantity of *benzoic aldehyde* and $ZnCl_2$ it yields styryl-quinoline (Heymann a. Königs, *B.* 21, 1424).—4. When heated with isoamyl iodide it yields the amylo-iodide (which may be extracted by

repeatedly boiling the product with water) and also an insoluble residue whence boiling alkalis liberate 'lepamine' $C_{20}H_{32}N_2$ (Greville Williams, *C. J.* 16, 375). Lepamine is a fragrant oil (c. 275°), V.D. (obs. and calc. 10·4). Lepamine yields the salts $C_{20}H_{32}N_2H_2Cl_2$ (melting below 100°) and $C_{20}H_{32}N_2H_2PtCl_6$.—5. By the action of a boiling aqueous solution of caustic potash upon mixtures of the alkylo-iodides of lepidine and quinoline, blue or green substances, called cyanines are obtained (*v.* QUINOLINE).

Salts.—B'HCl: needles.—$B'_2H_2PtCl_6$ 2aq: orange-red triclinic needles. [226°–230°] (Knorr); [c. 233°] (Königs).—$B'HAuCl_4$. [188°]. Prismatic needles. Decomposed when heated for some time at 110°.—$B'HCdCl_3$.—$B'HNO_3$: slender prisms.—$B'H_2SO_4$. [229°]. S. (alcohol) ·4 at 18°; 1·1 at 78° (Krakau, *J. R.* 17, 362).—$B'_2H_2Cr_2O_7$: yellow needles (from hot water) which decompose at 110°.—B'_2AgNO_3: white needles.—Tartrate $B'C_4H_6O_6$ aq. Crystallises from alcohol.—Picrate $B'C_6H_2(NO_2)_3OH$. [208°] (H. a. D.); [213°] (Krakau). Small yellow needles (from alcoholic solutions).

Methylo-iodide B'MeI. [174°]. Yellow prisms (from alcohol) (Hoogewerff a. Van Dorp, *R. T. C.* 2, 41, 318).

Ethylo-iodide B'EtI. [143°]. Prisms.

Isoamylo-iodide $B'C_5H_{11}I$. [160°]. Yellow prisms (Hoogewerff a. Van Dorp, *R. T. C.* 3, 352).

Chloro-lepidine *v.* CHLORO-METHYL-QUINOLINE.

(*Py.* 1)-Methyl-quinoline tetrahydride $C_{10}H_{13}N$ *i.e.* $C_6H_4<\begin{matrix}CHMe.CH_2\\NH\ .\ CH_2\end{matrix}>$ (250°–253° i.V.) at 740 mm. Formed by adding sodium to a boiling alcoholic solution of oxy-(*Py.* 1)-methyl-quinoline (Knorr a. Klotz, *B.* 19, 3300). Formed also by the action of tin and HCl on lepidine. Colourless oil, with pungent odour.

(*Py.* 2)-Methyl-quinoline $C_6H_4<\begin{matrix}CH:C(CH_3)\\ | \\ N:CH\end{matrix}$. [10°–14°]. (250° at 710 mm.). Obtained by heating (*Py.* 2)-methyl-quinoline-(*Py.* 3)-carboxylic acid with soda-lime or alone at 160°. By CrO_3 and H_2SO_4 it is oxidised to quinoline-(*Py.* 2)-carboxylic acid [273°] (Doebner a. Miller, *B.* 17, 1715; 18, 1642). Formed also by saturating a mixture of propionic aldehyde and methylal with HCl and heating the product with aniline and conc. HClAq (Miller a. Kinkelin, *B.* 20, 1916). Prisms or colourless liquid.

Salts.—$B'_2H_2PtCl_6$ 2aq: orange-yellow needles.—$B'HAuCl_4$: [145°]. Prismatic yellow needles, sol. hot water, sl. sol. cold.—Picrate $B'C_6H_2(NO_2)_3OH$: [187°]; fine yellow needles.

Methylo-iodide B'MeI: [221°]; long yellow needles, sparingly sol. alcohol.

Amylo-iodide $B'C_5H_{11}I$: [215°]; yellow needles.

(*Py.* 2)-Methyl-quinoline dihydride $C_{10}H_{11}N$ *i.e.* $C_6H_4<\begin{matrix}CH:CMe\\ | \\ NH.CH_2\end{matrix}$. Is one of the products formed by the action of methyl-iodide (*In.* 2)-methyl-indole (methyl-ketole) (Fischer a. Steche, *A.* 242, 358). Oil. Forms a nitros-amine.

(*Py.* 3)-Methyl-quinoline $C_{10}H_9N$ *i.e.* $C_6H_4<\begin{matrix}CH:CH\\N:CMe\end{matrix}$. (α)-*Methyl-quinoline. Quinaldine.* (240° at 720 mm.) (D. a. M.); (246·5° i.V.) at 724 mm. (P. a. B.); (240° uncor.) (Drewson). Occurs in coal tar (Jacobsen a. Reimer, *B.* 16, 1084).

Formation.—1. By heating a mixture of aniline, nitrobenzene, and H_2SO_4 with ethylene glycol or paraldehyde (Doebner a. Miller, *B.* 14, 2812).—2. By adding a little NaOH to an aqueous solution of equivalent quantities of o-amido-benzoic aldehyde and acetone (Friedländer a. Gohring, *B.* 16, 1835).—3. By the reduction of *o*-nitro-styryl methyl ketone with $SnCl_2$ (Drewson, *B.* 16, 1953).—4. By heating a mixture of aniline, aldol, and HCl (Doebner a. Miller, *B.* 16, 2464; 17, 1699).—5. By heating a mixture of aniline, acetal, and H_2SO_4 (D. a. M.).—6. By heating a mixture of aniline, nitrobenzene, lactic acid, and H_2SO_4 (Wallach a. Wüsten, *B.* 16, 2007).—7. By heating crotonic aldehyde with aniline, nitrobenzene, and H_2SO_4 (Skraup, *B.* 15, 897).—8. By distilling its carboxylic acid with lime (Beyer, *J. pr.* [2] 33, 413; Rohde, *B.* 22, 267).—9. By heating chloro-methyl-quinoline (vol. ii. p. 82) with HI in HOAc in sealed tubes at 260° (Conrad a. Limpach, *B.* 20, 955).—10. By heating methyl-indole (methyl-ketole) with bromoform and alcoholic NaOH and reducing the resulting bromo-methyl-quinoline [78°] with P and HI at 180° (Magnanini, *B.* 20, 2610; 21, 1940; *G.* 17, 246).—11. By heating methyl-indole (methyl-ketole) with conc. HCl at 225° (Magnanini, *B.* 20, 2609).—12. By heating ethyl-acetanilide with $ZnCl_2$ at 225° (Pictet a. Bunzl, *B.* 22, 1847).

Preparation.—A mixture of aniline (2 pts.), paraldehyde (3 pts.), and conc. HClAq (4 pts.), is heated on a water-bath for a few hours (Doebner a. Miller, *B.* 16, 2464).

Properties.—Oil, smelling like quinoline, sl. sol. water. It gives with $AgNO_3$ a compound crystallising in white needles. Not affected by nitrous acid. A solution of chloride of iodine in HCl forms deep-yellow needles of a chloro-iodide [151°] (Dittmar, *B.* 18, 1612).

Reactions.—1. Scarcely attacked even after long boiling with chromic acid mixture, but completely oxidised by CrO_3 in HOAc. CrO_3 and H_2SO_4 yield quinoline (*Py.* 3)-carboxylic acid.—2. $KMnO_4$ oxidises it to acetyl-o-amido-benzoic acid (Doebner a. Miller, *B.* 15, 3075).—3. Cold conc. HNO_3 forms (*B.* 3)- and (*B.* 4)-nitro-(*Py.* 3)-methyl-quinolines. Boiling conc. HNO_3 forms nitro-quinoline carboxylic acid [220°].—4. *Tin* and HCl reduce it to a tetra-hydride.—5. On heating with *sulphur* H_2S is evolved and the product contains a base $C_{20}H_{16}N_2$aq [162°] which crystallises from alcohol in white needles (Von Miller, *B.* 21, 1828).—6. Combines at once with *formamide* forming a white mass, which crystallises from alcohol or ether in needles of $C_9H_6MeN:C(OH)NH_2$ [76°], and is decomposed by water (Cleve, *B.* 20, 76). 7. Combines with *aldehydes*, forming aldol-like products which readily split off water (Von Miller, *B.* 20, 2041). Thus *paraldehyde* when heated with quinaldine for 5 hours at 210° yields (*Py.* 3)-allyl-quinoline (249°–253°) (Eisele, *B.* 20, 2043); *isobutyric aldehyde* with $ZnCl_2$

forms $C_{14}H_{17}NO$ [93°] (Brünner, *B.* 20, 2041); *p-nitro-benzoic aldehyde* at 120° unites forming $C_9H_6N.CH_2.CH(OH).C_6H_4NO_2$ [160°] which when heated with Ac_2O loses water and becomes *p*-nitro-styryl-quinoline (Bulach, *B.* 20, 2046; *B.* 22, 285). In like manner, when quinaldine (1 mol.) is heated with furfuraldehyde (1 mol.) and a little $ZnCl_2$ for 2 hours at 100° the product is $C_9H_6N.CH:CH.C_4H_3O$ which crystallises from ligroïn in tufts of needles (Srpek, *B.* 20, 2044).—8. When heated with *phthalic anhydride* and $ZnCl_2$ at 200° it yields 'quinoline yellow' $C_9H_6N.CH:C_2O_2:C_6H_4$ which crystallises from alcohol in golden needles [235°], may be sublimed, and is insol. water, v. sl. sol. ether, m. sol. boiling alcohol, v. sol. HOAc. It dyes silk and wool yellow (Jacobsen a. Reimer, *B.* 16, 1082).

S a l t s.—The n i t r a t e and h y d r o c h l o r i d e are easily soluble.—$B'_2H_2PtCl_6$. [226°] (F. a. G.); [229°] (P. a. B.); [230°] (Beyer). Sparingly soluble orange prisms.—A u r o c h l o r i d e: yellow crystalline pp.—$B'HHgCl_3$. [165·5°]. White needles.—B'HI. [186°]. V. sol. water.—$B'H_2SO_4$. [213°]. Deliquescent prisms (Hoogewerff a. Van Dorp, *R. T. C.* 3, 344).—$B'_2H_2Cr_2O_7$: long yellowish-red needles, sol. hot, sl. sol. cold, water.—P i c r a t e $B'C_6H_2(NO_2)_3OH$. [191°]. Needles, sl. sol. water and cold alcohol.

M e t h y l o-i o d i d e B'MeI. [195°]. Lemon-yellow needles, v. sol. water, sol. alcohol, insol. ether. Yields $(B'MeCl)_2PtCl_4$ crystallising in orange tables; $(B'MeCl)AuCl_3$ crystallising from hot water in lemon-yellow needles; and $(B'Me)_2Cr_2O_7$ crystallising in orange plates, sl. sol. water, exploding at 90°.

M e t h y l o-o x i d e $(B'Me)_2O$. Formed by adding aqueous KOH to the methylo-iodide (Bernthsen a. Hess, *B.* 18, 32; Möller, *A.* 242, 302). Yellow amorphous flakes, sl. sol. water, v. sol. alcohol and ether. Easily decomposes, becoming red. HIAq converts it into B'MeI, while HCl yields B'MeCl.

E t h y l o-i o d i d e B'EtI. *Ethyl-quinaldinium iodide.* [234°]. Prepared by heating quinaldine with EtI at 100°. Yellow prisms (from alcohol), decomposed on fusion (Hoogewerff a. Van Dorp, *R. T. C.* 3, 345, 350; Spaltholz, *B.* 16, 1851). Aqueous KOH converts it into the flocculent oxide $(B'Et)_2O$ which readily changes on exposure to air to a crimson resin. The oxide yields the following salts: $B'EtAuCl_4$: golden needles.—$(B'EtCl)_2PtCl_4$: ruby-red prisms, sol. hot water.—$(B'Et)_2Cr_2O_7$. Reddish-yellow needles, exploding at 100°. On heating quinoline ethylo-iodide (2 pts.) with quinaldine ethylo-iodide (1 pt.) and aqueous KOH diethyl-isocyanine iodide is formed, which crystallises from its crimson alcoholic solution in lustrous green prisms (*v.* QUINOLINE).

P r o p y l o-i o d i d e B'PrI. [167°]. Obtained by heating its components on the water-bath (Möller, *A.* 242, 306). Small greenish-yellow prisms (from alcohol), sl. sol. cold, v. sol. hot, alcohol and water. Gives with aqueous KOH a yellow amorphous oxide $(B'Pr)_2O$, sol. alcohol and ether. It yields the salts—$(B'PrCl)_2PtCl_4$ crystallising in orange plates, $B'PrAuCl_4$ crystallising in canary-yellow needles, v. sl. sol. cold water, and $(B'Pr)_2Cr_2O_7$ crystallising in brownish-red prisms.

I s o b u t y l o-i o d i d e $B'C_4H_9I$. [172°]. Obtained by cohobating its components at 115° (M.). Straw-yellow plates, sol. hot alcohol. Yields an unstable oxide which on heating changes to a violet colouring matter.

I s o a m y l o-i o d i d e $B'C_5H_{11}I$. [175°]. Formed by cohobating its components for 12 hours at 145°. Small yellow prisms, v. sol. water and hot alcohol. Converted by aqueous KOH into an oxide which condenses to a crimson dye on heating.

(*Py.* 3)-**Methyl-quinoline tetrahydride**

$$C_6H_4\begin{cases}CH_2.CH_2\\ \quad\quad | \\ NH.CHMe\end{cases}. \quad \textit{Tetra-hydro-quinaldine.}$$

(248° at 710 mm.). Formed by reducing $CH_3.CO.CH_2.CH_2.C_6H_4NO_2$ [1:2] (Jackson, *B.* 14, 890). It is also a product of the action of HCl on a mixture of aldehyde and aniline (Doebner a. Miller, *B.* 17, 1698). Prepared by reducing quinaldine with tin and HCl (Doebner a. Miller, *B.* 16, 2467). Colourless liquid with pleasant smell, sl. sol. water, v. sol. alcohol, ether, and benzene. $FeCl_3$ gives a blood-red colour to aqueous solutions of its salts; CrO_3 acts in like manner. Nitrous acid produces an oily nitrosamine and a crystalline nitro-nitrosamine [152°] (Möller, *A.* 242, 314). Heated with benzotrichloride it gives a green dye-stuff.—$B'_2H_2PtCl_6$: yellow needles.

ν-**Methyl-quinoline dihydride** $C_{10}H_{11}N$ *i.e.* $C_6H_4\begin{cases}CH:CH\\ NMe.CH_2\end{cases}$. This base is probably formed by heating *ν*-methyl-indole with MeI (Fischer a. Steche, *B.* 20, 2201).

ν-**Methyl-quinoline tetrahydride** $C_{10}H_{13}N$ *i.e.* $C_6H_4\begin{cases}CH_2.CH_2\\ NMe.CH_2\end{cases}$. *Kairoline.* (243° at 720 mm.). Prepared by heating quinoline tetrahydride with MeI (Hoffmann a. Königs, *B.* 16, 731), or by reduction of quinoline methylo-iodide with tin and HCl, the yield by the latter process being 50 p.c. of the theoretical (Feer a. Königs, *B.* 18, 2388). Oil. Resembles quinine in physiological action, and has been used as a febrifuge. Nitrous acid gives a yellowish-red colouration in dilute solutions. Gives a green dye-stuff on heating with benzo-trichloride.

S a l t s.—B'HCl aq. [244°]. Prepared by heating quinoline tetrahydride with MeOH and conc. HClAq at 160° (Ostermayer, *B.* 18, 595). Crystallises from alcohol or chloroform in tetrahedra; v. sol. alcohol, sl. sol. ether.—B'HClICl. [86°]. Large yellow needles.—$B'H_2PtCl_6$. [177°]. Red crystalline pp.—P i c r a t e. [125°]. Long yellow needles.

N i t r o s o- d e r i v a t i v e $C_{10}H_{12}(NO)N$. Green plates; v. sol. alcohol, ether, and benzene, sl. sol. ligroïn. Does not give Liebermann's reaction. Not affected by boiling NaOHAq.

M e t h y l o-h y d r o x i d e ×B'MeOH. Strong alkaline base; sol. water.

E t h y l o-i o d i d e $C_9H_{10}NMeEtI$. [179°]. Formed from ethyl-quinoline tetrahydride and MeI (Claus a. Stegelitz, *B.* 17, 1331). Crystals. Not affected by KOHAq. With Ag_2O it gives a crystalline base. V. sol. water, insol. ether.—$(C_9H_{10}MeEtCl)_2PtCl_4$.

References.—AMIDO-METHYL-HYDRO-QUINOLINE, NITRO-METHYL-QUINOLINE TETRAHYDRIDE, and OXY-METHYL-QUINOLINE TETRAHYDRIDE.

(B. 1)-Methyl-quinoline $C_{10}H_9N$ *i.e.*
CH:CMe.C.CH:CH
CH:CH . C.N :CH . (251°). This is probably the constitution of the base which is formed, together with (*B.* 3)-methyl-quinoline, by heating *m*-toluidine, o-nitro-phenol, glycerin, and H_2SO_4 together (Skraup a. Brunner, *M.* 7, 139). Its acid sulphate is more soluble in alcohol than that of the (*B.* 3)-isomeride. The platinochloride melts at 224°, the picrate at 198°. The picrate is much less soluble than that of the accompanying isomeride. The chromate is v. sol. water.

Derivative.—*v.* CHLORO-(*B.* 1)-METHYL-QUINOLINE, which may, however, perhaps be CHLORO-(*B.* 3)-METHYL-QUINOLINE.

(B. 2) - Methyl - quinoline $C_{10}H_9N$ *i.e.*
CMe:CH. C.CH:CH
CH :CH. C.N :CH . *p-Toluquinoline.* (258°) at 745 mm. S.G. $\frac{0}{}$ 1·0815; $\frac{20}{}$ 1·0681. Formed by heating a mixture of *p*-toluidine, *p*-nitro-toluene, glycerin, and H_2SO_4 (Skraup, *M.* 2, 158). Liquid, smelling like quinoline. Yields pyridine di-carboxylic (quinolinic) acid on oxidation with $KMnO_4$. HOCl forms chloro-oxy-methyl-quinoline $C_6H_3Me\langle{}^{CH:CH}_{NCl.CO}$.

Salts.—$B'HCl\frac{1}{2}aq$: slender needles; v. sol. water and alcohol.—$B'_2H_2PtCl_6$ 2aq: slender yellow prisms.—B'HI. [186°] (Möller, *A.* 242, 307).—$B'H_2SO_4$ aq. Prisms; v. e. sol. water.—Picrate $B'C_6H_2(NO_2)_3OH$. [229°]. Yellow powder.

Chloro-iodide $C_{10}H_9NICl$. [c. 170°]; easily soluble in alcohol. The hydrochloride $C_{10}H_9NICl,HCl$ is formed by adding a solution of chloride of iodine in HCl to a solution of (*B.* 2)-methyl-quinoline. It forms easily soluble reddish-yellow needles, [c. 112°], blackened by NH_3 (Dittmar, *B.* 18, 1612).

Methylo-iodide B'MeI. Slender yellowish prisms. When heated with (*Py.* 1)-methyl-quinoline methylo-iodide, and aqueous KOH it forms 'di-methyl-methylo-cyanine' $C_{22}H_{21}N_2I$ 2aq, which crystallises from alcohol in violet-blue needles; sl. sol. water, melting (when anhydrous) at 275°–277° (Hoogewerff a. Van Dorp, *R. T. C.* 3, 342).

Derivatives.—*V.* TRI-CHLORO-(*B.* 2)-METHYL-QUINOLINE, CHLORO-OXY-(*B.* 2)-METHYL-QUINOLINE, DI-CHLORO-DI-NITRO-OXY-(*B.* 2)-METHYL-QUINOLINE, and OXY-(*B.* 2)-METHYL-QUINOLINE.

(B. 3) - Methyl - quinoline $C_{10}H_9N$ *i.e.*
CH :CH.C.CH:CH
CMe:CH.C.N :CH . *m-Toluquinoline.* (250° uncor.); 259·7° cor. at 747 mm.). S.G. $\frac{0}{0}$ 1·0839; $\frac{20}{20}$ 1·0722. Formed, together with smaller quantities of an isomeride, probably (*B.* 1)-methyl-quinoline, by heating a mixture of *m*-toluidine, *m*-nitro-toluene, glycerin, and H_2SO_4 (Skraup, *M.* 3, 381; *B.* 15, 893), or of *m*-toluidine, o-nitro-phenol, glycerin, and H_2SO_4 (Skraup a. Brunner, *M.* 7, 139). The two bases may be separated by crystallising their acid sulphates from alcohol, in which the sulphate of the base here described is the less soluble. Yellowish, highly refractive liquid; not solid at –20°. Yields on oxidation quinoline (*B.* 3)-carboxylic acid [247°].

Salts.—Hydrochloride: large transparent prisms.—$B'H_2PtCl_6$ 2aq. [224°]. Orange prisms.—$B'H_2SO_4$.—$B'_2(H_2SO_4)_3xaq$.—Chromate: [89°]; v. sl. sol. water.—Picrate: [237°].

Methylo-iodide $B'MeI\frac{1}{2}aq$: golden needles.

(B. 4) - Methyl - quinoline $C_{10}H_9N$ *i.e.*
CH:CH .C.CH:CH
CH:CMe.C.N :CH . *o-Toluquinoline.* (248° cor.) at 751 mm. S.G. $\frac{0}{0}$ 1·085; $\frac{20}{20}$ 1·073. Formed by heating o-toluidine with glycerin, o-nitro-toluene, and H_2SO_4 (Skraup, *M.* 2, 153). Strongly refractive liquid, smelling like quinoline; not solidified in a mixture of solid CO_2 and ether; v. sl. sol. water, sol. alcohol and ether. Oxidised by $KMnO_4$ to pyridine dicarboxylic (quinolinic) acid.

Salts.—$B'HCl2\frac{1}{2}aq$: very soluble transparent prisms.—$B'_2H_2PtCl_6$ 2aq: orange prisms.—$B'H_2SO_4$: prisms; sl. sol. cold, v. sol. hot, water.—$B'C_6H_2(NO_2)_3OH$. [200°]. Pale-yellow leaflets.

Methylo-iodide B'MeI. Crystalline powder.

(B. 4) - Methyl - quinoline tetrahydride $C_{10}H_{13}N$. Oil. Obtained by reducing (*B.* 4)-methyl-quinoline (Ziegler, *B.* 21, 866).

Nitrosamine $C_9H_9MeN.NO$. Formed by treating (*B.* 4)-methyl-quinoline tetrahydride with $NaNO_2$ and HOAc (Ziegler). Oil. Slowly converted by alcoholic HCl into an isomeric nitroso-derivative, which crystallises from benzene in lustrous steel-blue crystals [140°], and may be reduced to an amido-(*B.* 4)-methyl-quinoline tetrahydride, giving a hydrochloride melting at 166°.

(B. 2, 4)-Di-methyl-quinoline $C_{11}H_{11}N$ *i.e.*
CMe:CH
| >C_5H_3N. (268° cor.). S.G. $\frac{}{4}$ 1·0665.
CH:CMe
Formed by heating (1, 3, 4)-*m*-xylidine with glycerin, nitrobenzene, and H_2SO_4 (Behrend, *B.* 17, 2716). Colourless oil. Yields a sulphonic acid melting at 166°.—$B'_2H_2PtCl_6$: yellow needles.—$B'H_2SO_4$: minute needles. Its bichromate forms long yellow needles.

(B. 1, 2) or (B. 2, 3)-Di-methyl-quinoline
CMe:CMe   CMe:CH
| >C_5H_3N or | >C_5H_3N. (274°).
CH:CH   CMe:CH
Obtained by heating a mixture of o-xylidine $C_6H_3Me_2(NH_2)$ [1:2:4], nitrobenzene, glycerin, and H_2SO_4 (Berend, *B.* 17, 1489).—$B'_2H_2PtCl_6$ aq: minute yellow needles.—$B'H_2SO_4$ $x$aq: glistening prisms.—$B'H_2Cr_2O_7$: slightly soluble orange prisms.

(B. 1, 4)-Di-methyl-quinoline $C_{11}H_{11}N$ *i.e.*
CH:CMe
| >C_5H_3N. [5°]. (265°) at 736 mm. S.G.
CH:CMe
$\frac{}{4}$ 1·0752 (B.); $\frac{21}{}$ 1·070. Formed by warming the sulphate of *p*-xylidine $C_6H_3Me_2(NH_2)$ [1:4:2] with nitrobenzene and glycerin (Berend, *B.* 18, 3165; Lellmann a. Alt, *A.* 237, 308). Oxidised by dilute HNO_3 at 170° to (*B.* 4)-methyl-quinoline (*B.* 1)-carboxylic acid.—$B'_2H_2PtCl_6$: yellow needles.—$B'_2H_2Cr_2O_7$. [149°]. Orange needles.

Tetra-hydride $C_{11}H_{15}N$. (271°). Formed by reduction with zinc and HCl (Berend, *B.* 18, 3165). Pleasant-smelling liquid.—B'HCl: slender needles (from alcohol) or six-sided plates (from water).

(B. 4, Py. 3)-Di-methyl-quinoline $C_{11}H_{11}N$ *i.e.*
CH:CH .C.CH:CH
| ‖ | . *o-Methyl-quinaldine.*
CH:CMe.C. N :CMe

(252°). Formed by heating a mixture of o-toluidine, paraldehyde, and HClAq at 100° (Doebner a. Miller, *B.* 16, 2469). Formed also by heating its carboxylic acid with KOH (Panajotoff, *B.* 20, 40). Colourless liquid, v. sol. alcohol and ether, sl. sol. water. Volatile with steam.—*Platinochlorides* $B'_2H_2PtCl_6$ 2aq: dark-yellow needles. —$B'_2H_2Cr_2O_7$: orange-yellow needles, sol. hot, sl. sol. cold, water. On oxidation with chromic acid it yields an acid $C_{11}H_9NO_2$ identical with that obtained from *o*-amido-benzoic acid and aldehyde (Von Miller a. R. Meyer, *B.* 23, 2260).

Methylo-iodide B′MeI. [221°]. Prepared by heating the base with MeI at 100° (Möller, *A.* 242, 309). Lemon-yellow needles (from indole). Alkalis liberate an unstable base, which on heating yields the original *o*-methyl-quinaldine. It also yields the salts: $(B'MeCl)_2PtCl_4$ crystallising in yellow needles, v. sl. sol. cold water, $B'MeAuCl_4$, and $(B'Me)_2Cr_2O_7$ crystallising from water in orange plates.

Ethylo-iodide B′EtI. [229°]. From the base and EtI at 140° (Möller). Lemon-yellow needles (from alcohol). Yields the salts: $(B'Et)_2PtCl_6$, crystallising in orange-yellow needles, and $B'EtAuCl_4$ crystallising in lemon-yellow plates, m. sol. hot water.

Tetrahydride $C_6H_3Me\langle{}^{CH_2.CH_2}_{NH.CHMe}$ (with | between CH_2 and CHMe).

Tetrahydro-methyl-quinaldine. (261°). Formed by reducing (*B.* 4, *Py.* 3)-di-methyl-quinoline (Doebner a. Miller, *B.* 16, 2469). Colourless liquid. Gives a red colouration with $FeCl_3$.— $B'_2H_2PtCl_6$: concentric red needles.

(*B.* 3, *Py.* 3)-**Di-methyl-quinoline** $C_{11}H_{11}N$ *i.e.*
CH :CH.C.CH:CH
| || | . *m-Methyl-quinaldine.*
CMe:CH.C. N :CMe
[61°]. (264°). Formed by heating a mixture of *m*-toluidine, paraldehyde, and HCl (Doebner a. Miller, *B.* 16, 2471). Long colourless needles, v. sol. alcohol, ether, and benzene, sl. sol. water. Oxidised by chromic acid to methyl-quinoline *m*-carboxylic acid [284°] (Miller a. Rist, *B.* 23, 2263, 3483).—$B'_2H_2Cr_2O_7$: thick orange needles, nearly insol. cold water.—$B'_2H_2PtCl_6$: small yellow needles.

(*B.* 2, *Py.* 3)-**Di-methyl-quinoline**
CMe:CH.C.CH:CH
| || | . *p-Methyl-quinaldine.* [60°]
CH :CH.C. N :CMe
(D. a. M.); [55°] (Jacobsen a. Reimer, *B.* 16, 2603). (266°) (D. a. M.); (260°) (J. a. R.). Formed by heating a mixture of *p*-toluidine, paraldehyde, and HCl (Doebner a. Miller, *B.* 16, 2470). Large colourless trimetric prisms, smelling like anise-seed. V. sol. alcohol, ether, and benzene, sl. sol. hot water. Oxidised by chromic acid to methyl-quinoline *p*-carboxylic acid [256°] (Miller a. Schunck, *B.* 23, 2263). Heated with phthalic anhydride and $ZnCl_2$ at 200° it yields methyl-quinophthalone or methyl-quinoline yellow $C_{11}H_9N{:}C_2O_2{:}C_6H_4$ [203°] which crystallises from alcohol in golden needles (J. a. R.).— $B'_2H_2PtCl_6$: nearly colourless slender needles, sl. sol. hot water. — $B'_2H_2Cr_2O_7$: long yellow needles, m. sol. hot water. — The hydrochloride, nitrate, sulphate, and acetate, are easily soluble crystalline salts.

Methylo-iodide B′MeI. [237°]. Formed from the base and MeI in the cold (Möller, *A.* 242, 311). Lemon-yellow needles, sl. sol. cold alcohol, insol. ether, v. sol. water. Yields the salts $(B'Me)_2PtCl_6$, $B'MeAuCl_4$, and $(B'Me)_2Cr_2O_7$, all three crystallising in needles.

Tetrahydride $C_6H_3Me\langle{}^{CH_2.CH_2}_{NH.CHMe}$. (267°). Formed by reducing the base with tin and HCl (Doebner a. Miller, *B.* 16, 2471). Liquid, sl. sol. water, v. sol. alcohol and ether. Its aqueous solution is coloured blood-red by $FeCl_3$.

(*B.* 4, *Py.* 1)-**Di-methyl-quinoline**
CH: CH.C.CMe:CH
| || | . (274° i. V.). Formed by
CH:CMe.C. N :CH
distilling oxy-(*B.* 4, *Py.* 1)-di-methyl-quinoline with zinc-dust (Knorr, *A.* 245, 369). Light yellow oil with pungent taste and smell, v. sol. alcohol and ether, almost insol. water. — $B'_2H_2PtCl_6$ aq. [220°].—$B'HAuCl_4$. [181°].

(*B.* 3, *Py.* 1)-**Di-methyl-quinoline**
CH:CH .C.CMe:CH
CMe:CH.C .N :CH . (c. 283° i. V.). Formed
by distilling (*Py.* 3)-oxy-(*B.* 3, *Py.* 1)-di-methyl-quinoline with zinc-dust (Knorr, *A.* 245, 371). Oil, volatile with steam.—$B'_2H_2PtCl_6$ 2aq. [227°]. Reddish-brown prisms.

(*B.* 2, *Py.* 1)-**Di-methyl-quinoline**
CMe:CH.C.CMe:CH
CH :CH.C . N . CH . (γ)-*Methyl-p-toluquinoline.*
(280° i. V.). Formed by distilling (*Py.* 3)-oxy-(*B.* 2; *Py.* 1)-di-methyl-quinoline with zinc-dust (Knorr, *A.* 245, 366). Pungent oil, v. sol. alcohol and ether. Oxidised by chromic acid to a methyl-quinoline carboxylic acid (Von Miller a. Daniel, *B.* 23, 2264).—$B'_2H_2PtCl_6$ 2aq: needles, decomposing at 231°.—$B'HAuCl_4$: needles, decomposing near 192°.—$B'_2H_2Cr_2O_7$: needles, decomposing near 150°. — $B'C_6H_2(NO_2)_3OH$: needles, decomposing near 230°.

(*Py.* 2, 3)-**Di-methyl-quinoline**
$C_6H_4\langle{}^{CH:CMe}_{N\ :CMe}$. [66°]. (261° uncor.) at 729 mm.
Formed by adding tiglic aldehyde (1 mol.) to a mixture of aniline hydrochloride (4 mols.) and HCl heated to 85° (Rohde, *B.* 20, 1912; 22, 268). Formed also in small quantity by heating a mixture of acetic and propionic aldehydes with aniline and HClAq at 100°. Tables or plates; v. sl. sol. water, v. sol. ether, v. e. sol. alcohol. Chromic acid mixture oxidises it to (*Py.* 3)-methyl-quinoline (*Py.* 2)-carboxylic acid. On condensation with benzil, by heating at 100° for 24 hours, it yields a base [176°], of which the solutions of the salts exhibit green fluorescence. This base changes on heating for some time at 180° to a polymeride [240°].

Salts.—B′HCl 2aq: radiating needles, v. e. sol. water and alcohol.—$B'_2H_2PtCl_6$ 2aq: orange needles, turning black at 230°.—$B'HNO_3$: prisms, v. e. sol. water and alcohol.—$B'H_2SO_4$ aq. [235°]: slender radiating needles, v. e. sol. water, m. sol. alcohol.—$B'_2H_2Cr_2O_7$: long orange needles, m. sol. hot water; turns brown at 150°. Picrate: [225°].

Methylo-iodide B′MeI ½aq. [218°]. Sickle-like groups of needles (from alcohol); m. sol. water and alcohol.

(*Py.* 1, 2)-**Di-methyl-quinoline**
$C_6H_4\langle{}^{CMe:CMe}_{N\ :CH}$. [65°]. (290° i.V.) at 737 mm.

Formed by distilling (*Py.* 3, 2, 1)-oxy-di-methyl-quinoline with zinc-dust (Knorr, *A.* 245, 362). On oxidation by chromic acid mixture it yields (*Py.* 2)-methyl quinoline (*Py.* 1)-carboxylic acid (Seitz, *B.* 23, 2257).—$B'_2H_2PtCl_6$ 2aq. [240°].—$B'HAuCl_4$. [177°]. Plates.—$B'_2H_2Cr_2O_7$: red needles.—Picrate $B'C_6H_2(NO_2)_3OH$. [c. 205°]. Yellow needles.

Methylo-iodide B'MeI. [191°]. Light-yellow needles (from alcohol).

(*Py.* 1, 3)-**Di-methyl-quinoline** $C_6H_4<\begin{smallmatrix}CMe:CH\\N\;:CMe\end{smallmatrix}$. (264° uncor.). S.G. $\frac{15}{}$ 1·061.

Formation.—1. By saturating a mixture of paraldehyde (120 g.) and acetone (200 g.) with gaseous HCl, allowing the mixture to stand for a day or two and then pouring it slowly into a solution of aniline (200 g.) in conc. HClAq (400 g.). In this reaction the ketone $CH_3.CH:CH.CO.CH_3$ is doubtless first formed (C. Beyer, *J. pr.* [2] 32, 125; 33, 401).—2. Together with methane, by heating acetone with aniline hydrochloride at 180; the yield being 3 p.c. of the theoretical (Riehm, *A.* 238, 3; *B.* 18, 3296).—3. Together with the bases $C_6H_5N:CMe_2$ (228°), V.D. 66·4 (calc. 66·5), and $C_{12}H_{15}N$ (?) (275°), by heating aniline with acetone and a dehydrating agent such as $ZnCl_2$ or P_2O_5.—4. By heating aniline with mesityl oxide at 130° (Engler a. Riehm, *B.* 18, 2245).—5. By heating acetanilide with acetone; the yield being 8 p.c. of the theoretical.—6. From acetone and benzanilide.—7. By the action of NaOHAq on a mixture of *o*-amido-acetophenone and acetone (O. Fischer, *B.* 19, 1037).—8. By dissolving the anilide of methylene di-methyl diketone (acetyl-acetone) in conc. H_2SO_4, warming, diluting with cold water, and neutralising with NH_3 (Combes, *C. R.* 106, 142).

Properties.—Oil, with sweetish smell, somewhat like quinoline; volatile with steam. Not affected by nitrous acid.

Reactions.—1. CrO_3 oxidises it to (*Py.* 3)-methyl-quinoline (*Py.* 1)-carboxylic acid.—2. By heating with phthalic anhydride and a little $ZnCl_2$ at 200° it is converted into a 'phthalone' $C_{11}H_9N:C_2O_2:C_6H_4$, which crystallises from alcohol in orange needles [238°] (Beyer, *J. pr.* [2] 33, 407).

Salts.—B'HCl: slender, stellate flat needles (by sublimation), v. sol. water and alcohol.—$B'_2H_2PtCl_6$. [229°].—$B'_2H_2PtCl_6$ 2aq.—$B'_2H_2ZnCl_4$ 1½aq.—$B'H_2SO_4$. [225°–228°]. Concentric needles, v. sol. water, sl. sol. alcohol.—$B'_2H_2Cr_2O_7$. [172°]. Orange needles, v. sol. hot, v. sl. sol. cold, water.—$B'C_6H_2(NO_2)_3OH$. [190°]. Needles (from acetone).

Methylo-iodide B'MeI. [226°].

Ethylo-iodide B'EtI. [214°]. Needles (from alcohol).

Di-methyl-quinoline $C_6H_4(C_3HMe_2N)$. [65°]. (267°) at 713 mm. Occurs among the products of the action of aniline on a mixture of isobutyric aldehyde, methylal, and HCl (Von Miller a. Kinkelin, *B.* 20, 1937). Monoclinic prisms.—$B'_2H_2PtCl_6$ 2aq. [268°]. Groups of needles (from HClAq).—$B'C_6H_2(NO_2)_3OH$. [220°]. Aggregates of tables (from hot alcohol).

(*Py.* 1, 4)-**Di-methyl-quinoline tetrahydride** $C_6H_4<\begin{smallmatrix}CHMe.CH_2\\NMe\;.CH_2\end{smallmatrix}$. (255° i.V.). Formed by adding Na to a boiling alcoholic solution of oxy-(*Py.* 1, 4)-di-methyl-quinoline (methyl-lepidone) (Knorr a. Klotz, *B.* 19, 3302). Colourless liquid.

(*Py.* 3, 4)-**Di-methyl-quinoline tetrahydride** $C_6H_4<\begin{smallmatrix}CH_2\;.CH_2\\NMe.CHMe\end{smallmatrix}$. (248°) at 710 mm. Formed by heating (*Py.* 3)-methyl-quinoline tetrahydride with MeI (Doebner a. Miller, *B.* 16, 2468). Formed also by reducing the methylo-iodide of (*Py.* 3)-methyl-quinoline with tin and HCl (Feer a. Königs, *B.* 18, 2388). Colourless liquid. On heating with benzotrichloride it gives a green dye-stuff.—$B'_2H_2PtCl_6$: sparingly soluble red granular pp.

Methylo-iodide B'MeI. [205°]. Colourless needles, v. e. sol. water and hot alcohol, insol. ether (Möller, *A.* 242, 318). Not acted on by alkalis, but converted by moist Ag_2O into the ammonium base, which is split up by distillation into MeOH and (*Py.* 3, 4)-di-methyl-quinoline. Yields the salts $(B'Me)_2PtCl_6$ crystallising from water in small brick-red crystals, $B'MeAuCl_4$ crystallising in lemon-yellow needles, and $(B'Me)_2Cr_2O_7$ crystallising in small hexagonal plates.

Di-methyl-quinoline $C_{11}H_{11}N$. (245°). Occurs in commercial quinaldine (Einhorn, *B.* 18, 3144).—$B'_2H_2PtCl_6$. [238°].

(*Py.* 1, 2, 4)-**Tri-methyl-quinoline dihydride** $C_{12}H_{15}N$ *i.e.* $C_6H_4<\begin{smallmatrix}CMe:CMe\\NMe.CH_2\end{smallmatrix}$. (244° i.V.) at 746 mm. Formed by heating methyl-indole (methyl-ketole) $C_6H_4<\begin{smallmatrix}CH\\NH\end{smallmatrix}>CMe$ with MeI and a little MeOH for 20 hours at 100° (Fischer a. Steche, *B.* 20, 818; *A.* 242, 353). Formed by heating (*In.* 1,2)-di-methyl-indole with MeOH and MeI in sealed tubes at 100° (Fischer a. Steche, *A.* 242, 364; Wolff, *B.* 21, 125). Formed also by heating indole with MeI, MeOH, and Na_2CO_3 at 130° (Ciamician a. Zatti, *B.* 22, 1980; Zatti a. Ferratini, *B.* 23, 2302; Fischer a. Meyer, *B.* 23, 2631). Formed likewise by heating scatole (1 pt.) with MeI (2½ pts.) and MeOH (1 pt.) for 12 hours at 130° (F. a. M.). Oil, turning red in air, miscible with alcohol, ether, benzene, and chloroform. Nitrous acid gives a reddish-brown oil, becoming crystalline. $FeCl_3$ added to its solution in HClAq ppts. golden-yellow plates or needles of a compound v. sol. hot water, v. sl. sol. conc. HClAq.

Salts.—The hydrochloride is v. sol. water.—Platinochloride [c. 212°].—$B'H_2SO_4$: plates.—B'HI. [253°]. Prisms (from alcohol).—$B'C_6H_2(NO_2)_3OH$. [148°]. Golden-yellow needles (from alcohol).

(*Py.* 1,2,4)-**Tri-methyl-quinoline tetrahydride** $C_6H_4<\begin{smallmatrix}CHMe.CHMe\\NMe.\;\;CH_2\end{smallmatrix}$ (?) (239° i.V.) at 749 mm. Formed by reducing the dihydride with zinc and HClAq (Fischer a. Steche, *A.* 242, 356). Colourless liquid, sl. sol. water, v. sol. ether, alcohol, and benzene. $FeCl_3$ gives a brown amorphous pp. in its solution in HClAq.—Picrate: [162°] (F. a. S.); [164°] (Ciamician a. Zatti, *B.* 22, 1981); yellow plates (from alcohol).—Platinochloride: bright-red crystals.

Methylo-iodide B'MeI. [251°]. Plates or needles (from alcohol), m. sol. water.

(*Py.* 1, 3, 4)-**Tri-methyl-quinoline tetrahydride** $C_6H_4<\begin{smallmatrix}CHMe.CH_2\\NMe.CHMe\end{smallmatrix}$. Hydro-iodide

B'HI. [215°]. Formed from (*Py.* 1, 3)-di-methyl-quinoline by reducing in alcoholic solution with Na and heating the product with MeI and MeOH at 100° (Fischer a. Meyer, *B.* 23, 2631).

(*Py.* **1, 2, 4)-Tri-methyl-quinoline tetrahydride** $C_6H_4<\begin{matrix}CHMe.CHMe\\NMe.CH_2\end{matrix}$. Hydro-iodide B'HI. [205°]. Formed like the preceding from (*Py.* 1, 2)-di-methyl-quinoline (F. a. M.). Crystalline.

(*B.* **1, 2, 4)-Tri-methyl-quinoline** $C_{12}H_{13}N$ *i.e.* $\begin{matrix}CMe:CMe\\CH\ :CMe\end{matrix}>C_5H_3N$. [43°]. (286° uncor.). Formed by heating ψ-cumidine [63°] with glycerin, nitrobenzene, and H_2SO_4 (Berend, *B.* 18, 376). White prisms. — $B'HNO_3$: sparingly soluble needles. — $B'H_2SO_4$: white prisms.— $B'_2H_2PtCl_6$ 2aq: very sparingly soluble orange-red needles.

(*B.* **2, 4 ;** *Py.* **3)-Tri-methyl-quinoline** $C_{12}H_{13}N$ *i.e.* $\begin{matrix}CMe:CH\ .C.CH:CH\\CH\ :CMe.C.\ N\ :CMe\end{matrix}$. *op-Di-methyl-quinaldine.* [46°]. (260°) at 719 mm. Formed by heating *m*-xylidine with paraldehyde and conc. HClAq on the water-bath (Panajotoff, *B.* 20, 32). Small plates (from alcohol) or monoclinic prisms (from petroleum-ether); insol. water, v. e. sol. alcohol. Readily volatile with steam. Yields on oxidation (*B.* 4, *Py.* 3)-di-methyl-quinoline (*B.* 2)-carboxylic acid. Forms, with chloral, a compound $C_{14}H_{12}Cl_3N$aq, melting at 108°, and crystallising in yellowish needles, v. sol. alcohol.

Salts.—B'HCl: white needles.— $B'_2H_2PtCl_6$ 2aq: orange-yellow needles, sl. sol. water.—$B'H_2SO_4$ aq: white needles, v. sol. water and alcohol, sl. sol. ether.—$B'HNO_3$: transparent triclinic prisms.—$B'_2H_2Cr_2O_7$: orange-yellow needles.—$B'C_6H_2(NO_2)_3OH$. [185°]. Yellow needles.

Methylo-iodide B'MeI aq. Yellow needles; v. sol. water.

Tetrahydride $C_6H_2Me_2<\begin{matrix}CH_2.CH_2\\NH.CHMe\end{matrix}$. (200°–250°). Formed by reducing the base with tin and HCl (P.).—$B'_2H_2PtCl_6$: orange plates.

(*B.* **1 or 3, 2 ;** *Py.* **3)-Tri-methyl-quinoline** $\begin{matrix}CMe:CMe.C.CH:CH\\CH\ :CH\ .C.\ N\ :CMe\end{matrix}$ or $\begin{matrix}CMe:CH.C.CH:CH\\CMe:CH.C.\ N\ :CMe\end{matrix}$. Formed from *o*-xylidine, aldehyde, and HCl (Merz, *B.* 17, 1158). Monoclinic crystals.— $B'_2H_2PtCl_6$: minute needles.

(*B.* **2 ;** *Py.* **1, 3)-Tri-methyl-quinoline** $\begin{matrix}CMe:CH.C.CMe:CH\\CH\ :CH.C.\ N\ :CMe\end{matrix}$. [64°] (P.); [40°] (C.); (278°) (P.); (281°) (C.). Formed by saturating a mixture of acetone (40 g.) and paraldehyde (30 g.) with HCl at 0°, allowing to stand 12 hours in a freezing mixture, pouring into a solution of *p*-toluidine (65 g.) in fuming HClAq (130 g.) and heating on the water-bath for 7 hours (Pfitzinger, *J. pr.* [2] 38, 41). Formed also by dissolving the *p*-toluide of methylene di-methyl diketone $CH_3.CO.CH_2.C(NC_6H_4Me).CH_3$ in conc. H_2SO_4, warming, diluting, and neutralising with NH_3 (Combes, *C. R.* 106, 145). White needles, containing water of crystallisation which is given off in a desiccator, the anhydrous base crystallising in tables and absorbing water (1 mol.) from the air. Sl. sol. water, v. sol. alcohol, ether, and petroleum-ether. Volatile with steam. It has a bitter, acrid taste, and an irritating vapour.

Salts.—B'HCl 2aq: white needles, v. e. sol. hot water and alcohol. [260°].—$B'_2H_2PtCl_6$ 2aq: yellow needles, v. sl. sol. water, almost insol. alcohol. [220°] (C.).—$B'H_2SO_4$. [222°]. White needles or rhombohedra (containing aq), m. sol. cold alcohol.—$B'_2H_2Cr_2O_7$. Yellowish-red needles, v. sl. sol. cold water.—$B'C_6H_2(NO_2)_3OH$. [201°]. Greenish-yellow needles (from hot acetone).

Methylo-iodide B'MeI. [226°]. Needles (containing aq), sol. water, alcohol, and ether.

(*B.* **2 ;** *Py.* **2, 3)-Tri-methyl-quinoline** $\begin{matrix}CMe:CH.C.CH:CMe\\CH\ :CH.C.\ N\ :CMe\end{matrix}$. [87°]. (285°). Formed from tiglic aldehyde (1 mol.), *p*-toluidine (4 mols.) and HCl (8 mols.) (Von Miller a. Ohler, *B.* 23, 2268). White nodules (from ligroïn); insol. water, m. sol. ligroïn, v. sol. ether. Yields on oxidation (*Py.* 2, 3)-di-methyl-quinoline (*B.* 2)-carboxylic acid [270°].

Salts. — $B'_2H_2PtCl_6$ 2aq: laminæ. — The chromate crystallises in orange laminæ, v. sl. sol. water.—The hydrochloride and sulphate are v. e. sol. water.—Picrate. [212°]. Straw-coloured laminæ.

(*B.* **4 ;** *Py.* **1, 3)-Tri-methyl-quinoline** $\begin{matrix}CH:CH\ .C.CMe:CH\\CH:CMe.C.\ N\ :CMe\end{matrix}$. (280°). Formed by the action of H_2SO_4 on the *o*-toluide of methylene dimethyl diketone $CH_3.CO.CH_2.C(NC_7H_7).CH_3$ (Combes, *C. R.* 106, 145). Oil.—Platinochloride [257°].

(*B.* **4 ;** *Py.* **3, 4)-Tri-methyl-quinoline tetrahydride** $\begin{matrix}CH:CH\ .C.CH_2.CH_2\\CH:CMe.C.NMe.CHMe\end{matrix}$. (244°). Formed by the action of MeI on (*B.* 4 ; *Py.* 3)-di-methyl-quinoline tetrahydride (Doebner a. Miller, *B.* 16, 2470). Colourless liquid.

(*Py.* **1, 2, 3)-Tri-methyl-quinoline** $C_6H_4<\begin{matrix}CMe:CMe\\N\ :CMe\end{matrix}$. [65°]. (285°). Formed by heating the anilide of di-methyl ethylidene diketone $CH_3.CO.CHMe.C(NC_6H_5).CH_3$ with H_2SO_4, and separated by passing NH_3 through the diluted product (Combes, *C. R.* 106, 144).—$B'_2H_2PtCl_6$. [215°].

Tri-methyl-quinoline $C_{12}H_{13}N$. (270°–280°). A by-product in the preparation of quinaldine from paraldehyde, aniline, and HCl (Doebner a. Miller, *B.* 18, 3352). — $B'_2H_2PtCl_6$ 2aq: pale-yellow needles.

(*B.* **1, 2, 4 ;** *Py.* **3)-Tetra-methyl-quinoline** $\begin{matrix}CMe:CMe.C.CH:CH\\CH\ :CMe.C.\ N\ :CMe\end{matrix}$. [c. 20°]. (300°). Formed by heating solid ψ-cumidine [63°] with paraldehyde and HClAq at 105° (Doebner a. Miller, *B.* 17, 1710). Crystalline; v. sol. alcohol and ether, insol. water.—$B'_2H_2Cr_2O_7$: long yellow needles.

(*B.* **2, 4 ;** *Py.* **1, 3)-Tetra-methyl-quinoline** $\begin{matrix}CMe:CH.C.CMe:CH\\CH:CMe.C.\ N\ :CMe\end{matrix}$. [84°]. (285° uncor.). Formed from acetone and *m*-xylidine (Levin a. Riehm, *B.* 19, 1394). White plates (from ether). —$B'H_2SO_4$: [235°–242°]; needles, v. sol. water, m. sol. alcohol.—B'HCl: white needles (by sublimation). — $B'_2H_2PtCl_6$. — $B'_2H_2Cr_2O_7$: orange needles, sl. sol. water.

Tetramethylquinoline $C_{13}H_{15}N$. (265°–273°). Occurs in crude quinaldine, obtained from par-

aldehyde, aniline, and HClAq (Einhorn, *B.* 18, 3145). On oxidation with CrO_2Cl_2 it yields an aldehyde $C_{13}H_{13}NO$, crystallising from water in needles (containing 3aq), melting at 74° when hydrated and 102° when anhydrous; it is oxidised by ammoniacal $AgNO_3$ to an acid crystallising in needles [224°].

Salt.—$B'_2H_2PtCl_6$.

References.—AMIDO-, CHLORO-, NITRO-, and OXY-, METHYL-QUINOLINES, and METHYL-DI-QUINOLYL.

(γ)-METHYL-ISOQUINOLINE $C_{10}H_9N$ *i.e.* $C_6H_4<\begin{array}{l}CMe:CH\\CH:N\end{array}$. (256° uncor.). Formed by the distillation of either of the compounds $\begin{array}{l}CMe_2.CO\\C_6H_4.CO\end{array}>NH$ and $\begin{array}{l}CMe_2.CO\\C_6H_4.CO\end{array}>NMe$ with zinc-dust (Le Blanc, *B.* 21, 2300). Liquid, not solidified at −75°. — $B'_2H_2PtCl_6$. [253·5°]. Brownish-red crystals.—$B'C_6H_2(NO_2)_3OH$. [195°]. Slender needles.

(α)-Methyl-isoquinoline $C_6H_4<\begin{array}{l}CH:CH\\CMe:N\end{array}$. One of the products got by distilling papaveroline over zinc-dust (Krauss, *M.* 11, 361. Oil. Volatile with steam.—$B'_2H_2PtCl_6\,1\frac{1}{2}aq$. [229°]. Orange-yellow pp.—Picrate. [210°]. Light yellow pp.

Derivative.—*v.* CHLORO-METHYL-ISOQUINOLINE.

METHYL-QUINOLINE-ACRYLIC ACID *v.* METHYL-QUINOLYL-ACRYLIC ACID.

(*Py.* 3)-METHYL-QUINOLINE (*B.* 2)-CARBOXYLIC ACID $C_{11}H_9NO_2$ *i.e.* $\begin{array}{l}CO_2H.C:CH.C.CH:CH\\\quad CH:CH.C.N:CMe\end{array}$. *Quinaldine p-carboxylic acid.* [259°]. Formed by the reaction of a mixture of paraldehyde, *p*-amido-benzoic acid, and HClAq (Doebner a. Miller, *B.* 17, 939). Formed also by oxidation of the corresponding di-methyl-quinoline (Schunck, *B.* 23, 2263). White needles, which may be sublimed. Sol. hot alcohol, v. sl. sol. water. — HA'HCl aq: long slender needles or small prisms.—$(HA')_2H_2PtCl_6\,4aq$: monoclinic tables.—$(HA')_2H_2Cr_2O_7$: red needles, sol. hot water.—$CaA'_2\,2aq$: feathery crystals.—$CuA'_2\,6aq$: small plates.—AgA': sparingly soluble crystalline powder.—$^{\times}PbA'_2$: prisms.

(*Py.* 3)-Methyl-quinoline (*B.* 3)-carboxylic acid $\begin{array}{l}CH:CH.C.CH:CH\\CO_2H.C:CH.C.N:CMe\end{array}$. *Quinaldine m-carboxylic acid.* [285°]. Formed by heating a mixture of paraldehyde, *m*-amido-benzoic acid, and HClAq (Doebner a. Miller, *B.* 17, 941). Formed also by the oxidation of the corresponding aldehyde by Ag_2O (Eckhardt, *B.* 22, 281). Formed also by oxidation of the corresponding di-methyl-quinoline (Rist, *B.* 23, 2262), and from the corresponding amido-methyl-quinoline by Sandmeyer's reaction (Rist, *B.* 23, 3485). Long silky needles which may be sublimed. Sol. alcohol, nearly insol. water. — HA'HCl aq: small tables, sl. sol. cold water.—$(HA')_2H_2PtCl_6$: monoclinic prisms. — $(HA')_2H_2Cr_2O_7$: yellow needles, v. sol. hot, sl. sol. cold, water. — $CaA'_2\,2aq$: sparingly soluble prisms.—$CuA'_2\,3aq$: green tables.—AgA': crystalline pp.

(*Py.* 3)-Methyl-quinoline (*B.* 4)-carboxylic acid $\begin{array}{l}CH:CH\text{——}C.CH:CH\\CH:C(CO_2H).C.N:CMe\end{array}$. *Quinaldine o-carboxylic acid.* [151°]. Formed by heating a mixture of o-amido-benzoic acid (25 g.), paraldehyde (13 g.), and HClAq at 100° (Doebner a. Miller, *B.* 17, 943). Formed also by oxidation of the corresponding di-methyl-quinoline (R. Meyer, *B.* 23, 2259). Colourless needles (containing $\frac{1}{2}$aq), v. sol. hot water and alcohol. Split up by heat into CO_2 and quinaldine.—HA'HCl: concentric tables, v. sol. water.—$(HA')_2H_2PtCl_6\,2aq$: large red prisms, sol. hot, sl. sol. cold, water.—$CuA'_2\,1\frac{1}{2}aq$: small dark-green needles.—$^{\times}AgA'$: amorphous pp., changing into slender needles when heated with water for a long time.

(*B.* 4)-Methyl-quinoline (*B.* 1)-carboxylic acid $\begin{array}{l}CH:C(CO_2H)\\CH:C(CH_3)\end{array}>C_5H_3N$. *o-Methyl-quinoline ana-carboxylic acid.* [286°]. Prepared by heating the corresponding di-methyl-quinoline with dilute HNO_3 at 170° (Lellmann a. Alt, *A.* 237, 310). White powder. Yields (*B.* 4)-methyl-quinoline on distillation with lime. A solution of its ammonium salt gives a dirty-green pp. with $FeSO_4$, a light-green pp. with $CuSO_4$, and a white pp. with lead acetate.

Salts. — HA'HCl aq: silky needles. — $(HA')_2H_2PtCl_6\,6aq$: yellow needles.— $(HA')_2H_2PtCl_6\,2aq$: needles. — $(HA')_2H_2PtCl_6$. — CaA'_2: crystalline pp.

(*Py.* 3)-Methyl-quinoline (*Py.* 1)-carboxylic acid $C_6H_4<\begin{array}{l}C(CO_2H):CH\\N\text{=====}CMe\end{array}$. *Aniluvitonic acid.* [242°].

Formation. — 1. By boiling a mixture of aniline and pyruvic acid with water; or by boiling anilpyruvic acid with water. In this reaction $CH_3.CH:CH.CO.CO_2H$ may perhaps be assumed as an intermediate acid (Böttinger, *B.* 14, 90, 133; *A.* 191, 321). — 2. By oxidising (*Py.* 1,3)-di-methyl-quinoline with CrO_3 (Beyer, *J. pr.* [2] 33, 411; Seitz, *B.* 23, 2257).—3. By heating isatin with acetone and dilute (5 p.c.) NaOHAq (Pfitzinger, *J. pr.* [2] 38, 582).

Properties.—Laminæ or needles (containing aq); sol. water and alcohol, v. e. sol. dilute acids. Tastes bitter.

Reactions.—1. Yields quinaldine on *distillation with lime* (Küsel, *B.* 19, 2249).—2. *Oxidised* by $KMnO_4$ to pyridine tricarboxylic acid.—3. *Bromine* in chloroform forms an oily addition-product, which gives up all its bromine on treatment with boiling water (Böttinger, *B.* 16, 2357).

Salts.—HA'HCl aq: needles; loses its HCl when treated with cold water.—$(HA')_2H_2PtCl_6\,2aq$. —HA'HBr 2aq.—BaA'_2 aq.—AgA': small plates.

(*Py.* 2)-Methyl-quinoline (*Py.* 3)-carboxylic acid $C_6H_4<\begin{array}{l}CH:CMe\\N:C.CO_2H\end{array}$. [144°]. Formed by oxidation of (*Py.* 2, 3)-methyl-ethyl-quinoline (derived from aniline and propionic aldehyde) with CrO_3 and H_2SO_4 (Doebner a. Miller, *B.* 17, 1715; 18, 1641). Long silky needles or monoclinic prisms (from ether-alcohol); sol. hot water and alcohol. Split up at 160° into CO_2 and (*Py.* 2)-methyl-quinoline.—CuA'_2: sl. sol. water.

(*Py.* 3)-Methyl-quinoline (*Py.* 2)-carboxylic acid $C_6H_4<\begin{array}{l}CH:C.CO_2H\\N:CMe\end{array}$. *Quinaldine carboxylic acid.* [234°]. Formed by saponification of its ether, which is produced by the action of o-amido-benzoic aldehyde on an alkaline aqueous solution of acetoacetic ether (Friedländer a. Göhring, *B.* 16, 1836; *B.* 19, 37). Formed also by oxidising (*Py.* 2, 3)-di-methyl-quinoline with

chromic acid (Rohde, *B.* 22, 267). Colourless needles, sl. sol. water, m. sol. alcohol. Split up on fusion into CO_2 and quinaldine.

Ethyl ether EtA′. [71°]. Long white needles, insol. water. May be distilled.—$(EtA')_2H_2PtCl_6$ 2aq: sparingly soluble yellow needles.

Methylo-iodide of the *ethyl ether* EtA′MeI. [205°]. Orange needles, sl. sol. cold water and alcohol, v. sol. hot water. Ag_2O converts it into the oxide $(EtA'Me)_2O$, an amorphous pp. which, when freshly prepared, is sol. benzene and chloroform, insol. water, alcohol, ether, and ligroïn; after a time it becomes insol. benzene and chloroform. The oxide decomposes when heated between 180° and 240°. HCl converts it into EtA′MeCl, which yields $(EtA'MeCl)_2PtCl_6$, crystallising in golden plates [217°].

(*Py.* 1)-**Methyl-quinoline** (*B.* 2)-**carboxylic acid** $\begin{matrix}CO_2H.C:CH.C.CMe:CH\\ HC:CH.C.\ N\ :CH\end{matrix}$. *Lepidine p-carboxylic acid.* [250°–270°]. Obtained by oxidation of the corresponding di-methyl-quinoline by chromic acid mixture (K. Daniel, *B.* 23, 2264). Stellate groups of needles. Yields lepidine on distillation with soda-lime.

Methyl-quinoline carboxylic acid $C_{13}H_9NO_2$ *i.e.* $C_6H_4(C_5HMeN.CO_2H)$. [190°]. Formed by oxidising the fraction 275°–285° (? di-methyl-quinoline) of the product of the action of aniline on a mixture of isobutyric aldehyde, methylal, and HCl (Von Miller a. Kinkelin, *B.* 20, 1940). Small crystals, m. sol. water and alcohol; gives off CO_2 on fusion.

(*Py.* 4)-**Methyl-quinoline tetrahydride** (*B.* 3)-**carboxylic acid**

$$\begin{matrix}CH:CH.C.CH_2.CH_2\\ CO_2H.C\ :CH.C.NMe.CH_2\end{matrix}.$$

Kairoline m-carboxylic acid. [164°]. Obtained by heating quinoline tetrahydride (*B.* 3)-carboxylic acid with MeI at 150° (Fischer a. Körner, *B.* 17, 765). Needles; sl. sol. water, v. sol. alcohol.

(*Py.* 4)-**Methyl-quinoline tetrahydride** (*Py.* 1)-**carboxylic acid** $C_6H_4<\begin{matrix}CH(CO_2H).CH_2\\ N\ (CH_3)\ .CH_2\end{matrix}$. *Methyl-tetrahydro-cinchonic acid.* Formed by heating the hydrochloride of quinoline tetrahydride (*Py.* 1)-carboxylic acid with MeOH and MeI at 100°, and decomposing the resulting salt with Ag_2O (Weidel, *M.* 3, 66). Crystallises from cold alcohol in large prisms (containing 2aq); v. sol. water and alcohol, nearly insol. ether. Reduces warm ammoniacal $AgNO_3$. Decomposes on distillation, yielding an anhydride $C_{22}H_{24}N_2O_3$, which is a colourless oil (298° at 744 mm.), insol. ether, alcohol, and dilute acids, and is converted by heating with HClAq at 150° into MeCl and quinoline tetrahydride (*Py.* 1)-carboxylic acid (Weidel a. Hazura, *M.* 5, 643). On heating the anhydride with aqueous KOH it is converted into 'homohydrocinchonic acid' $C_{11}H_{13}NO_2$, which crystallises in pearly leaflets [125°], insol. water, sol. alcohol and ether, and forms a hydrochloride $C_{11}H_{13}NO_2HCl$ aq, crystallising in trimetric prisms (a:b:c = ·93:1:2·07); and a methylo-iodide $C_{11}H_{13}NO_2MeI$ aq, forming monoclinic crystals; converted by Ag_2O into $C_{11}H_{12}MeNO_2$aq, crystallising in glittering prisms, v. e. sol. water.

Salts.—The metallic salts are extremely deliquescent. — HA′HCl aq: large monoclinic crystals.—$(HA')_2H_2PtCl_6$: large orange crystals.—HA′HI aq: large monoclinic crystals.

(*B.* 2; *Py.* 3)-**Di-methyl-quinoline** (*Py.* 1)-**carboxylic acid** $\begin{matrix}CMe:CH.C.C(CO_2H):CH\\ CH\ :CH.C.N{=\!=\!=}CMe\end{matrix}$. [262°]. Formed by the action of aqueous NaOH on a mixture of *p*-methyl-isatin and acetone (Pfitzinger, *J. pr.* [2] 38, 584). Shining plates (from water).

(*B.* 4; *Py.* 3)-**Dimethyl-quinoline** (*B.* 2)-**carboxylic acid**

$$\begin{matrix}CO_2H.C\ :CH\ .C.CH:CH\\ CH:CMe.C.\ N:CMe\end{matrix}.$$

Formed by oxidising (*B.* 2, 4; *Py.* 3)-trimethyl-quinoline with CrO_3 and dilute H_2SO_4 (Panajotoff, *B.* 20, 38). Needles (by sublimation); sl. sol. water and cold alcohol. On distillation with lime it gives (*B.* 4; *Py.* 3)-di-methyl-quinoline.

Salts.—$(HA')_2H_2PtCl_6$ 4aq: orange needles.—BaA'_2: white needles, v. sol. water.—AgA′ aq: amorphous precipitate becoming crystalline.—$C_6H_2(NO_2)_3OH$. [221°]. Yellow needles; sl. sol. water, v. sol. alcohol.

(*Py.* 2, 3)-**Di-methyl-quinoline** (*B.* 2)-**carboxylic acid** $\begin{matrix}CO_2H.C:CH.C.CH:CMe\\ HC:CH.C.\ N\ :CMe\end{matrix}$. [270°]. Formed by oxidising (*B.* 2; *Py.* 2, 3-tri-methyl-quinoline (Miller a. Ohler, *B.* 23, 2268). Silky needles, sl. sol. water and alcohol. Gives on distillation (*Py.* 2, 3)-di-methyl-quinoline [68°].—CuA'_2 aq.

(*Py.* 3)-**Methyl-quinoline** (*B.* 2; *Py.* 1)-**di-carboxylic acid** $\begin{matrix}CO_2H.C\ :CH.C.C(CO_2H):CH\\ CH:CH.C.N{=\!=\!=}CMe\end{matrix}$. Formed by heating *p*-amido-benzoic acid (30 g.) with pyruvic acid (20 g.) and aldehyde (12 g.) in alcoholic solution on a water-bath (Von Miller a. R. Meyer, *B.* 23, 2262). White powder, insol. alcohol and other solvents. Cakes together at 160°. Gives quinaldine on distillation with lime.—CuA'_2: green crystalline pp.

(*Py.* 3)-**METHYL-QUINOLINE** (*B.* 3)-**CARBOXYLIC ALDEHYDE** $C_{11}H_9NO$ *i.e.* $\begin{matrix}CH:CH.C.CH:CH\\ COH.C\ :CH.C.N:CMe\end{matrix}$. [61°]. Prepared by adding $KMnO_4$ to a dilute solution of sodium methyl-quinolyl-acrylic acid covered with benzene and frequently shaking (Eckhardt, *B.* 22, 277). Slender hair-like crystals (containing $1\frac{1}{2}$ aq!). Melts at 61° when anhydrous and 73° when hydrated. V. sol. dilute HClAq, sl. sol. acetic acid, v. sol. alcohol, ether, and benzene, m. sol. ligroïn and hot water. Volatile with steam. Reduces ammoniacal $AgNO_3$. Gives a crystalline sulphite, and a red colour with phenyl-hydrazine acetate. Ag_2O oxidises it to the corresponding carboxylic acid [285°]. On heating with methyl-quinoline and $ZnCl_2$ for 2 hours at 150° it yields a condensation-product [69°].

Salts.—B′HCl: pale-yellow needles.—$B'H_2PtCl_6$. [211°]. Triclinic crystals (from alcohol containing HCl). —$B'C_6H_2(NO_2)_3OH$. [182°]. Needles, blackening at 174°.

Phenyl-hydrazide $C_{17}H_{15}N_3$. The salt $C_{17}H_{15}N_3HCl$ separated as brick-red hair-like crystals on adding a hot solution of phenyl-hydrazine hydrochloride to a hot solution of the base in HClAq. In presence of H_2SO_4 the salt $(C_{17}H_{15}N_3)_4(H_2SO_4)_3$ 9aq separates in small brick-red needles.

(*Py.* 3)-**Methyl-quinoline** (*B.* 2)-**carboxylic aldehyde** $\frac{CHO.C\ :CH.C.CH:CH}{CH:CH.C.\ N\ :CMe}$ [106°]. Formed by oxidising the corresponding methyl-quinolyl-acrylic acid with $KMnO_4$, accompanied by agitation with benzene (Miller a. Kinkelin, *B.* 18, 3237). Needles (from water); m. sol. ligroïn and hot water, v. e. sol. alcohol, ether, benzene, and acids. On heating with quinaldine at 150° it forms $C_9H_6N.CH:CH.C_9H_5NMe$, a yellow insoluble substance melting above 300°.—$B'_2H_2PtCl_6$ 2aq: orange prisms.

Phenyl-hydrazide $C_{17}H_{15}N_3$. [160°]. Golden prisms (from alcohol).

(*B.* 2, 4)-**Di-methyl-quinoline** (*Py.* 3)-**carboxylic aldehyde** $\frac{CMe:CH\ .C.CH:CH}{CH\ :CMe.C.\ N\ :C.CHO}$ [107°]. Formed by oxidising (*B.* 2, 3)-di-methyl-quinolyl-acrylic acid with $KMnO_4$ (Panajotoff, *B.* 23, 1471). Yellowish plates, v. sol. alcohol and ether, sl. sol. water. Sol. acids; insol. alkalis.

Tri-methyl-quinoline carboxylic aldehyde $C_{13}H_{13}NO$. [101·5°]. Formed from tetra-methyl-quinoline (derived from paraldehyde, aniline, and HCl) by treatment with CrO_2Cl_2 followed by water (Einhorn, *B.* 18, 3144). Crystallises from water in needles (containing 3aq) which melt at 74°. When anhydrous it melts at 101·5°. It reduces ammoniacal $AgNO_3$, forming a mirror. It yields an oxim [203°] and a phenyl-hydrazide [207°].

METHYL-QUINOLINE MERCAPTAN *v.* METHYL-QUINOLYL MERCAPTAN.

(*B.* 2)-**METHYL-QUINOLINE** (*B.* 4)-**SULPHONIC ACID** $C_{10}H_9NSO_3$ *i.e.* $\frac{C(CH_3):CH}{CH:C(SO_3H)}>C_5H_3N$. *p-Toluquinoline sulphonic acid.* Formed by boiling a mixture of *p*-toluidine sulphonic acid, nitrobenzene, glycerin, and H_2SO_4 (Fischer a. Wittmack, *B.* 17, 441). Formed also by the sulphonation of (*B.* 2)-methyl-quinoline (Herzfeld, *B.* 17, 1552). Colourless plates, sl. sol. boiling water.—KA': v. sol. water. —BaA'_2 (dried at 130°): amorphous, sl. sol. water.

(*B.* 4)-**Methyl-quinoline** (*B.* 1)-**sulphonic acid** $\frac{CH:C(SO_3H)}{CH:CMe}>C_5H_3N$. Obtained by heating *o*-toluidine sulphonic acid $C_6H_3Me(NH_2)SO_3H$ [1:2:4] with glycerin, nitrobenzene, and H_2SO_4 (Herzfeld, *B.* 17, 904). Formed also by sulphonating (*B.* 4)-methyl-quinoline (Herzfeld, *B.* 17, 1550). Flat prisms (from water); v. sol. water.—KA': long soluble tables.—BaA'_2: soluble trimetric tables.

(*B.* 4)-**Methyl-quinoline** (*B.* 2)-**sulphonic acid** $\frac{SO_3H.C\ :CH}{CH:CMe}>C_5H_3N$. Formed by heating *o*-toluidine sulphonic acid $C_6H_3Me(NH_2)SO_3H$ [1:2:5] with glycerin, nitrobenzene, and H_2SO_4 (Herzfeld, *B.* 17, 903). Colourless sparingly soluble prisms.

(*Py.* 3)-**Methyl-quinoline** (*B.* 2)-**sulphonic acid** $\frac{SO_3H.C\ :CH.C.CH:CH}{CH:CH.C.\ N\ :CMe}$. *Quinaldine p-sulphonic acid.* Formed in small quantity in the sulphonation of quinaldine. Prepared by heating amido-benzene *p*-sulphonic acid (100 pts.) with paraldehyde (80 pts.) and HCl (100 pts.) for 2 hours on the water-bath (Doebner a. Miller, *B.* 17, 1703). Small monoclinic crystals, v. sol. hot water. On fusion with KOH it yields oxy-methyl-quinoline [213°].

(*Py.* 3)-**Methyl-quinoline** (*B.* 4)-**sulphonic acid** $\frac{CH:CH \text{——} C.CH:CH}{CH:C(SO_3H).C.\ N\ :\ CMe}$. *Quinaldine o-sulphonic acid.* Formed, in small quantity, in sulphonating quinaldine (Doebner a. Miller, *B.* 17, 1703). Long flat triclinic prisms, v. sol. hot water. On fusion with potash it yields oxy-methyl-quinoline [74°].

(*Py.* 3)-**Methyl-quinoline** (*B.* 1 or 3)-**sulphonic acid** $\frac{CH:C(SO_3H).C.CH:CH}{CH:CH \text{——} C.\ N\ :CMe}$ or $\frac{CH:CH \text{——} C.CH:CH}{C(SO_3H):CH.C.\ N\ :CMe}$. *Quinaldine m-sulphonic acid.* The chief product of the sulphonation of quinaldine (Doebner a. Miller, *B.* 17, 1703). Glistening monoclinic prisms; sol. hot, sl. sol. cold, water. On fusion with potash it gives oxy-methyl-quinoline [234°]. Distillation with KCy yields the nitrile of the corresponding carboxylic acid (Richard, *B.* 23, 3488).

(*Py.* 1)-**Methyl-quinoline sulphonic acid** $C_6H_3(SO_3H)<\frac{CMe:CH}{N\ :\ CH}$. *Lepidine sulphonic acid.* Formed by heating 'homohydrocinchonic acid' $C_{10}H_9NSO_3$ with H_2SO_4 at 180° (Weidel a. Hazura, *M.* 5, 652). Crystallises from water in thin plates (containing aq); nearly insol. cold, v. sol. hot water.

(*Py.* 1)-**Methyl-quinoline** (*B.* 2)-**sulphonic acid** $\frac{SO_3H.C:CH.C.CMe:CH}{HC:CH.C.N = CH}$. Formed by heating lepidine (1 pt.) with H_2SO_4 (8 pts.) at 300° (Busch a. Koenigs, *B.* 23, 2680). Silky needles (containing *x*aq), v. sol. hot water.—AgA' aq: white jelly, becoming crystalline.

(*Py.* 1, 3)-**Di-methyl-quinoline sulphonic acid** $C_{11}H_{11}NSO_3$ *i.e.* $C_6H_3(SO_3H)<\frac{CMe:CH}{N\ \ :CMe}$. Formed by sulphonating the corresponding di-methyl-quinoline (Beyer, *J. pr.* [2] 33, 407). Tables or flat needles, not melting below 303°. On fusion with potash it yields oxy-di-methyl-quinoline [44°].

(*B.* 1, 4)-**Di-methyl-quinoline** (*B.* 2)-**sulphonic acid** $\frac{SO_3H.C\ :CMe}{CH:CMe}>C_5H_3N$. *p-Xyloquinoline sulphonic acid.* Formed by heating (*B.* 1, 4)-di-methyl-quinoline with fuming H_2SO_4. Formed also from xylidine sulphonic acid by heating with nitrobenzene, glycerin, and H_2SO_4 (Nölting a. Frühling, *B.* 21, 3157).—KA': needles or plates, v. sol. water.—BaA'_2 aq: plates, v. sol. hot water.—BaA'_2 2aq.

(*B.* 1, 4)-**Di-methyl-quinoline** (*B.* 3)-**sulphonic acid** $\frac{CH:CMe}{SO_3H.C\ :CMe}>C_5H_3N$. Formed by heating xylidine sulphonic acid (derived from *p*-xylene sulphonic acid) with nitrobenzene, glycerin, and H_2SO_4 (Nölting a. Frühling, *B.* 21, 3156). Short white plates, sl. sol. cold water, v. sol. hot water and dilute acetic acid.—KA'aq: v. e. sol. water.—BaA'_2 aq: needles, v. sol. hot water.

(*B.* 2, 4)-**Di-methyl-quinoline sulphonic acid** $C_6HMe_2(SO_3H)(C_5H_3N)$. Formed by heating the corresponding di-methyl-quinoline with fuming H_2SO_4 at 165° (Berend, *B.* 17, 2716). Minute needles (from alcohol-ligroïn).

(*B.* 2, 4; *Py.* 3)-**Tri-methyl-quinoline** (*B.* 1)-**sulphonic acid.** Formed from the corresponding tri-methyl-quinoline by heating with $H_2S_2O_7$ at 125° (Panajotoff, *B.* 20, 36). Small yellow needles (from dilute HClAq), not melting at 260°: insol. cold water.—BaA'_2 3aq: silky needles.

METHYL-QUINOLINIC ACID *v.* METHYL-PYRIDINE DICARBOXYLIC ACID.

METHYL-QUINOLINIUM HYDRATE *v.* *Methylo-hydrate* of QUINOLINE.

(*Py.* 1)-**METHYL-**(*Py.* 3 : *B.* 3)-**DIQUINOLYL** $C_{19}H_{14}N_2$ *i.e.* $C_6H_4\left<\begin{matrix}CMe:CH\\ N\ :C\end{matrix}\right>$—$C_6H_3\left<\begin{matrix}CH:CH\\ N\ :CH\end{matrix}\right.$. [138°]. Obtained by heating flavaniline (10 pts.), with nitrobenzene (5 pts.), glycerin (30 pts.), and H_2SO_4 (30 pts.) (Fischer, *B.* 19, 1036). Colourless crystals. Strong base. Its salts with mineral acids have a splendid blue fluorescence in dilute solution.

Methylo-iodide B'MeI: fine yellowish needles, easily soluble in water.

Di-(*Py.* 3)-**methyl-diquinolyl** $C_{20}H_{16}N_2$ *i.e.* $\begin{matrix}CH\ :CH\\ CMe:\ N\end{matrix}\!>\!C_6H_3.C_6H_3\!<\!\begin{matrix}CH:CH\\ N\ :CMe\end{matrix}$. [207°] (above 360°). Prepared by gradually adding paraldehyde (90 g.) to a solution of benzidine (80 g.) in conc. HClAq (400 g.) at 100°. After heating for ten hours the product is diluted with water, treated with $NaNO_2$, boiled, and ppd. by KOH (Hinz, *A.* 242, 326). Slender white needles, sol. alcohol, benzene, and chloroform, sl. sol. water and ether.—$B''H_2PtCl_6$ 2aq: light-yellow pp., sl. sol. hot water.—$B''2HNO_3$: small colourless needles, v. sol. water, sl. sol. alcohol.—$B''H_2Cr_2O_7$: slender yellow needles, sl. sol. hot water.

Di-methyl-diquinolyl $C_{20}H_{16}N_2$aq [162°]. Formed by heating quinaldine with sulphur (Von Miller, *B.* 21, 1828). Crystallises from alcohol in white needles (containing aq). Its picrate crystallises in needles. The platinochloride forms needles, v. sl. sol. water.

Tetra-methyl-diquinolyl $C_{22}H_{20}N_2$ *i.e.* $\begin{matrix}CH\ :CMe\\ CMe:\ N\end{matrix}\!>\!C_6H_3.C_6H_3\!<\!\begin{matrix}CMe:CH\\ N\ :CMe\end{matrix}$. *Tetra-methyl-diquinolyline.* [232°]. Formed by heating benzidine with acetone and conc. HClAq at 180° (Schestopal, *B.* 20, 2506). White plates, insol. water, sl. sol. ether, v. sol. alcohol. When heated with benzoic aldehyde and $ZnCl_2$ at 180° it forms a compound crystallising from alcohol in yellow needles.

Salts.—$B''H_2Cl_2$. Needles, v. sol. water and alcohol.—$B''H_2SO_4$. Needles (from water) or prisms (from alcohol).—$B''H_2PtCl_6$: needles.—$B''H_2Cr_2O_7$: needles, sl. sol. cold water.—Picrate: insol. water and cold alcohol. —$B''I_2Cl_2$ 2HCl: flesh-coloured needles.

Methylo-iodide $B''Me_2I_2$. [270°].

Ethylo-iodide $B''Et_2I_2$. [158°].

(*Py.* 3)-**METHYL-QUINOLYL-**(*B.* 2)-**ACRYLIC ACID** $C_{13}H_{11}NO_2$ *i.e.* $CO_2H.CH:CH.\underset{\textstyle CH:CH.C.\ N\ :CMe}{C\ :CH.C.CH:CH}$. *Quinaldine-acrylic acid.* Obtained by heating a mixture of paraldehyde (40 g.), *p*-amido-cinnamic-acid hydrochloride (50 g.), and conc. HCl (50 g.) (Miller a. Kinkelin, *B.* 18, 3235). Small concentric needles. Decomposes between 240° and 250°. Sol. hot alcohol, sl. sol. cold alcohol and water. By an alkaline solution of $KMnO_4$ it is oxidised to methyl-quinoline carboxylic aldehyde $C_9H_5Me.CHO$.

Salts.—A'H,HClaq: easily soluble concentric prisms.—$A'H,HNO_3$aq: needles or prisms, sl. sol. dilute HNO_3. — $(A'H,HCl)_2PtCl_4$ 2aq; reddish-yellow prisms.

(*Py.* 3)-**Methyl-quinolyl** (*B.* 3)-**acrylic acid** $C_{13}H_{11}NO_2$ *i.e.* $\underset{\textstyle CO_2H.CH:CH.C\ \ :CH.C.\ N\ :CMe}{CH:CH.C.CH:CH}$ [246°]. Obtained by heating *m*-amido-cinnamic acid with paraldehyde and conc. HClAq at 150° (Eckhardt, *B.* 22, 272). Small white monoclinic prisms (from alcohol), tending to become yellow; sl. sol. ether, chloroform, and petroleum-ether, m. sol. alcohol, benzene, and acetone. When heated above its melting-point a small sublimate of slender needles [223°] is obtained. $KMnO_4$ oxidises it to the corresponding methyl-quinoline carboxylic aldehyde. On warming with chloral on the water-bath two compounds are formed. One of these compounds $C_{12}H_6NO_2.CH_2.CH(OH)CCl_3$ crystallises from alcohol in prisms [201°], which dissolve in nitric acid with violet-fluorescence, and which yield the salts $C_{15}H_{12}Cl_3NO_3HCl$ [over 300°] and $AgC_{15}H_{11}Cl_3NO_3$ crystallising in slender needles. The other compound $C_{28}H_{25}Cl_5N_2O_5$ crystallises from alcohol in needles [128°] which dissolve in nitric acid with blue fluorescence, and which forms a salt $C_{28}H_{25}Cl_5N_2O_5HCl$ [217°].

Salts.—HA'HClaq: deliquescent trimetric needles.—$(HA')_2H_2PtCl_6$ 2aq: yellow needles or plates.—$HA'HNO_3$aq: needles, sol. water. — $HA'C_6H_2(NO_2)OH$aq. [152°]. Bundles of slender needles, sol. alcohol, hot water, and HOAc, sl. sol. ether.—CaA'_2 3aq: slender needles (from water), v. sol. dilute HClAq and acetic acid.—AgA'2aq: minute crystalline lancelets.—AgA'4aq: needles.

(*Py.* 3)-**Methyl-quinolyl-**(*B.* 1?)-**acrylic acid** $C_{13}H_{11}NO_2$. Formed on one occasion in the preparation of the preceding isomeride (E.). Crystallises in yellowish monoclinic plates (containing aq) [184°] and in white crystals (containing ½ EtOH) [204°]. Its ammoniacal solution, unlike that of its isomeride, is not ppd. by salts of Ba, Ca, and Mg.

(*B.* 2, 4)-**Di-methyl-**(*Py.* 3)-**quinolyl-acrylic acid** $\underset{\textstyle CH\ :CMe.C.\ N\ :C.CH:CH.CO_2H}{CMe:CH\ .C.CH:CH}$. Formed by boiling the compound of chloral and (*B.* 2, 4; *Py.* 3)-tri-methyl-quinoline with aqueous K_2CO_3 (Panajotoff, *B.* 20, 42). Yellowish needles, decomposing at 180°, forming a product melting at 210°.

METHYL-QUINOLYL-AMMONIUM IODIDE *v.* *Methylo-iodide* of QUINOLINE.

(*Py.* 1)-**METHYL-QUINOLYL ETHYL SULPHIDE** $C_6H_4\!<\!\begin{matrix}CMe:CH\\ N\ :CSEt\end{matrix}$. Formed by treating methyl-quinolyl mercaptan with NaOEt and EtI (Roos, *B.* 21, 628). Oil, volatile with steam. —$B'_2H_2PtCl_6$ ½aq.—B'HI. [214°]. Long yellow needles.

(*Py.* 3)-**Methyl-quinolyl ethyl sulphide** $C_6H_4\!<\!\begin{matrix}C(SEt):CH\\ N{=\!=\!=}CMe.\end{matrix}$ [56°]. Formed from sodium methyl-quinolyl mercaptide and EtI (R.). White needles, v. sol. alcohol and ether, insol. water.

TETRA - METHYL - DIQUINOLYLINE *v.* TETRA-METHYL-DIQUINOLYL.

(*Py.* 1)-**METHYL**-(*Py.* 3)-**QUINOLYL MERCAPTAN** $C_6H_4<\begin{matrix}CMe{:}CH\\ N\ {:}C.SH\end{matrix}$. [253°]. Formed by heating (*Py.* 3, 1)-oxy-methyl-quinoline with P_2S_5 at 150°, extracting the product with HClAq and ppg. with water (Roos, *B.* 21, 625). Brownish needles (from alcohol); insol. water, sl. sol. cold alcohol, v. sol. ether. Not attacked by hydroxylamine or phenyl-hydrazine. H_2O_2 oxidises it to a disulphide. NaOEt and EtI form methyl-quinolyl ethyl sulphide.

(*Py.* 3)-**Methyl**-(*Py.* 1)-**quinolyl-mercaptan.** $C_6H_4<\begin{matrix}C(SH){:}CH\\ N\text{———}CMe\end{matrix}$. [187°]. Formed by the action of P_2S_5 on (*Py.* 1, 3)-oxy-methyl-quinoline (Roos, *B.* 21, 628). Crystallises from water in plates (containing aq); v. sol. hot water, alcohol, and ether. With NaOEt and EtI it yields $C_9H_5MeN(SEt)$ [56°].

Di-(*Py.* 1)-**methyl-di**-(*Py.* 3)-**quinolyl disulphide** $C_6H_4<\begin{matrix}CMe{:}CH\\ N\ {:}C.\end{matrix}\ S.S.\ \begin{matrix}CH{:}CMe\\ C\ \ :\ \ N\end{matrix}>C_6H_4$. [167°]. Prepared by oxidising the corresponding mercaptan with hydrogen peroxide (Roos, *B.* 21, 627). White plates (from benzene); v. sol. alcohol, ether, and benzene, insol. water and alkalis.

(*Py.* 3) - **METHYL** - (*B.* 4) - **QUINOLYL PHENYL KETONE** $C_{17}H_{13}NO$ *i.e.* $\begin{matrix}CH{:}CH\ .\ C.CH{:}CH\\ CH{:}CBz.C.\ N\ {:}CMe\end{matrix}$. (*B.* 4)-*Benzoyl-quinaldine.* [108°]. Colourless felted needles. Formed by boiling o-amido-benzophenone (1 pt.) and paraldehyde (2 pts.) with dilute H_2SO_4 (15 pts.) (Geigy a. Koenigs, *B.* 18, 2406).

(*Py.* 3)-**methyl**-(*B.* 2)-**quinolyl phenyl ketone** $C_6H_5.CO.\begin{matrix}C\ \ :\ CH.C.CH{:}CH\\ CH{:}\ CH.C.\ N\ {:}CMe\end{matrix}$. [68°]. (above 300°). Formed by adding paraldehyde (1 mol.) to a hot solution of *p*-amido-benzophene (1 mol.) in conc. HClAq and digesting the mixture on a water-bath (Hinz, *A.* 242, 323). Plates (from alcohol); v. sol. hot water, alcohol, and ether.—$B'_2H_2PtCl_6$ 2aq: needles. Melts at 110° when anhydrous.—$B'_2H_2Cr_2O_7$: needles.

Methylo-iodide B'MeI. [220°].

(*B.* 2)-**METHYL-QUINOXALINE** $C_9H_8N_2$ *i.e.* $\begin{matrix}CMe{:}CH.C.N{:}CH\\ CH\ {:}CH.C.N{:}CH\end{matrix}$. *Toluquinoxaline.* (244° uncor.). Obtained by the action of glyoxal on (1, 3, 4)-tolylene-diamine, and purified by means of its compound with $NaHSO_3$ (Hinsberg, *B.* 17, 321; *A.* 237, 336). Liquid, turning yellow in air and light; miscible with cold water, alcohol, ether, and benzene; less soluble in hot water. With tin and HClAq it gives a blue colouring matter. Forms a dibromide $C_9H_8Br_2N_2$ crystallising from chloroform in needles, which blacken and decompose at 170°.—$B'_2H_2PtCl_6$: yellow needles; sl. sol. water and alcohol.—$B'_2H_2C_2O_4$. Needles [136°]; sl. sol. water.

Compound with sodium bisulphite $B'(NaHSO_3)_2$ 2aq: slender needles; v. sol. water, m. sol. alcohol.

Ethylo-iodide B'EtI. Colourless crystals; v. sol. water, sol. alcohol and chloroform.

Derivatives.—*V.* CHLORO-TOLUQUINOXALINE.

(*B.* 2; *Qu.* 2) - **Di - methyl - quinoxaline** $\begin{matrix}CMe{:}CH.C.N{:}CH\\ CH\ {:}CH.C.N{:}CMe\end{matrix}$. '*Methyl-tolylene-quinoxaline.*' [54°]. (268° uncor.). Formed by the action of chloro-acetone (2 mols.) on an aqueous solution of (1, 3, 4)-tolylene-diamine (Hinsberg, *B.* 19, 485; *A.* 237, 368). Formed also by the action of tolylene o-diamine upon methyl-glyoxal or its oxim, nitroso-acetone (Pechmann, *B.* 20, 2544). White crystals, turning red in the air; v. e. sol. cold water, alcohol, and ether. Ppd. from its aqueous solution on boiling or on adding KOH. Not affected by nitrous acid or Ac_2O.—$B'_2H_2PtCl_6$: yellow needles: sl. sol. water.

Tri-methyl-quinoxaline $\begin{matrix}CMe{:}CH.C.N{:}CMe\\ CH\ {:}CH.C.N{:}CMe\end{matrix}$. [91°]. (271°). Formed by the action of di-methyl diketone (diacetyl) on (1, 3, 4)-tolylene-diamine acetate (Pechmann, *B.* 21, 1414). Hexagonal crystals (from ligroïn).

Tetra-methyl-diquinoxaline, so called, $\begin{matrix}CMe{:}N.C.CH{:}C.N{:}CMe\\ CMe{:}N.C.CH{:}C.N{:}CMe\end{matrix}$. [above 300°]. Obtained by warming tetra-amido-benzene with excess of di-methyl diketone $CH_3.CO.CO.CH_3$ (Nietzki a. Müller, *B.* 22, 444). Reddish star-shaped plates (from aniline). Nearly insol. water, alcohol, and ether. Its solution in conc. H_2SO_4 is bluish-green, and becomes blue on dilution.

METHYL-QUINOXALINE DICARBOXYLIC ACID $C_{11}H_8N_2O_4$ *i.e.* $\begin{matrix}CMe{:}CH.C.N\ {:}C.CO_2H\\ CH\ {:}CH.C.N\ {:}C.CO_2H\end{matrix}$. *Toluquinoxaline dicarboxylic acid.* Prepared by the action of an aqueous solution of (1, 3, 4)-tolylene-diamine on sodium di-oxy-tartrate (carboxytartronate) at 80° (Hinsberg, *A.* 237, 353). Colourless needles or prisms; v. sol. water, v. sl. sol. benzene. When crystallised from water its molecule contains ½aq. The anhydrous acid decomposes at 130° into CO_2 and a mono-carboxylic acid. $SnCl_2$ forms a compound crystallising in dark-green needles, sl. sol. water.

METHYL-QUINOXYL *v.* (*Py.* 1)-OXY-METHYL-QUINOLINE.

METHYL-RESORCIN *v.* ORCIN.

Di-methyl-resorcin *v.* *Di-methyl derivative* of RESORCIN.

Tri - methyl - resorcin $C_6H(CH_3)_3(OH)_2$ [1:3:5:2:6]. *Di-oxy-mesitylene. Mesorcin.* [150°]. (275° cor.).

Preparation.—Nitro-mesidine, obtained by partial reduction of di-nitro-mesitylene, is treated with HNO_2 and converted into nitro-mesitol; by reduction of this and treatment again with HNO_2 mesorcin is obtained (Knecht, *B.* 15, 1375).

Properties.—White plates: sl. sol. cold water. May be sublimed. Reduces ammoniacal $AgNO_3$ in the cold. By Fe_2Cl_6 it is oxidised to oxy-isoxyloquinone. Heated with H_2SO_4 it gives a substance whose alkaline solution is pink with an intense green fluorescence.

Di-acetyl derivative $C_9H_{10}(OAc)_2$. [63°]. (305° cor.).

METHYL-ROSANILINES *v.* METHYL-TRI-AMIDO-DI-PHENYL-TOLYL-CARBINOLS.

Methyl - pararosanilines *v.* METHYL - TRI - AMIDO-TRI-PHENYL-CARBINOLS.

DI-METHYL - ROSINDOLE $C_{23}H_{20}N_2$ *i.e.* $C_6H_5C<\begin{matrix}C_9H_8N\\ C_9H_7N\end{matrix}$ (?). [c. 270°]. Formed

together with benzoyl-methyl-indole by heating methyl-indole (methyl-ketole) with benzoyl chloride and $ZnCl_2$. Also formed by oxidation of the leuco- compound benzylidene-methyl-indole. Amorphous yellow pp., v. sol. alcohol and ether; or yellowish-red prismatic crystals, sl. sol. alcohol, v. sl. sol. ether. The amorphous modification is converted into the crystalline by long boiling with water. It dissolves in acids and in alcoholic NaOH or KOH with a red colour. Its salts are red dyestuffs closely resembling rosaniline. By zinc-dust and NH_3 it is reduced to benzylidene-methyl-indole [248°].—B'HCl : small metallic green crystals; sl. sol. water (Fischer a. Wagner, *B.* 20, 815).

METHYL SALICYLIC ACID *v.* OXY-TOLUIC ACID and the *Methyl derivative* of o-OXY-BENZOIC ACID.

METHYL-SALICYLIC ALDEHYDE *v. Methyl derivative* of o-OXY-BENZOIC ALDEHYDE.

DI-METHYL-SELENAZOLE *v.* SELENIUM, ORGANIC COMPOUNDS.

METHYL-SELENIDE *v.* SELENIUM, ORGANIC COMPOUNDS.

METHYL SILICATE $C_4H_{12}SiO_4$ *i.e.* $Si(OMe)_4$. (122°). S.G. $\frac{0}{}$ 1·0589. V.D. 5·38 (calc. 5·26). Formed by the action of $SiCl_4$ on dry methyl alcohol (Friedel a. Crafts, *A. Ch.* [4] 9, 32). Colourless liquid with fragrant ethereal odour; m. sol. water, the solution depositing gelatinous silica when kept for a month. When heated with $SiCl_4$ in various proportions it gives rise to the compounds $ClSi(OMe)_3$, (115°), S.G. $\frac{0}{}$ 1·195, V.D. 5·58 (calc. 5·42); $Cl_2Si(OMe)_2$, (c. 100°), S.G. $\frac{0}{}$ 1·260, V.D. 5·66 (calc. 5·57); and $Cl_3Si(OMe)$, (c. 84°), V.D. 5·66 (calc. 5·73).

Hexa-methyl disilicate $Me_6Si_2O_7$. (202°). S.G. $\frac{0}{}$ 1·144. V.D. 9·19 (calc. 8·93). Formed when, in the preparation of Me_4SiO_4, the methyl alcohol is not quite dry. Formed also by heating Me_4SiO_4 (2 mols.) with water (1 mol.) and methyl alcohol.

METHYL-STIBINE *v.* ANTIMONY, *Compounds with organic radicles*, vol. i. 293.

METHYL-STILBAZOL *v.* STYRYL-METHYL-PYRIDINE.

METHYL-STILBENE *v.* *s*-PHENYL-TOLYL-ETHYLENE.

Di-methyl-stilbene *v.* DI-TOLYL-ETHYLENE.

Tetra-methyl-stilbene *v.* DI-XYLYL-ETHYLENE.

METHYL-STRYCHNINE *v.* STRYCHNINE.

METHYL-STYRENE *v.* TOLYL-ACETYLENE.

METHYL STYRYL KETONE *v.* STYRYL METHYL KETONE.

METHYL-SUCCINIC ACID *v.* PYROTARTARIC ACID.

u-Di-methyl-succinic acid $C_6H_{10}O_4$ *i.e.* $CO_2H.CH_2.CMe_2.CO_2H$. *Isoadipic acid. Isobutane dicarboxylic acid.* Mol. w. 146. [140°]. H.C.v. 671,400. H.C.p. 671,700. H.F. 237,300 (Stohmann, Kleber, a. Langbein, *J. pr.* [2] 40, 212).

Formation.—1. From its imide, which is formed, together with di-methyl-malonamic acid, by oxidising mesitylic acid $C_8H_{13}NO_3$ with $KMnO_4$ in acid solution (Pinner, *B.* 15, 582).—2. By boiling with HClAq the isobutane tricarboxylic ether $CO_2Et.CMe_2.CH(CO_2Et)_2$ obtained by the action of α-bromo-isobutyric ether on sodio-malonic ether (Leuckart, *B.* 18, 2350; Bischoff, *B.* 23, 1943). Formed also by heating the corresponding isobutane tricarboxylic acid (Barnstein, *A.* 242, 133).—3. By oxidising with chromic acid mixture the terpene $C_{20}H_{32}$ obtained from copaiva balsam (Levy a. Engländer, *A.* 242, 192).—4. By oxidising tropilene C_7H_8 with nitric acid (S.G. 1·38) (Ladenburg, *A.* 217, 139).—5. By heating its nitrile (obtained from isobutylene bromide and KCy) with HClAq at 150° (Hell a. Rothberg, *B.* 22, 1740).

Properties.—Thick colourless prisms (from benzene), crystallising from water in efflorescent monoclinic forms; $a:b:c = 2·029:1:1·191$; $\alpha = 118° 36'$; $\beta = 95° 16'$; $\gamma = 101°$. V. sol. water, alcohol, ether, and acetone, v. sl. sol. chloroform and ligroïn. At about 185° it splits up into CO_2 and its anhydride.

Salts.—KHA″ $2\frac{1}{2}$aq: small prisms (P.).—KHA″ 5aq (B.).—NaHA″ $3\frac{1}{2}$aq. Monoclinic prisms; $a:b:c = 1·8365:1:4·1801$; $\beta = 90° 43'$ (L. a. E.).—Na_2A'' 11aq: needles, v. sol. water. — NH_4HA''. — $(NH_4)_2A''$. — BaA″ 2aq (B.). — BaA″ $2\frac{1}{2}$aq: monoclinic plates; $a:b:c = 1·601:1:1·790$; $\beta = 97° 26'$. Sl. sol. hot, m. sol. cold, water, insol. alcohol (L. a. E.). — CaA″ aq: minute plates, sl. sol. water, insol. alcohol.— —CdA″ 6aq. — CuA″ 2aq. — PbA″ aq. — Ag_2A'': white pp., v. sl. sol. water.

Methyl ether Me_2A'': (200°). S.G. $\frac{16}{16}$ 1·0568.

Ethyl ether Et_2A''. (215°). S.G. $\frac{17}{17}$ 1·0134 (B.); $\frac{17}{}$ ·9976 (L. a. E.).

Anhydride $\begin{matrix}CMe_2.CO\\CH_2\ .CO\end{matrix}\!\!>\!O$. [29°]. (218°) (B.); (220°) (L. a. E.).

Chloride $C_2H_2Me_2(C_2O_2Cl_2)$. (201°) (B.); (193°) (L. a. E.). Formed by heating the acid with PCl_5 at 125°. Reacts with phenyl-hydrazide, forming the compound $\begin{matrix}CMe_2.CO\\CH_2\ .CO\end{matrix}\!\!>\!N.NHPh$ [132°], which yields a nitrosamine [76°].

Imide $\begin{matrix}CMe_2.CO\\CH_2\ .CO\end{matrix}\!\!>\!NH$. [106°]. Formed from the chloride and NH_3. Plates (from ether). Yields $C_6H_8KNO_2$ $2\frac{1}{2}$aq, crystallising in prisms, v. sol. alcohol.

Nitrile $CN.CH_2.CMe_2.CN$. *Isobutylene cyanide.* (219°). Formed by leaving a mixture of isobutylene bromide and alcoholic KCy to stand for two weeks, heating to 140° to expel alcohol, and extracting the residue with ether (Hell a. Rothberg, *B.* 22, 1740). Clear liquid, v. sol. water.

Anti-*s*-di-methyl-succinic acid $C_6H_{10}O_4$ *i.e.* $CO_2H.CHMe.CHMe.CO_2H$. *Maleïnoid di-methyl-succinic acid. Butane dicarboxylic acid.* [120°] (O. a. R.; H. a. R.; B. a. V.); [124°] (Z.). S. 30 at 14°.

Formation.—1. Together with the isomeric 'para' or fumaroid acid [194°] by reduction of di-methyl-maleïc acid (Otto a. Rössing, *B.* 20, 2736).—2. Together with the isomeric acid [194°] by heating with HClAq the mixture of their ethers obtained by adding α-bromo-propionic ether to an alcoholic solution of α-cyano-propionic ether and NaOEt (Zelinsky, *B.* 21, 3160).—3. A mixture of the ethers of the two isomeric *s*-di-methyl-succinic acids is also formed, with other bodies, when α-bromo-propionic ether is heated with finely-divided silver (Hell a. Rothberg, *B.* 22, 60).—4. The mixture of 'anti-' and 'para' di-methyl-succinic acids is also formed by hydro-

lysis of butane tricarboxylic acid derived from sodium methyl-malonic ether and α-bromo-propionic ether (Leuckart, *B.* 18, 2346; Bischoff a. Voit, *B.* 22, 389).—5. From its anhydride, which is formed, together with the anhydride of the fumaroid isomeride, by heating the fumaroid acid [194°] for several hours at 200° (Bischoff a. Voit, *B.* 23, 641).

Properties.—Concentrically grouped prismatic needles, more sol. hot than cold water, v. sol. ether, alcohol, acetone, and chloroform, sl. sol. CS_2 and benzene, almost insol. ligroïn. A neutral solution of its ammonium salt gives a yellowish-red pp. with $FeCl_3$, a greenish-blue pp. with cupric sulphate, but no pp. with salts of Ba, Zn, Mg, Co, and Ni. Bromine at 130° converts it into di-methyl-maleïc acid [95°].

Salts.—CaA″2aq: crystalline powder, sl. sol. cold water.—BaA″3aq: thin plates, sl. sol. water.—Ag_2A'': white crystalline pp.

Methyl ether Me_2A''. (200°). From Ag_2A'' and MeI at 100°. Oil, with pleasant odour (Zelinsky a. Krapivin, *B.* 22. 646).

Ethyl ether Et_2A''. (222°). S.G. $\frac{0}{0}$ 1·0218; $\frac{18}{0}$ 1·0072 (Z. a. K.); $\frac{15}{15}$ 1·0315 (B. a. V.). H.C. 1,296,860 (Ossipoff, *C. R.* 109, 224). Oil, decomposed by heat into the anhydride and Et_2O.

Chloride (186°–197°).

Imide $\begin{matrix}\text{CHMe.CO}\\ \text{CHMe.CO}\end{matrix}\!>\!\text{NH}$. [106°] (B. a. V.): [110°] (Z. a. K.). Obtained by distilling the dry ammonium salt in gaseous NH_3. Stellate groups of prisms (from dilute alcohol) or thin needles (from benzene), v. sol. water, alcohol, benzene and chloroform, sl. sol. ether, v. sl. sol. ligroin. reconverted into the acid [120°] by alkalis.

Anilide CONHPh.CHMe.CHMe.CONHPh. [222°]. Formed from the chloride and aniline. Needles (from alcohol).

Phenyl-imide $\begin{matrix}\text{CHMe.CO}\\ \text{CHMe.CO}\end{matrix}\!>\!\text{NPh}$. [146°]. Formed by heating the acid (1 mol.) with aniline (2 mols.) till the aniline begins to distil. Slender needles, v. sol. alcohol, ether, and benzene, sl. sol. water.

Anhydride $\begin{matrix}\text{CHMe.CO}\\ \text{CHMe.CO}\end{matrix}\!>\!\text{O}$. [87°]. When formed by heating the 'anti' acid to 200°, it yields only the 'anti' acid again when heated with water; but when formed from the 'para' acid by like treatment the product (a mixture of anhydrides?) yields a mixture of 'para' and 'anti' acids, the amount of the latter increasing with the duration of the heating. Formed also from the 'anti' acid by heating with AcCl. In all cases it melts at 87°. When heated with bromine in chloroform at 90° it yields di-methyl-maleïc acid.

'*Para*'-*s*-di-methyl-succinic acid $C_6H_{10}O_4$ *i.e.* $MeCH(CO_2H).CHMeCO_2H$. *Fumaroid variety of s-di-methyl-succinic acid. Isoadipic acid. Hydropyrocinchonic acid.* [194°] (O. a. B.); (B. a. V.). (192°) (Z.). H.F. 238,000. H.C.v. 670,700. H.C.p. 671,000 (Stohmann, Kleber, a. Langbein, *J. pr.* [2] 40, 212). S. 1 at 22°.

Formation.—1. By heating α-bromo-propionic acid with reduced silver at 155° (Wislicenus, *B.* 2, 720; *cf. anti*-DI-METHYL-SUCCINIC ACID, *Formation* 3).—2. By boiling (αβ)-di-methyl-acetyl-succinic ether with conc. alcoholic KOH (Hardtmuth, *A.* 192, 143).—3. By boiling an aqueous solution of sodium di-methyl-maleate with sodium-amalgam (Weidel, *A.* 173, 109; *M.* 3, 612).—4. From its amide which is formed by the action of NH_3 on an oily product of the action of bromine on a solution of cyano-ethine in dilute H_2SO_4 (E. von Meyer, *J. pr.* [2] 26, 358).—5. Together with the isomeride [120°] by the reduction of di-methyl-maleïc anhydride by HIAq at 220° or by sodium-amalgam (Otto a. Beckurts, *B.* 18, 838; Otto a. Rössing, *B.* 20, 2736).—6. By heating cyano-di-methyl-succinic acid with HClAq (Zelinsky, *B.* 21, 3166).—7. Together with the 'anti' isomeride, by all the modes of formation described above for that acid.—8. By heating the 'anti' isomeride for several hours with conc. HClAq at 180°–190° (Bischoff a. Voit, *B.* 23, 643).

Properties.—Small triclinic needles (from alcohol), sl. sol. water, m. sol. alcohol. On heating at 200° it yields a mixture of its anhydride and that of the 'anti' acid; after several hours' heating it is almost wholly converted into the anhydride of the 'anti' acid. Its neutral solution is ppd. by $FeCl_3$, $CuSO_4$, $BaCl_2$, and lead acetate. On treatment with bromine it yields di-methyl-maleïc acid.

Salts.—NH_4HA'' (dried at 100°). Monoclinic prisms, v. sol. water.—CaA″2aq: prisms (Bischoff a. Rach, *A.* 234, 76).—CaA″aq (Z.).—CaA″1½aq (W.). Monoclinic needles.—SrA″.—BaA″4aq.—PbA″.—PbA″½aq: short prisms.—CuA″.—Ag_2A''.

Methyl ether Me_2A''. (199°). Oil (Zelinsky a. Krapivin, *B.* 22, 650). Yields the acid [192°] on saponification.

Ethyl ether Et_2A''. (220°). S.G. $\frac{0}{0}$ 1·013; $\frac{12}{0}$ 1·002. H.C. 1,303,570. Oil, with pleasant odour. Yields on saponification a mixture of the acids [120°] and [192°].

Chloride (186°–197°).

Imide $\begin{matrix}\text{MeCH — CO}\\ \text{CHMe.CO}\end{matrix}\!>\!\text{NH}$. [78°]. From the ether and NH_3. Crystallises from benzene. Yields only the 'para' acid on saponification.

Anilide MeCH(CONHPh).CHMe.CONHPh. [235°]. From the chloride and aniline. Needles, sol. ether and HOAc. Yields only the 'para' acid on saponification.

Phenyl-imide $\begin{matrix}\text{MeCH .CO}\\ \text{CHMe.CO}\end{matrix}\!>\!\text{NPh}$. [126°]. Formed by heating the acid with aniline. Caustic potash converts it into a mixture of 'anti' and 'para' acids.

Anhydride $\begin{matrix}\text{MeCH .CO}\\ \text{CHMe.CO}\end{matrix}\!>\!\text{O}$. [38°]. Formed from the acid and AcCl. May be reconverted into the original acid. By heating the 'para' acid to 180°–196° a mixture of anhydrides [87°] is formed, which yields on saponification a mixture of 'anti' and 'para' acids.

Derivative.—*v.* DI-CHLORO-DI-METHYL-SUCCINIC ACID.

Tri-methyl-succinic acid $C_7H_{12}O_4$ *i.e.* $CO_2H.CHMe.CMe_2.CO_2H$. [105°]. *Electrical conductivity*: Bischoff, *B.* 23, 1466. Formed by the hydrolising action of H_2SO_4 on pentane tricarboxylic ether obtained from sodium methyl-malonic ether and α-bromo-isobutyric ether (Bischoff a. Mintz, *B.* 23, 649). Yields an anhydride melting between 67° and 82°.

This acid is probably identical with *s*-di-

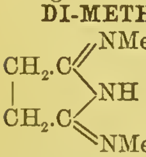
methyl-glutaric acid (Bischoff a. Jannsnicker, *B.* 23, 3403).

Tetra-methyl-succinic acid $C_8H_{14}O_4$ *i.e.* $CO_2H.CMe_2.CMe_2.CO_2H$. *Hexane dicarboxylic acid.* Mol. w. 174. [192°]. Formed, together with the isomeric tri-methyl-glutaric acid [97°], by heating α-bromo-isobutyric ether (3 pts.) with dry silver powder (2 pts.) at 125° for 8 hours. The product is fractionally distilled, and the fraction 200°–250° saponified by heating with HBrAq at 100°. The resulting acids may be separated by steam distillation, tetra-methyl-succinic acid alone passing over (Hell, *B.* 7, 320; 10, 2229; Auwers a. V. Meyer, *B.* 22, 2014, 3005; 23, 299).

Properties.—Short branching crystals, melting at 200° when quickly heated, and 192° when slowly heated; sl. sol. cold water, m. sol. hot water, ether, chloroform, and CS_2, v. sol. alcohol and benzene, almost insol. ligroïn.

Anhydride [147°]. (230·5°). Formed by heating the acid alone, with HClAq at 200°, or with AcCl at 100°. Formed also by treating the acid (6 g.) with red phosphorus (·8 g.) and bromine (16 g.). Slender needles (from ligroïn). May be sublimed. Soon becomes resinous. Nearly insol. cold water and cold Na_2CO_3Aq, slowly dissolved by these liquids on heating, being converted into the acid.

DI-METHYL-SUCCINIMIDINE $C_6H_{11}N_3$ *i.e.*



. The hydrochloride of this base is formed by the action of methylamine on succinimido-ether. — B'HCl: glistening prisms, [248°], v. sol. water, sl. sol. alcohol (Pinner, *B.* 16, 1658).

METHYL-SUCCINURIC ACID. *Amide* $NH_2.CO.NMe.CO.CH_2.CH_2.CONH_2$ (?). [205°–207°]. Formed from methyl-succinyl-urea $CO<\begin{matrix}NMe.CO.CH_2\\NH\ .CO.CH_2\end{matrix}$ and alcoholic NH_3 at 100° (Menschutkin, *A.* 178, 210). Plates, v. sl. sol. boiling alcohol.

DI-METHYL-SULPHAMIC ACID $C_2H_7NSO_3$ *i.e.* $NMe_2.SO_2.OH$ [165°]. Formed, together with hydrogen di-methyl-ammonium sulphate $NMe_2H_2.O.SO_2.OH$, by boiling its chloride with water (Behrend, *B.* 15, 1610; *A.* 222, 130). Large six-sided plates (from alcohol), v. sol. water, m. sol. alcohol, sl. sol. ether. By boiling with water, alkalis, or dilute nitric acid, it is converted into $(NMe_2H_2)SO_4H$. It expels CO_2 from carbonates.

Salts.—BaA'_2 aq: plates, v. sol. water.—PbA'_2 aq.—AgA' aq: v. e. sol. water, ppd. by adding ether to its alcoholic solution.

Ethyl ether EtA'. From the chloride and NaOEt. Oil.

Chloride $NMe_2.SO_2Cl$. (183° at 760 mm.; 114° at 75 mm.). Formed by heating dimethylamine hydrochloride (1 mol.) with SO_2Cl_2 ($1\frac{1}{2}$ mols.) on the water-bath, the yield being 50 p.c. of the theoretical. The product is mixed with water, and the chloride extracted with ether, shaken with aqueous Na_2CO_3, dried over $CaCl_2$, and distilled (Behrend). Golden-yellow oil, partially decomposing on distillation with evolution of HCl. V. sol. alcohol, ether, benzene, and chloroform, insol. water, HClAq, and KOHAq. Boiling water decomposes it into HCl, H_2SO_4, $NMe_2.SO_2OH$, and dimethylamine. Sodium-amalgam reduces it to H_2S, dimethylamine, and H_2SO_4. Tin and HClAq act in like manner. Zinc-dust yields tetra-methyl-sulphamide.

Amide v. DI-METHYL-SULPHAMIDE.

Dimethylamide v. TETRA-METHYL-SULPHAMIDE.

Di-ethyl-amide $NMe_2.SO_2.NEt_2$. (229°). From the chloride and NEt_2H. Oil, partially decomposed on distillation.

***u*-DI-METHYL-SULPHAMIDE** $NMe_2.SO_2.NH_2$. [96°]. Formed by passing NH_3 into the chloride of di-methyl-sulphamic acid (Behrend, *B.* 15, 1611; *A.* 222, 126). Six-sided prisms with pyramidal ends, v. sol. water and alcohol, m. sol. ether.

s-**Di-methyl-sulphamide** $NHMe.SO_2.NHMe$. [78°]. Prepared by the action of methylamine on SO_2Cl_2 in ethereal solution at 0° (Franchimont, *R. T. C.* 3, 418). Prisms, v. e. sol. water and alcohol, v. sl. sol. benzene. Tastes sweet. Nitric acid converts it into $SO_2(NMe.NO_2)_2$.

Tetra-methyl sulphamide $SO_2(NMe_2)_2$. [73°]. Formed from SO_2Cl_2 and $NHMe_2$ dissolved in chloroform (Behrend, *B.* 14, 722; *A.* 222, 119). Formed also from $NMe_2.SO_2Cl$ and $NHMe_2$. Colourless plates (from alcohol), v. sol. alcohol and ether, v. sl. sol. water, aqueous acids and alkalis. May be sublimed. Dry HCl at 120° decomposes it into $NMe_2.SO_2Cl$ and $NHMe_2$. Conc. HNO_3 yields NMe_2NO_2 (Franchimont, *R. T. C.* 3, 420).

METHYL SULPHATES. Mono-methyl sulphate $CH_3O.SO_2.OH$. *Methyl-sulphuric acid.* Formed by mixing methyl alcohol (1 pt.) with H_2SO_4 (2 pts.), allowing the hot mixture to cool, diluting with water, adding $BaCO_3$, filtering and evaporating. The barium salt thus obtained is then decomposed by H_2SO_4 (Dumas a. Péligot, *A. Ch.* [2] 58, 54; 61, 199; *A.* 15, 40; Kane, *P. M.* 7, 397). Formed also from $Cl.SO_2.OH$ and methyl alcohol (Claesson, *J. pr.* [2] 19, 240). Liquid, not solidified at −30°; v. e. sol. water, m. sol. alcohol, miscible with dry ether. Yields Me_2SO_4 and H_2SO_4 on distillation. When the potassium salt is heated with potassium acetate methyl acetate is formed; methyl ethers of other acids are formed in like manner.

Salts.—$KMeSO_4$ aq: very deliquescent monoclinic tables; $a:b:c = ·742:·779:1$; $\beta = 86° 51'$ (Schabus, *J.* 1854, 552).—$Ca(MeSO_4)_2$: very deliquescent octahedra.—$Ba(MeSO_4)_2$ 2aq: monoclinic tables; $a:b:c = ·824:1·907:1$; $\beta = 83° 30'$. S.G. $\frac{19·2}{}$ 2·273.—$Pb(MeSO_4)_2$ aq: long deliquescent prisms, v. sol. water.—$UrO_2(MeSO_4)_2$ aq: very deliquescent crystals (Péligot, *A.* 56, 231).

Chloride $MeO.SO_2Cl$. (132·5°) at 722 mm. Formed from SO_2Cl_2 (1 mol.) and MeOH (1 mol.) (Behrend, *J. pr.* [2] 15, 32). Formed also from MeOCl and SO_2 (Sandmeyer, *B.* 19, 861). Pungent oil, decomposed by water into HCl and $MeO.SO_2.OH$.

Di-methyl sulphate Me_2SO_4. Mol. w. 126. (188°). S.G. $\frac{22}{}$ 1·324 (D. a. P.).

Formation.—1. From Me_2O and SO_3.—2. By dry distillation of $MeHSO_4$ (Dumas a. Péligot; Claesson, *J. pr.* [2] 19, 244; *B.* 13, 1699).—3. By distilling methyl alcohol (1 pt.) with conc. H_2SO_4 (9 pts.), washing the distillate with water,

drying the oily layer with $CaCl_2$, and rectifying (Dumas a. Péligot, *A. Ch.* [2] 58, 32).

Properties.—Oil, decomposed by boiling water and by alkalis into MeOH and H_2SO_4. An ethereal solution of NH_3 forms $MeO.SO_2.ONH_3Me$. Distillation with fused NaCl forms MeCl and Na_2SO_4. Distillation with KOBz yields MeOBz and K_2SO_4. Sodium formate yields methyl formate and sodium sulphate. It forms double compounds with sulpho-acetates, sulpho-benzoates, and isethionates (Geuther, *A.* 218, 288).

METHYL SULPHIDE $(CH_3)_2S$. Mol. w. 62. (41°) (R.); (37°) (K.). S.G. $\frac{20}{}$ ·845. H.F.p. 12,730. H.F.v. 11,570. S.V. 75·6 (Lossen, *A.* 254, 71). Formed by passing MeCl into a solution of K_2S in MeOH (Regnault, *A. Ch.* [2] 71, 391; *A.* 34, 26). Prepared by distilling a concentrated solution of $MeNaSO_4$ (from 500 c.c. MeOH) with aqueous KOH (500 g.) that has been previously half saturated with H_2S; the yield being moderate (150 g.). Colourless mobile liquid with very unpleasant odour (Klason, *B.* 20, 3407).

Reactions.—1. Takes fire when dropped into dry *chlorine*, but if the temperature be kept low oily substitution products $(CH_2Cl)_2S$, $(CHCl_2)_2S$, and $(CCl_3)_2S$ may be obtained (Riche, *A. Ch.* [3] 43, 283). The compound $(CCl_3)_2S$ boiled at 156°–160° and gave a V.D. 5·68 (calc. 9·41).—2. *Iodo-acetic ether* forms $S(CH_2.CO_2Et)_2$, tri-methyl-sulphine iodide, and $Me_2S(CH_2.CO_2Et)_2$ (Letts, *Tr. E.* 28, 618).—3. *Bromo-acetic ether* forms $Me_2SBr.CH_2.CO_2Et$ which crystallises in pearly scales and yields when treated with moist Ag_2O unstable $Me_2S(OH).CH_2.CO_2Et$ (Letts).

Combinations.—Me_2SBr_2. Crystals (Cahours, *A.* 135, 355). When dissolved in water it gives off HBr. When its alcoholic solution is treated with zinc and the product evaporated and mixed with $HgCl_2$, there is formed a pp. of $(SMe_2)_2HgCl_2ZnBr_2$ (Patein, *Bl.* [2] 50, 201).—Me_2SI_2. Crystals resembling iodine.—Me_2SHgCl_2.—$(Me_2S)_2PtCl_4$ (Loir, *A.* 107, 234). Yellow crystalline powder. Melts with decomposition at 218° (Blomstrand, *J. pr.* [2] 38, 365).—$(Me_2S)_2PtCl_2$. [159°]. Formed by the action of Me_2S on potassium platinum chloride at 60° (Blomstrand, *J. pr.* [2] 38, 358). Exists in two allotropic forms, crystallising in lemon-yellow monoclinic crystals, and in yellow dimetric plates (containing $CHCl_3$).—$(Me_2S)(Et_2S)PtCl_2$. Formed from $(Et_2S)_2PtCl_2$ and Me_2S.—$(Me_2S)_2PtCl_2Br_2$.—$(Me_2S)_2PtBr_4$: reddish-brown monoclinic crystals (from chloroform).—$(Me_2S)_2PtBr_2$. Formed from $(Me_2S)_2PtSO_4$ and KBr (B.). Yellow monoclinic crystals.—$(Me_2S)_2PtI_2Cl_2$: greenish-black crystalline powder. — $(Me_2S)_2PtI_2Br_2$. — $(Me_2S)_2PtI_4$: black crystalline powder.—$(Me_2S)_2PtI_2$. [172°]. Formed from $(Me_2S)_2Pt(NO_3)_2$ and KI (B.). Red crystals.—$(Me_2S)_2Pt(NO_3)_2$. [156°]. Formed from $(Me_2S)_2PtCl_2$ and $AgNO_3$ (B.). Small brownish needles.—$(Me_2S)_2Pt(NO_2)_2$. Formed from $(Me_2S)_2PtSO_4$ and potassium nitrite (B.). Small white plates, soluble in chloroform.—$(Me_2S)_2PtSO_4$ 2aq. [91°]. Formed from silver sulphate and $(Me_2S)_2PtCl_2$. Yellowish crystalline mass, v. sol. water.—$(Me_2S)_2PtCrO_4$: reddish-brown pp. got by adding K_2CrO_4 to a solution of $(Me_2S)_2PtSO_4$. Sl. sol. water, insol. alcohol and chloroform.

Methylo-iodide SMe_3I. *Tri-methyl-sulphine iodide.* Formed, even in the cold, by the union of Me_2S with MeI (Cahours, *C. R.* 80, 1317; 81, 1163; *A. Ch.* [5] 10, 13; *A.* 135, 355; 136, 151). Formed also by heating MeI at 100° with ppd. As_2S_3 or with Na_2S (Klinger, *B.* 15, 881; *A.* 252, 357) and by heating SEt_3I with MeOH at 140° (Klinger a. Maassen, *A.* 252, 252). Large prisms (from water), v. sol. hot water, sl. sol. alcohol, insol. ether. Its aqueous solution is partially decomposed on evaporating at 100°, forming Me_2S and iodine. Moist Ag_2O yields $SMe_3.OH$, a strongly alkaline base whence the other salts may be prepared by neutralisation with acids. An aqueous solution of SMe_3I gives with alcoholic $HgCl_2$ a pp. of Me_3SIHgI_2 which forms pale-yellow needles, nearly insol. water and ether, sol. alcohol (Patein, *Bl.* [3] 2, 159). Bromine forms Me_3SIBr_2, which separates from hot alcohol in orange-red crystals [95°] which in alcoholic solution give with platinic chloride a pp. of $(Me_3SCl)_2PtCl_4$ (Dobbin a. Masson, *C. J.* 47, 56). Tri-methyl-sulphine di-bromo-iodide is converted by dry NH_3 into $Me_3SIBr_2N_2H_6$, an amorphous light-green mass [75°–80°]. Chlorine forms Me_3SICl_2, which separates from alcohol in yellow crystals [104°], converted by aqueous ammonia into iodide of nitrogen and by gaseous ammonia into $Me_3SICl_2 2NH_3$ an unstable compound which loses ammonia and absorbs water when exposed to air (D. a. M.). The compound $(Me_3SI)_3As_2I_6$ is formed by heating As_2S_3 with MeI at 100° and crystallises in blue-black needles (Klinger a. Maassen, *A.* 252, 260). The compound Me_3SISnI_2 crystallises in yellow needles, sl. sol. cold water. The compound $(Me_3SI)_2CdI_2$, formed by heating CdS with MeI at 100°, crystallises from water or alcohol in white needles, melting at 185° when slowly heated and 195° when quickly heated, and converted by aqueous CdI_2 into Me_3SICdI_2 [168°].

Methylo-chloride Me_3SCl. From the base and HCl. Deliquescent prisms. Gives the salts $(Me_3SCl)_2PtCl_4$ crystallising from hot water in sparingly soluble orange-yellow prisms and Me_3SAuCl_4 crystallising in thick prisms, v. e. sol. water. Me_3SCl shaken with an ethereal solution of iodine yields reddish-black crystals of Me_3SI_2Cl, which is probably also formed from Me_3SI and ICl (Dobbin a. Masson). Me_3SCl is converted by ICl into Me_3SICl_2. Dry chlorine forms Me_3SCl_3, a yellow liquid, solidifying on exposure to air. Decomposed by water, alcohol, and ether, into Me_3SCl and chlorine.

Methylo-bromide Me_3SBr. Formed from $Me_3S.OH$ and HBr. Also formed from Me_2S and MeBr. Prisms, v. sol. water. Converted by iodine in ethereal solution into Me_3SBrI_2. With ICl it forms $Me_3SClBrI$ as yellow crystals [87°], completely decomposed at 190°.

Methylo-sulphydrate $Me_3S.SH$ aq. From $Me_3S.OH$ and H_2S (Brown a. Blaikie, *J. pr.* [2] 23, 395).

Methylo-sulphide $(Me_3S)_2S$. *Tri-methyl-sulphine sulphide.* An aqueous solution of this body may be got by saturating one half of a conc. solution of $Me_3S.OH$ with H_2S, and adding the other half. This solution, if allowed to evaporate in dry air or in coal-gas, when it reaches a certain strength forms Me_2S, thus: $(Me_3S)_2S = 3Me_2S$ (Crum Brown a. Blaikie, *Pr. E.* 9, 563; *C. N.* 37, 130). On gently heating a solution of $(Me_3S)_2S$ in a sealed tube, Me_2S

separates as an upper layer. The aqueous solution has the characters of an alkaline sulphide, dissolving sulphur (forming $(Me_3S)_2S_5$) and Sb_2S_3. Acids decompose it with evolution of H_2S.

Methylo-thiosulphate $(Me_3S)_2S_2O_3$ aq. Formed by exposing an aqueous solution of $(Me_3S)_2S$ to atmospheric oxidation. Formed also by exposing $(Me_3S)_2S_5$ to air. Hygroscopic four-sided prisms, sl. sol. alcohol. Decolourises a solution of iodine. At 135° it is decomposed into Me_2S and $Me_3S.O.SO_2.SMe$, a white crystalline mass [100°] which does not act upon iodine but slowly oxidises to sulphate (Crum Brown a. Blaikie, *J. pr.* [2] 23, 395).

Methylo-sulphite $(Me_3S)_2SO_3$ $x$aq. Formed from the hydroxide by saturating one half of its solution with SO_2, and adding the other half (Crum Brown a. Blaikie, *Pr. E.* 9, 712). Crystals. Gives off water of crystallisation at 140°. At 170° it gives off Me_2S, leaving a liquid residue, which solidifies on cooling, and is apparently $(Me_3S)SO_3Me$.

Methylo-dithionate $(Me_3S)_2S_2O$ 6aq. Formed from $Me_3S.OH$ and dithionic acid. Deliquescent cubes, insol. alcohol. Decomposes at 220° into SO_2 and $(Me_3S)_2SO_4$, and the latter then further decomposes into Me_2S and $Me_3S.SO_4Me$.

Methylo-metaphosphate $Me_3S.PO_3$. From $AgPO_3$ and Me_3SI. Hygroscopic glassy mass, giving off Me_2S on heating.

Methylo-ferrocyanide $(Me_3S)_4FeCy_6$ 9aq. From Me_3SI and silver ferrocyanide. Transparent green plates, which lose their water in a desiccator, and then give off Me_2S at 220°.

Methylo-ferricyanide $(Me_3S)_3FeCy_6$ $7\frac{1}{2}$aq. From Me_3SI and silver ferricyanide (Crum Brown a. Blaikie, *Pr. E.* 10, 253). Pale-orange efflorescent plates.

The *methylo-chromate* and *methylo-iodate* explode at 140°.

Methylo-carbonate $(Me_3S)_2CO_3$. Formed from Me_3SI and Ag_2CO_3, the liquid being evaporated to a syrup and left to crystallise over H_2SO_4. Deliquescent prisms, with strong alkaline reaction. At 100° it is split up into CO_2, water, Me_2S, and methyl alcohol.

Methylo-oxalate $(Me_3S)_2C_2O_4$ aq. Formed from $Ag_2C_2O_4$ and Me_3SI. Deliquescent crystals. Split up at 140° into Me_2S and methyl oxalate.

Methylo-acetate ×$Me_3S.OAc$. Formed from Me_3SI and AgOAc (Crum Brown a. Blaikie, *Pr. E.* 10, 53; *C. N.* 39, 51). Split up at 100° into Me_2S and MeOAc.

Methylo-benzoate ×$Me_3S.OBz$. From the iodide and AgOBz. Thin plates (from alcohol). Decomposed by heat into Me_2S and MeOBz.

Ethylo-iodide SMe_2EtI. *Di-methyl-ethyl-sulphine iodide.* [110°]. Formed either from Me_2S and EtI or MeEtS and MeI (Klinger a. Maassen, *A.* 243, 212; 252, 246; *cf.* Krüger, *J. pr.* [2] 14, 193). Hygroscopic crystalline mass, v. e. sol. alcohol, insol. ether. Yields on distillation Et_3SI and Me_3SI. In alcoholic solution it reacts with AgCy at 90°, forming $SMe_2EtCyAgCy$, a deliquescent crystalline body, v. sol. alcohol, insol. ether, and decomposed by heat into AgCy and SMe_2EtCy (Patein, *C. R.* 106, 861). Forms the following compounds:—$(Me_2SEtI)_2CdI_2$ [180°], crystallising in small needles, sl. sol. water.—$Me_2SEtICdI_2$ [99°], crystallising from hot conc. CdI_2Aq in long needles.—$Me_2SEtIHgI_2$. [66°] (Patein, *Bl.* [3] 2, 159).

Ethylo-chloride Me_2SEtCl. The following compounds of this body have been prepared (Klinger a. Maassen, *A.* 243, 212):—$Me_2SEtCl(HgCl_2)_2$: [119°]; long needles, insol. hot water.—$Me_2SEtCl(HgCl_2)_6$: [200°]; white crystalline powder, slightly soluble in water.—$(Me_2SEtCl)_2PtCl_4$: [c. 213°]; small orange crystals, sl. sol. water, insol. alcohol and ether.—$Me_2SEtClAuCl_3$: [244°]; long yellow needles, m. sol. hot water.

Di-methyl disulphide $C_2H_6S_2$ *i.e.* Me_2S_2. (117°) (C.); (112° at 744 mm.) (Pierre, *A.* 80, 128). S.G. $\frac{18}{}$ 1·046 (C.). V.D. 3·30. S.V. 100·6 (Lossen, *A.* 254, 71). Formed by passing MeCl through an alcoholic solution of K_2S_2, or by distilling $Ca(SO_4Me)_2$ with K_2S_2 (Cahours, *A. Ch.* [3] 18, 157; *A.* 61, 92). Liquid, with intolerable odour of onions, v. sl. sol. water, miscible with alcohol and ether. Burns with blue flame. Chlorine converts it first into crystalline $Me_2S_2Cl_2$, and finally into a liquid mixture of $(CCl_3)_2S$ and SCl_2 (Riche, *A.* 92, 356). Dilute nitric acid converts it into methyl methane thiosulphonate $MeSO_2.SMe$.

Derivative.—*v.* PER-CHLORO-METHYL DI-SULPHIDE.

Di-methyl trisulphide Me_2S_3. (170°) at 760 mm. S.G. $\frac{0}{0}$ 1·2162; $\frac{10}{0}$ 1·2059; $\frac{17}{0}$ 1·199. Formed together with Me_2S_4 and S from methyl mercaptan and S_2Cl_2 (Klason, *B.* 20, 3414). Formed also from MeCl and K_2S_5 (Cahours). Pale-yellow liquid, with very disagreeable odour.

Derivative.—*v.* HEXA-BROMO-DI-METHYL TRI-SULPHIDE.

METHYL SULPHITE $C_2H_6SO_3$ *i.e.* $SO(OMe)_2$. (121·5°). S.G. $\frac{16.2}{4}$ 1·0456. V.D. 3·68 (calc. 3·80). Formed by the action of methyl alcohol on S_2Cl_2 or on $SOCl_2$ (Carius, *A.* 110, 209; 111, 93). Colourless liquid, with pleasant odour, miscible with alcohol and ether. It dissolves slowly in water with evolution of SO_2 and formation of MeOH.

METHYL SULPHOCYANIDE C_2H_3NS *i.e.* MeSCy. (133°). S.G. $\frac{16}{}$ 1·115 (C.); $\frac{4}{4}$ 1·069 (Nasini a. Scala, *G.* 17, 66). R_∞ 33·8. S.V. 78·1 (Lossen, *A.* 254, 73). H.F.p. −31,410. H.F.v. −31,990 (Thomsen, *Th.*). Obtained by distilling potassium sulphocyanide with calcium methyl sulphate (Cahours, *A. Ch.* [3] 18, 261; *A.* 61, 95). Liquid with alliaceous odour, v. sl. sol. water, miscible with alcohol and ether. Boiling nitric acid oxidises it to methane sulphonic acid. Chlorine acts upon it according to the equation:—$3MeSCN + 11Cl_2 = Cl_3Cy_3 + 2CSCl_4 + CSCl_2 + 9HCl$ (James, *J. pr.* [2] 35, 462). Cold aqueous KOH does not attack it, but alcoholic potash forms Me_2S_2, ammonia, KCy, and K_2CO_3. Alcoholic KSH forms KSCy and Me_2S. When heated at 180° it partially changes to methyl thiocarbimide.

Methyl polysulphocyanide $(CH_3CNS)_3$ (?) [188°]. Prepared by heating methyl sulphocyanide to 180° with a trace of HCl (Hofmann, *B.* 13, 1349). Sublimable. Colourless crystals. Sol. acetic acid, insol. acids and alkalis. By heating with alcoholic NH_3 to 150° it gives a well-crystallising base.

METHYL-SULPHONAMIDES v. METHYL SULPHAMIDES.

DI-METHYL-SULPHONE $C_2H_6SO_2$ *i.e.* Me_2SO_2. Mol. w. 94. [109°]. (238°). R_∞ 32·09 in a 2·46 aqueous solution (Kanonnikoff, *J. R.* 15, 451). Formed by oxidising Me_2S with fuming HNO_3 (Saytzeff, *A.* 144, 148) or with aqueous $KMnO_4$ (1:30) (Beckmann, *J. pr.* [2] 17, 454). Thick needles (from alcohol). Not affected by reducing agents.

DI-METHYL-SULPHONE DI-CARBOXYLIC ACID $O_2S(CH_2.CO_2H)_2$. *Sulphono-di-acetic acid.* [182°]. Formed by oxidation of thio-di-glycollic (sulphido-diacetic) acid in alkaline solution with $KMnO_4$ (Lovén, *B.* 17, 2817). Long trimetric tables. V. sol. water, alcohol, and ether. At 200° it splits up into di-methyl-sulphone and CO_2.

Salts.—$A''Ba$ 5aq: fine felted sparingly soluble needles.—$A''Ba$ aq: small prisms.

Ethyl ether $A''Et_2$: thick oil.

Amide $O_2S(CH_2.CONH_2)_2$: glistening plates, v. sol. hot water, slightly in cold.

METHYL-SULPHONIC ACID v. METHANE SULPHONIC ACID.

METHYL SULPHOXIDE $(CH_3)_2SO$. The nitrate $(CH_3)_2SOHNO_3$ is formed by oxidising methyl sulphide with conc. HNO_3Aq and crystallises in deliquescent needles, whence $BaCO_3$ sets free the oxide (Saytzeff, *A.* 144, 148). Oil, v. sol. water. Solidifies when strongly cooled. Reduced by zinc and H_2SO_4 to methyl sulphide Me_2S.

METHYL-SULPHURIC ACID v. METHYL SULPHATES.

METHYL SULPHYDRATE v. METHYL MERCAPTAN.

METHYL-TARCONIC ACID v. NARCOTINE.

DI-METHYL-TARTARIC ACID $C_6H_{10}O_6$ *i.e.* $CO_2H.CMe(OH).CMe(OH).CO_2H$. *Di-oxy-di-methyl-succinic acid.* Formed, together with lactic acid, by the action of zinc and a little HClAq on pyruvic acid in alcoholic solution (Böttinger, *A.* 188, 315; *B.* 9, 1064, 1621). Syrup.—KHA'': small six-sided plates, v. sl. sol. water.—K_2A'': needles, m. sol. water.—BaA'' 3½aq: prismatic needles, sl. sol. water.—CaA'': crystalline pp., nearly insol. water.

METHYL-TAURINE v. METHYL-AMIDO-ETHANE SULPHONIC ACID.

METHYL-TAURO-CYAMINE v. METHYL-GUANIDO-ETHANE SULPHONIC ACID.

METHYL-TEREPHTHALIC ACID v. TOLUENE DICARBOXYLIC ACID.

Di-methyl-terephthalic acid v. XYLENE DICARBOXYLIC ACID.

METHYL-TELLURIDE v. TELLURIUM, ORGANIC COMPOUNDS.

METHYL TETRADECYL KETONE $C_{16}H_{32}O$ *i.e.* $CH_3.CO.C_{14}H_{29}$. [43°]. (231°). Formed by distilling a mixture of barium pentadecoate and barium acetate (Krafft, *B.* 15, 1707). Yields myristic and acetic acids on oxidation.

DI-METHYL-THETINE $C_4H_8SO_2$ *i.e.* $CH_2<^{SMe_2}_{CO}>O$. *Anhydride* of the *methylo-hydroxide* of the *methyl derivative* of *thioglycollic acid.* Obtained by decomposing its hydrobromide with moist Ag_2O, or its sulphate with baryta (Crum Brown a. Letts, *Tr. E.* 28, 571; *B.* 6, 1384; 7, 695). Crystals (containing aq). Hygroscopic, but gives up the water over H_2SO_4. V. sol. water, m. sol. alcohol. Neutral in reaction. Decomposes when heated into CO_2 and $(Me_3S)_2CO_3$, the methylo-carbonate of di-methyl sulphide. Yields di-methyl-sulphone when oxidised by $KMnO_4$. The following compounds may be styled its salts:—$Me_2SBr.CH_2.CO_2H$. Formed from bromo-acetic acid and Me_2S. Large deliquescent rectangular plates (from alcohol). Acid to litmus. With lead oxide it forms $C_4H_8SO_22PbBr_2$. Decomposed by heat or by boiling alcohol into SMe_3Br, methyl bromide, and $S(CH_2.CO_2H)_2$ (Letts, *Tr. E.* 28, 591). Yields methane sulphonic acid on oxidation (Letts, *Tr. E.* 28, 601).—$(C_4H_9SO_2Br)_2PtBr_4$ (?): dark-red crystals.—$Me_2SCl.CH_2.CO_2H$. Formed from the sulphate and $BaCl_2$. Deliquescent crystals, v. sol. water, v. sl. sol. alcohol.—$(C_4H_8SO_2)_2HI$(?).—$Me_2SI_3.CH_2.CO_2H$. Formed by leaving di-methyl-thetine in contact with dilute HIAq. Crystals, insol. water, sol. alcohol and ether.—$SO_4(SMe_2.CH_2.CO_2H)$. *Di-methyl-thetine sulphate.* Formed from $Me_2SBr.CH_2.CO_2H$ and silver sulphate. Crystalline mass, sol. water, v. sl. sol. alcohol. Acid to litmus. When heated over 140° it fuses and splits up into CO_2 and $(Me_3S)_2SO_4$, the methylo-sulphate of di-methyl sulphide. — $Me_2S(NO_3).CH_2.CO_2H$. From $Me_2SBr.CH_2.CO_2H$ and $AgNO_3$. Colourless crystals with acid reaction. Yields di-methyl-sulphone when oxidised by conc. HNO_3.

METHYL-THIALDINE $C_7H_{15}NS_2$. [79°]. Obtained on treating crude thio-acetic aldehyde with an aqueous solution of methylamine (W. Markwald, *B.* 19, 2378). Long needles (from alcohol); insol. water, sl. sol. cold alcohol, v. e. sol. hot alcohol and ether. Its solutions possess a feeble alkaline reaction. Volatilises in steam with partial decomposition. With acids it forms very soluble salts.

μ-METHYL-THIAZOLE C_4H_5NS *i.e.* $^{S.CMe}_{CH:CH}>N$. (128° cor.). Formed by boiling thioacetamide $CH_3.CS.NH_2$ with chloro-acetal (Hantzsch, *A.* 250, 270), or with di-chloro-di-ethyl oxide (Hantzsch, *B.* 21, 943). Mobile liquid, miscible with water. Its hydrochloride and hydrobromide form hygroscopic needles. With mercuric chloride it forms compounds melting at 112° and 154°. $B'_2H_2PtCl_6$. [199°]. Hexagonal plates or flat needles (from water).—Picrate. [146°]. Yellow needles; sl. sol. water, v. sol. alcohol and benzene.

(α)-Methyl-thiazole $^{S——CH}_{CH:CMe}>N$. (132°).

Obtained by distilling oxy-methyl-thiazole (from chloro-acetone and metallic sulphocyanides) with zinc-dust (Hantzsch a. Arapides, *B.* 21, 942); *A.* 249, 24). Formed also by boiling with alcohol the diazo- compound derived from amido-methyl-thiazole (from chloro-acetone and thio-urea) (Popp, *A.* 250, 277). Colourless liquid, sinking under water, but slowly dissolving; v. sol. alcohol and ether. The hydrochloride is deliquescent. It forms two compounds with $HgCl_2$, melting at 119° and 148°. The aurochloride melts at 185°, and the picrate at 174°. — $B'_2H_2PtCl_6$. [204°]. Orange prisms; m. sol. water, sl. sol. alcohol.

$\alpha\mu$ - **Di - methyl - thiazole** C_5H_7NS *i.e.* $\begin{matrix}S.CMe\\CH:CMe\end{matrix}\gg N$. (145° cor.). S.G. $\frac{15}{}$ 1·0601. Formed from thioacetamide and chloro - acetone (Hantzsch, *B.* 21, 943 ; *A.* 250, 265). Colourless liquid ; more sol. cold than hot water. Reduced in alcoholic solution by sodium to ethylamine and propyl mercaptan (Schatzmann, *A.* 261, 1).—$B'_2H_2PtCl_6$. [215°]. Prisms; m. sol. water. — $B'HCl(HgCl_2)_4 4aq$. [110°]. White needles; v. e. sol. water.—$B'(HgCl_2)_2$. [177°]. Sl. sol. cold water, v. e. sol. dilute HClAq.—*Picrate.* [138°].

Methylo-iodide B'MeI. Pointed crystals ; v. sol. water.

$\beta\mu$-**Di-methyl-thiazole** $\begin{matrix}S.CMe\\CMe:CH\end{matrix}\gg N$. (150° cor.). Formed by condensing thioacetamide with (α)-chloro-propionic aldehyde (Hubacher, *A.* 259, 240). Oil, v. sl. sol. water, v. sol. alcohol and ether. Volatile with steam.—$B'_2H_2PtCl_6$. [202°]. —*Picrate.* [167°].

Tri-methyl thiazole C_6H_9NS *i.e.* $\begin{matrix}S — CMe\\CMe:CMe\end{matrix}\gg N$. (167°). S.G. $\frac{16}{}$ 1·013. Formed by heating thioacetamide with chloro-methyl ethyl ketone at 100° (Poubleff, *A.* 259, 258). Liquid, m. sol. cold, insol. hot, water.—×B'HCl. [174°].—$B'_2H_2PtCl_6$. [233°].—*Aurochloride* [156°].—*Picrate* [133°]. *Mercuric double chloride* [119°].

References. — METHYL - AMIDO - METHYL - THI - AZOLE, METHYL - IMIDO - DI - METHYL - THIAZOLE, OXY-METHYL-THIAZOLE, and TOLYL-AMIDO-METHYL-THIAZOLE.

METHYL-THIAZOLE CARBOXYLIC ACID $C_5H_5NSO_2$ *i.e.* $\begin{matrix}S.CMe\\CO_2H.C:CH\end{matrix}\gg N$. [145°]. Formed by heating the dicarboxylic acid [169°] at 171° (Roubleff, *A.* 259, 271). Small needles or prisms, v. sol. cold, v. e. sol. hot, water, m. sol. alcohol, sl. sol. ether, almost insol. benzene.

Methyl-thiazole carboxylic acid $\begin{matrix}S.CH\\CO_2H.C:CMe\end{matrix}\gg N$. [257°]. Formed by saponifying its ether with alcoholic potash (Wohmann, *A.* 259, 299). Pearly plates (from water) or needles (from alcohol), sl. sol. ether and hot water, almost insol. benzene.

Ethyl ether EtA'. [28°]. (233° i. V.) at 726 mm. Obtained from amido-methyl-thiazole carboxylic ether by diazotisation, conversion into chloro-methyl-thiazole carboxylic ether [51°] and reduction of this by zinc-dust and HOAc. Flat prisms, volatile with steam.

Methyl-thiazole dicarboxylic acid $\begin{matrix}S.C(CH_3\ )\\CO_2H.C:C(CO_2H)\end{matrix}\gg N$. [169°]. Formed by condensing thioacetamide with chloro-oxalacetic ether and saponifying with alcoholic soda (Roubleff, *A.* 259, 268). Long white needles, v. sol. cold water, sl. sol. ether and benzene.—BaA''2aq: needles.—HgA'' $3\frac{1}{2}$aq : crystalline pp.

Di-methyl-thiazole carboxylic acid $\begin{matrix}S.CMe\\CO_2H.C:CMe\end{matrix}\gg N$. [227°]. Formed by saponifying its ether (R.). Silky needles or small prisms, sl. sol. hot water, m. sol. alcohol and ether. May be sublimed. Yields on distillation with lime di-methyl-thiazole.—AgA' : white needles, sol. hot water.—HA'HCl : plates.

Ethyl ether EtA'. [51°]. (242° cor.). Formed from thioacetamide and chloro-aceto-acetic ether (Hantzsch, *A.* 250, 269). Needles (from ether); insol. water, v. sol. alcohol and ether.

METHYL - THIAZYL - PROPIONIC ETHER $\begin{matrix}S.CMe:N\\CH:C.CHMe.CO_2Et\end{matrix}$. Formed by condensing bromo-methyl-acetoacetic ether with thioacetamide in the cold (Roubleff, *A.* 259, 262). Thick oil. When saponified and heated with lime it yields methyl-ethyl-thiazole.

($\alpha\alpha'$)-METHYL-THIENYL-GLYOXYLIC ACID $C_7H_6SO_3$ *i.e.* $S\!<\!\begin{matrix}C(CO.CO_2H):CH\\C(CH_3) = CH\end{matrix}$. [80°]. Formed by oxidising ($\alpha\alpha'$)-methyl-thienyl methyl ketone with alkaline $KMnO_4$ (Ruffi, *B.* 20, 1747).—$CaA'_2 2aq$: needles.—$Ba'A_2 \frac{1}{4}aq$: needles.—AgA'.

($\alpha\beta$) - **Methyl - thienyl - glyoxylic acid** $SC_4H_2Me.COCO_2H$. [142°]. Formed by oxidising (α)-methyl-(β)-thienyl methyl ketone with an aqueous solution of $KMnO_4$ and KOH (Ruffi, *B.* 20, 1748). Needles (from water), subliming even in the cold.

Phenyl-hydrazide $SC_4H_2Me.C(N_2HPh).CO_2H$. [141°]. Crystalline.

Oxim $SC_4H_2Me.C(NOH).CO_2H$. [104°].

($\alpha\alpha'$) - **Di-methyl - (β) - thienyl - glyoxylic acid** $S\!<\!\begin{matrix}CMe:CH\\CMe:C.CO.CO_2H\end{matrix}$. Formed by oxidation of ($\alpha\alpha'$)-di-methyl-(β)-thienyl methyl ketone with alkaline $KMnO_4$ (Ruffi). Oil, slowly solidifying. Yields leuco-thiophene green when heated with di-methyl-aniline and $ZnCl_2$.—AgA'.

METHYL-THIENYL KETONE *v.* THIENYL METHYL KETONE.

(α)-METHYL-THIENYL METHYL KETONE C_7H_8SO *i.e.* $S\!<\!\begin{matrix}C(CO.CH_3):CH\\C(CH_3) = CH\end{matrix}$. *Acetomethyl-thienone.* [25°]. (233° cor.). Formed by the action of AcCl on (α)-methyl-thiophene in presence of $AlCl_3$ (Demuth, *B.* 18, 3025; 19, 1859 ; Ernst, *B.* 19, 3275). Large tables. On oxidation with $KMnO_4$ it yields thiophene dicarboxylic acid. Fuming HNO_3 forms a nitro- derivative [121°].

Oxim $C_7H_8S(NOH)$. [125°]. Needles (from dilute alcohol).

Phenyl-hydrazide $C_7H_8S(N_2HPh)$. [128°]. Needles (from alcohol).

(β) - **Methyl - thienyl methyl ketone** $C_4H_2SMe.CO.CH_3$. (216° cor.). Formed from (β)-methyl-thiophene and AcCl in presence of $AlCl_3$ (Demuth, *B.* 18, 3025).

($\alpha\beta'$) - **Di-methyl - thienyl methyl ketone** $C_8H_{10}SO$ *i.e.* $S\!<\!\begin{matrix}CMe:CH\\CAc:CMe\end{matrix}$ or $S\!<\!\begin{matrix}CMe:CAc\\CH\ :CMe\end{matrix}$. (227°). Formed by the action of AcCl on ($\alpha\beta'$)-di-methyl-thiophene dissolved in ligroïn in presence of $AlCl_3$ (Zelinsky, *B.* 20, 2019). Liquid. Coloured red by isatin and H_2SO_4.

Oxim $C_8H_{10}S(NOH)$. [70°]. Needles.

Phenyl-hydrazide $C_8H_{10}S(N_2HPh)$. [70°].

Di-methyl-thienyl methyl ketone $SC_4HMe_2.CO.CH_3$. (224°). S.G. $\frac{17}{}$ 1·091. Formed from the di-methyl-thiophene of coal-tar by treatment with AcCl and $AlCl_3$ (Messinger, *B.* 18, 2301). Liquid. Gives a red colour with isatin and H_2SO_4. Oxidised by alkaline $KMnO_4$ to thiophene tricarboxylic acid.

Oxim $C_8H_{10}S(NOH)$. [65°]. Needles.

TETRA-METHYL-THIO-ANILINE *v.* TETRA-METHYL-DI-AMIDO-DI-PHENYL SULPHIDE.

METHYL-THIOCARBAMINE CYAMIDE *v.* CARBIMIDO-METHYL-THIO-UREA.

METHYL-THIOCARBAMINE-ETHYL-CYAMIDE *v.* ETHYL-CARBIMIDO-METHYL-THIO-UREA.

DI-METHYL-THIOCARBAZIC ACID $C_3H_8NS_2$ *i.e.* $NMe_2.NH.CS.SH$. [112°]. Formed from di-methyl-hydrazine and CS_2 (Renouf, *B.* 13, 2172). Colourless plates.

METHYL-THIOCARBIMIDE $CH_3.N.CS$. Mol. w. 73. [34°]. (119°). V.D. 2·42 (calc. 2·53). S.G. $\frac{4}{4}$ 1·069. R_∞ 35·75 (Nasini a. Scala, *G.* 17, 66). H.F.p. −24,520. H.F.v. −25,100. H.C. (gas) 392,000 (Thomsen, *Th.* 4, 197). Formed by the action of $AgNO_3$ or $HgCl_2$ on the product of the union of CS_2 on methylamine (Hofmann, *B.* 1, 172). Formed also by heating pure methyl sulphocyanide for some time at 180°–185° (Hofmann, *B.* 18, 2196). Pungent crystals. Reacts with sodium cyanamide and alkyl iodides, forming methyl-alkyl-cyano-thio-ureas. Thus CN_2HNa and MeI give $CH_3NH.CS.NCy.CH_3$ [c. 195°], while allyl iodide yields the compound $NHMe.CS.NCyC_3H_5$ [78°], propyl iodide forms $NHMe.CS.NCy.C_3H_7$ [91°], and benzyl chloride forms $NHMe.CS.NCy.CH_2Ph$ [173°] (Hecht, *B.* 23, 1658).

METHYL THIOCARBONATES.

Methyl dithiocarbonic acid $C_2H_4S_2O$ *i.e.* $CH_3O.CS.SH$. *Methyl-xanthic acid. Methyl-xanthogenic acid. Xantho-methylic acid.* The potassium salt of this acid is formed by adding CS_2 to a solution of KOH in methyl alcohol (Dumas a. Péligot, *A. Ch.* [2] 24, 55; Desains, *A. Ch.* [3] 20, 504). It crystallises in silky fibres, S.G. $\frac{15.2}{}$ 1·6878 (Clarke, *B.* 11, 1505). Iodine converts it into $(CH_3O.CS)_2S_2$. With EtI it yields MeO.CS.SEt (184°).—PbA'_2.

Methyl dithiocarbonate $CH_3O.CS.SCH_3$. (168°) (S.); (171°) (C.). S.G. $\frac{18}{}$ 1·176 (S.); $\frac{15}{}$ 1·143 (C.). Formed from $CH_3.CS.SK$ and MeI (Salomon, *J. pr.* [2] 8, 117). Formed also together with CO and S by heating the compound $(CH_3O.CS)_2S_2$ (*v. supra*) (Cahours, *A. Ch.* [3] 19, 158).

Methyl trithiocarbonate Me_2CS_3. (200°–205°). S.G. $\frac{18}{}$ 1·159. Formed by distilling a mixture of concentrated solutions of K_2CS_3 and $Ca(SO_4Me)_2$ (Cahours, *A. Ch.* [3] 19, 163). Yellow liquid with pungent odour, nearly insol. water, miscible with alcohol and ether. Combines with bromine forming red crystals of $Me_2CS_3Br_2$ (Berend, *A.* 128, 333).

METHYL-THIO-COUMARILIC ACID $C_8H_4(CH_3)O.CO.SH$.

Ethyl ether $C_8H_4(CH_3)O.CO.SEt$: [92°]; glistening yellow needles; v. sol. ether, sl. sol. alcohol. Formed by heating methyl-coumarilic-ethyl-ether with P_2S_5. By treatment with alcoholic KOH it is reconverted into methyl-coumarilic acid (Hantzsch, *B.* 19, 2400).

METHYL-THIOFORMALDINE $C_4H_9S_2N$ *i.e.* $(CH_2)_3S_2NMe$. [65°]. (c. 185°). Formed from an aqueous solution of formic aldehyde by successive addition of H_2S and methylamine (Wohl, *B.* 19, 2346). Needles (from ether) with unpleasant smell, insol. water, sol. acids and alcohol, v. sol. ether. Volatile with steam. On boiling it is converted into a substance melting at 130°–140°. —B'HCl. [188°]. White needles, v. sol. water. Its solution is ppd. by $AgNO_3$, $HgCl_2$, and platinic chloride.

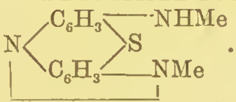
Methylo-iodide B'MeI. [161°–163°]. Slender needles, v. sol. water. Gives rise to B'MeCl and $(B'MeCl)_2PtCl_4$.

METHYL-THIOHYDANTOÏN $C_4H_6N_2SO$ *i.e.* $NH{:}C\genfrac{<}{>}{0pt}{}{S.CH_2}{NMe.CO}$ (?). Formed by warming methyl-thio-urea with chloro-acetic acid and water (Andreasch, *M.* 6, 840). Thick prisms or needles (from water), sol. hot water and alcohol. Boiling KOHAq yields thioglycollic acid. Nitrous acid forms a nitrosamine $C_4H_5(NO)N_2SO$ which is an orange-red powder, sol. hot water.

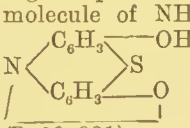
(α)-Di-methyl-thiohydantoïn $C_5H_8N_2SO$ *i.e.* $NMe{:}C\genfrac{<}{>}{0pt}{}{S.CH_2}{NMe.CO}$. [71°]. Formed by heating di-methyl-thio-urea with chloro-acetic acid in aqueous solution (Andreasch, *M.* 8, 408). Long colourless prisms, v. sol. water, alcohol, and ether. Smells like nicotine. Hot aqueous alkalis convert it into thioglycollic acid. Nitrous acid forms an isonitroso- compound $C_5H_7N_3SO_2$ [220°].

(β)-Di-methyl-thiohydantoïn $NH{:}C\genfrac{<}{>}{0pt}{}{S.CMe_2}{NH.CO}$. [114°]. Formed from di-argentic thiohydantoïn and MeI (Andreasch, *M.* 8, 416). Thin plates, v. sol. water, sl. sol. alcohol. Oxidised by $KClO_3$ and HCl to urea and other products.

DI-METHYL-THIONINE $C_{14}H_{13}NS$ *i.e.*

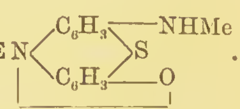


. Obtained by the action of Fe_2Cl_6 upon methyl-*p*-phenylene-diamine in the presence of H_2S and HCl. The free base is a crystalline powder, sl. sol. ether and alcohol, insol. water. The blue alcoholic solution has a strong red fluorescence. The hydrochloride is easily sol. water with a blue colour and reddish-brown fluorescence. The hydroiodide (B'HI) is a dark-blue powder, sol. hot water and alcohol, sl. sol. cold water; dyes silk blue. The free base by boiling with water is converted into methyl-thionoline with evolution of NH_2Me. By treating the product with 70 p.c. H_2SO_4 a second molecule of NH_2Me is split off and thionol



is formed (Bernthsen a. Goske, *B.* 20, 931).

METHYL-THIONOLINE



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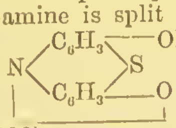
Formed by boiling di-methyl-thionine with water, methyl-amine being evolved. By treatment with 70 p.c. H_2SO_4 a second molecule of methyl-amine is split off, and there is formed thionol



(Bernthsen a. Goske, *B.* 20, 932).

Di-methyl-thionoline *v.* METHYLENE-VIOLET.

METHYL-THIOPARABANIC ACID $C_4H_4N_2SO_2$ *i.e.* $CS\genfrac{<}{>}{0pt}{}{NMe.CO}{NH.CO}$. *Oxalyl-methyl-thio-urea.* [105°]. Prepared by passing cyanogen into an alcoholic solution of methyl-thio-urea and boiling the ppd. $CSN_2H_3MeCy_2$ with conc.

HClAq (Andreasch, *B.* 14, 1447; *M.* 2, 277). Yellow plates, sol. water, alcohol, and ether. May be sublimed. Converted by warming with aqueous $AgNO_3$ into methyl-parabanic acid.

Di-methyl-thioparabanic acid $C_5H_6N_2SO_2$ *i.e.* $CS<{NMe.CO \atop NMe.CO}>$. *Thiocholestrophane. Oxalyl-di-methyl-thio-urea.* [113°]. Prepared by passing cyanogen into an alcoholic solution of *s*-di-methyl-thio-urea and boiling the ppd. cyanide with HClAq (Andreasch). Yellow monoclinic tables, sl. sol. cold water, v. e. sol. alcohol and ether. Split up by boiling alkalis into di-methyl-thio-urea and oxalic acid. On heating with $BaCO_3$ and water it gives di-methyl-oxamide and CSO. Boiling aqueous $AgNO_3$ forms cholestrophane.

(α)-METHYL-THIOPHENE C_5H_6S *i.e.* $S<{CMe:CH \atop CH:CH}$. *Thiotolene.* (111°). Occurs in coal-tar (V. Meyer, *B.* 18, 3009). Formed by the action of sodium on a mixture of (α)-iodo-thiophene and MeBr (V. Meyer a. Kreis, *B.* 17, 1562; Egli, *B.* 18, 544). Formed also by the action of P_2S_3 on acetyl-propionic (levulic) acid (Kues, *B.* 19, 556). Oil. Forms a tri-bromo- derivative [87°].

(β)-Methyl-thiophene $S<{CH:CMe \atop CH:CH}$. *Thiotolene.* Occurs, together with the preceding isomeride, in crude toluene from which it may be separated by shaking with H_2SO_4, and passing steam through the boiling acid diluted with 20 p.c. water. The mixture of methyl-thiophenes so obtained boils at 113 cor. and has a S.G. $\frac{18}{18}$ = 1·0194 (Meyer a. Kreis, *B.* 17, 787; Schulze, *B.* 17, 2853). Formed by distilling sodium pyrotartrate with P_2S_3 (Volhard a. Erdmann, *B.* 18, 455). Oil. Oxidised by alkaline $KMnO_4$ to (β)-thiophenic acid. Gives a tri-bromo- derivative [34°], and a bromo-di-nitro- derivative [125°].

Di-methyl-thiophene C_6H_8S. *Thioxene.* Crude thioxene is obtained in considerable quantity by passing steam through sulphuric acid used in purifying xylene diluted with 20 p.c. of water and heated to boiling (Schulze, *B.* 17, 2853).

(αβ′) - Di - methyl - thiophene $S<{CMe:CH \atop CH:CMe}$. *m-Thioxene.* (138° cor.). S.G. $\frac{20}{}$ ·9956. V.D. 4·02 (calc. 3·9). Formed by distilling β-acetyl-isobutyric acid with P_2S_3 (Zelinsky, *B.* 20, 2018). Gives on oxidation methyl-thiophene carboxylic and thiophene dicarboxylic acids.

Di-methyl-thiophene $SC_4H_2Me_2$. (139° cor.). S.G. $\frac{21}{21}$ ·9777. Formed from iodo-(β)-methyl-thiophene, MeI and sodium (Demuth, *B.* 19, 1859). Liquid.

(αα′) - Di - methyl - thiophene $S<{CMe:CH \atop CMe:CH}$. *Thioxene.* (137° cor.). S.G. $\frac{18}{18}$ ·9755. Occurs in coal-tar. Prepared from crude thioxene by conversion into iodo-di-methyl-thiophene and reducing this body with zinc-dust and alcoholic NaOH (Messenger, *B.* 18, 565, 1606). Formed by heating acetonyl-acetone (di-methyl-ethylene-diketone) $CH_3.CO.CH_2.CH_2.CO.CH_3$ (3 pts.) with powdered P_2S_5 (2 pts.) for an hour at 140°–150°; the yield is 50-60 p.c. of the theoretical (Paal, *B.* 18, 2252). Formed also from (α)-iodo-(α′)-methyl-thiophene by leaving it for some weeks in contact with sodium and MeI (Ruffi, *B.* 20, 1747). Colourless mobile liquid of slight odour. Dissolves sulphur considerably. Gives a red colour with isatin and H_2SO_4, a violet with phenanthraquinone and H_2SO_4, and a reddish-brown with phenyl-glyoxylic acid and H_2SO_4. By $KMnO_4$ it is oxidised to thiotolene-carboxylic acid [142°]. The di-bromo- derivative melts at [47°–50°], and the tri-bromo- derivative at [144°]. It also forms a bromo- derivative [194°], a second di-bromo-derivative [46°], a per-bromo- derivative C_6Br_8S [114°], and oily iodo- and nitro- derivatives (Messinger). With phenanthraquinone, HOAc, and H_2SO_4 (Laubenheimer's reagent) it gives a reddish-violet colouration.

(ββ′)-Di-methyl-thiophene $S<{CH:CMe \atop CH:CMe}$. (145°). S.G. $\frac{23}{22}$ 1·0078. Formed by distilling sodium *s*-di-methyl-succinate with P_2S_3 (Zelinsky, *B.* 21, 1836). Yellow oil. With a trace of isatin in conc. H_2SO_4 it gives an emerald-green colour. On oxidation it yields an acid crystallising in needles [139°], sl. sol. cold water.

(αβ) - Di - methyl - thiophene $S<{CMe:CMe \atop CH:CH}$. *om-Thioxene.* (137° cor.). S.G. $\frac{21}{}$ ·9938. Formed by distilling β-acetyl-*n*-butyric acid with P_2S_3 (Paal a. Püschel, *B.* 20, 2559; Grünewald, *B.* 20, 2585). Colourless, strongly refracting oil. In the indophenine reaction it gives a bluish-violet colour. Laubenheimer's reagent yields a reddish-violet colour. $KMnO_4$ oxidises it to methyl-thiophene carboxylic acid and thiophene (ββ′)-di-carboxylic acid.

Tri-methyl-thiophene $C_7H_{10}S$ *i.e.* $S<{CMe:CMe \atop CH\ :CMe}$. (162°). Formed by distilling $CH_3.CO.CHMe.CHMe.CO_2H$ with P_2S_3 (Zelinsky, *B.* 20, 2025).

Tetra-methyl thiophene $C_8H_{12}S$ *i.e.* $S<{CMe:CMe \atop CMe:CMe}$. (184° uncor.). S.G. $\frac{21}{21}$ ·9442. Formed from tri-methyl-thiophene by treatment of this substance (12 g.) dissolved in petroleum-ether with iodine (48·5 g.) and HgO (21 g.), distilling with steam, and allowing the iodo-tri-methyl-thiophene which comes over to stand with MeI and sodium (Zelinsky, *B.* 21, 1837). Oil. Does not give the indophenine reaction.

References. — Di-bromo-methyl-thiophene and Iodo-di-methyl-thiophene.

METHYL-THIOPHENE CARBOXYLIC ACID $C_6H_6SO_2$ *i.e.* $S<{CMe:CH \atop CH\ :C.CO_2H}$ or $S<{C(CO_2H):CH \atop CH{=\!=}CMe}$. *Thiotolene carboxylic acid.* [119°]. Formed by oxidising the corresponding di-methyl-thiophene with alkaline $KMnO_4$ in the cold (Zelinsky, *B.* 20, 2020). Needles, sl. sol. cold water, v. sol. ether. May be sublimed.—$CaA'_2\,2\frac{1}{2}aq$: plates.—AgA′.

(β)-Methyl-thiophene (α)-carboxylic acid $S<{C(CO_2H):CMe \atop CH{=\!=}CH}$. *c-Thiotolenic acid.* [144°]. Obtained by saponifying its ether, which is formed by the action of $ClCO_2Et$ and sodium-amalgam upon iodo-(β)-methyl-thiophene (Levi, *B.* 19, 656). Formed also by oxidising (β)-methyl-thienyl methyl ketone with alkaline $KMnO_4$ (Demuth, *B.* 19, 680); and by boiling the amide with alcoholic potash. Needles (from water), v. sol. hot water and alcohol. Not at-

tacked by $KMnO_4$. — CaA'_2 4aq: plates. — BaA'_2 5aq: small plates, sol. water.—AgA'.

Chloride $C_4H_2MeS.COCl$. (219°). Liquid, smelling like benzoyl chloride.

Amide $C_4H_2MeS.CONH_2$. [119°] (Z.); [123°] (Levi). Formed by the action of $Cl.CONH_2$ on (β)-methyl-thiophene in presence of $AlCl_3$ (Zelinsky, *B.* 20, 2024; Gattermann, *A.* 244, 58). Needles (from water), v. sol. water.

(α)-Methyl-thiophene (α')-carboxylic acid $S<\begin{matrix}C(CO_2H):CH\\C(CH_3)=CH\end{matrix}$. *Methyl thiophenic acid. oo-Thiotolenic acid.* [142°] (P.); [137°] (L.). Formed by oxidation of thioxene (from acetonyl-acetone) with alkaline $KMnO_4$ (Paal, *B.* 18, 2253). Obtained also from its ether, which is produced by heating iodo-(α)-methyl-thiophene with $ClCO_2Et$ and sodium-amalgam (Levi, *B.* 19, 656). White needles. Somewhat volatile with steam. Begins to sublime at c. 120° in long needles. V. e. sol. alcohol, ether, and boiling water, sl. sol. cold water. Gives no colour-reaction with isatin and H_2SO_4. Oxidised by alkaline $KMnO_4$ to the corresponding thiophene dicarboxylic acid.—CaA'_2 $3\frac{1}{4}$aq.—A'Ag^x: white crystalline powder.

Methyl-thiophene carboxylic acid $S<\begin{matrix}CMe:C.CO_2H\\CH\ :CH\end{matrix}$ (?). [134·5°]. Obtained by oxidising (αβ)-di-methyl-thiophene with an alkaline 1 p.c. solution of $KMnO_4$ (Grünewald, *B.* 20, 2586).

Di-methyl-thiophene carboxylic acid $C_7H_8SO_2$ *i.e.* $S<\begin{matrix}C(CO_2H).C:CH_3\\C(CH_3)\ :CH\end{matrix}$. [172°]. Obtained from its amide by hydrolysis (Zelinsky a. Gattermann, *A.* 244, 59). Needles (from dilute alcohol). —AgA'.

Amide $C_4HMe_2S.CONH_2$. [116°]. Formed by acting on di-methyl-thiophene with $Cl.CONH_2$ in presence of $AlCl_3$. Colourless needles (from water).

Tri-methyl-thiophene carboxylic acid $C_8H_{10}SO_2$ *i.e.* $S<\begin{matrix}C(CO_2H):C.CH_3\\C(CH_3)\ :C.CH_3\end{matrix}$. [208°]. Obtained by hydrolysis of its amide (Gattermann a. Zelinsky, *A.* 244, 60). Needles (from alcohol).

Amide $C_4Me_3S.CONH_2$. [147°]. Formed by the action of $ClCONH_2$ upon (αββ')-tri-methyl-thiophene in presence of $AlCl_3$. Crystallises from water.

(β)-METHYL-THIOPHENE SULPHONIC ACID $C_4H_2MeS.SO_3H$. Formed by warming (β)-methyl-thiophene with fuming H_2SO_4 (Muhlert, *B.* 19, 1620). Syrup, turning red on exposure to air.—KA' $\frac{1}{4}$aq.—ZnA'_2 $3\frac{1}{2}$aq.—PbA'' (at 110°).

Chloride $C_4H_2MeS.SO_2Cl$. Oil.

Amide $C_4H_2MeS.SO_2NH_2$. [80°]. Crystalline nodules (from ether).

METHYL-THIOPHENIC ACID *v.* METHYL-THIOPHENE CARBOXYLIC ACID.

METHYL-THIO-DIPHENYLAMINE *v.* METHYL-IMIDO-DI-PHENYL SULPHIDE.

METHYL DITHIOPHOSPHATES.

Di-methyl-di-thio-phosphoric acid $C_2H_7PO_2S_2$ *i.e.* $Me_2HPO_2S_2$. Formed, together with $Me_3PO_2S_2$, by the action of P_2S_5 (1 pt.) on methyl alcohol (5 pts.) in the cold (Kowalewsky, *A.* 119, 303). Thick liquid, soluble in water. Decomposes below 100°.—PbA'_2: prisms (from alcohol). Melts below 100°.

Tri-methyl dithiophosphate $Me_3PO_2S_2$. Formed as above. Liquid, v. sl. sol. water.

METHYL-THIO-PHTHALIMIDINE C_9H_9NS *i.e.* $C_6H_4<\begin{matrix}C(NMe)\\CH_2\ —\end{matrix}>S$. From thiophthalimidine and MeI (Way a. Gabriel, *B.* 23, 2483). It is converted by conc. HClAq at 190° into thiophthalide, and by oxidation into o-di-cyano-dibenzyl di-sulphide $(C_6H_4Cy.CH_2)_2S_2$ [124°].—B'HCl.—$B'_2H_2PtCl_6$.—$B'C_6H_2(NO_2)_3OH$: yellow needles.

METHYL-THIO-UREA $C_2H_6N_2S$ *i.e.* $NH_2.CS.NHMe$. [118°]. Formed from methyl-thiocarbimide and NH_3 (Andreasch, *M.* 2, 277). Prisms, v. sol. water and alcohol, sl. sol. ether.—B'HI: large plates, v. e. sol. water and alcohol. Melts below 100°. Decomposed by Ag_2O into AgI and methyl-cyanamide (Bernthsen a. Klinger, *B.* 11, 492).

Di-methyl-thio-urea $C_3H_8N_2S$ *i.e.* $CS(NHMe)_2$. [51·5°]. Formed from methyl-thiocarbimide and methylamine (Traumann, *A.* 249, 49; Hecht, *B.* 23, 286; *cf.* Andreasch, *M.* 2, 277). Transparent very hygroscopio plates. V. sol. water, alcohol, and acetone, sl. sol. ether and benzene, v. sl. sol. light petroleum.

METHYL-THYMO-ACRYLIC ACID *v. Methyl-derivative* of OXY-METHYL-PROPYL-CINNAMIC ACID.

DI-METHYL-TOLANE *v.* DI-TOLYL-ACETYLENE.

DI-METHYL-TOLENYL-AMIDINE.

Hydrochloride $C_{10}H_{14}N_2HCl$ *i.e.* $(NHMe.C(C_6H_4Me):NMe)HCl$. [200°]. Formed by adding the hydrochloride of *p*-tolenyl imido-ether $(EtO.C(C_6H_4Me):NH)HCl$ to an alcohol solution of methylamine (Glock, *B.* 21, 2654). Long silky needles (from water), v. sol. water and alcohol.—$B'_2H_2PtCl_6$ 2aq. [95°]. Dimetric crystals.

u-Di-methyl-tolenyl-amidine. *Hydrochloride* $(NMe_2.C(C_6H_4Me):NH)HCl$. Formed from the hydrochloride of *p*-tolenyl imido-ether and dimethylamine (G.). Short prisms.

METHYL-TOLINDOLE *v.* DI-METHYL-INDOLE.

METHYL-TOLISATIN *v. Di-methyl-*ISATIN.

DI-METHYL-TOLUBUTYLAMINE *v.* METHYL-BUTYL-PHENYL-DI-METHYL-AMINE.

METHYL-o-TOLUIDINE $C_8H_{11}N$ *i.e.* $[2:1]C_6H_4Me.NHMe$. *o-Tolyl-methyl-amine.* (207°). S.G. $\frac{15}{}$ ·973. Prepared by the action of tin and HClAq on the nitrosamine which is obtained from the crude product of the action of methyl alcohol and HCl on o-toluidine (Monnet, Reverdin, a. Nölting, *B.* 11, 2278). Obtained also by heating o-toluidine hydrobromide (or hydroiodide) with 5 p.c. more than an equivalent quantity of methyl alcohol for 8 hours at 150°, the yield being 46 p.c. of the theoretical (Reinhardt a. Staedel, *B.* 16, 29). It is also produced by distilling o-tolyl-amido-acetic acid (Widman, *J. pr.* [2] 38, 303). Colourless oil.—$B'_2H_2PtCl_6$.

Acetyl derivative $C_6H_4Me.NAcMe$. [56°]. (251°) (R. a. S.); (c. 260°) (M., R., a. N.).

Nitrosamine $C_6H_4Me.N(NO)Me$. Oil. Converted by alcoholic HCl into the isomeric *p*-nitroso-o-methyl-toluidine

$[5:1:2]NO.C_6H_3Me.NHMe$ or $C_6H_3Me<\begin{matrix}NHMe\\N\ —\end{matrix}>O$,

which crystallises in green plates, [151°], sol. benzene. On boiling with dilute aqueous NaOH

it is converted into nitroso-cresol and methylamine. Potassium permanganate oxidises it to nitro-methyl-toluidine [134°]. Its hydrochloride $C_8H_{10}N_2OH_2Cl_2$ aq crystallises in yellow cubes [110°]; v. sl. sol. conc. HClAq (Kock, *A.* 243, 308).

Methyl-*m*-toluidine [3:1]C_6H_4Me.NHMe. (207°). Formed by the action of MeI on *m*-toluidine, and purified by means of the acetyl derivative (Nölting, *B.* 11, 2279). Oil.—$B'_2H_2PtCl_6$.

Acetyl derivative C_6H_4Me.NAcMe. [66°]. (c. 250°). Sol. hot water, alcohol, and ether.

Methyl-*p*-toluidine [4:1]C_6H_4Me.NHMe. (208°). Formed by passing MeCl into boiling *p*-toluidine. The ethereal extract of the crude product is freed from *p*-toluidine by ppn. with H_2SO_4, evaporated, and mixed with Ac_2O. The resulting mixture of di-methyl-toluidine and acetyl-methyl-toluidine may then be fractionally distilled, and the acetyl derivative saponified by HClAq or NaOHAq (Thomsen, *B.* 10, 1582). Oil.—$B'_2H_2PtCl_6$.

Acetyl derivative C_6H_4Me.NAcMe. [83°]. (283°). Plates (from ether-alcohol); sl. sol. water, v. sol. alcohol and ether.

Propionyl derivative $C_{11}H_{15}NO$ *i.e.* C_6H_4Me.N(C_3H_5O)Me. (266°–269°). Formed from methyl-*p*-toluidine and propionic anyhydride (Norton a. Livermore, *B.* 20, 2270). Converted by dilute nitric acid into tri-nitro-methyl-*p*-toluidine [130°].

Nitrosamine C_6H_4Me.NMe(NO). [54°]. Insol. water, v. sol. alcohol and ether.

Di-methyl-o-toluidine $C_9H_{13}N_4O_6$ *i.e.* [2:1]C_6H_4Me.NMe_2. (183°). Formed by distilling its methylo-hydroxide (Thomsen, *B.* 10, 1586; Nölting, *B.* 11, 2279). Prepared by heating o-toluidine hydrobromide (or hydroiodide) with a little (5 p.c.) more than two equivalents of methyl alcohol for 8 hours at 150°, the yield being 93 p.c. of the theoretical (Reinhardt a. Staedel, *B.* 16, 29). Oil. Converted by HNO_3 (S.G. 1·5) into di-nitro-o-tolyl-methyl-nitramine (Van Romburgh, *R. T. C.* 3, 395).—$B'_2H_2PtCl_6$.—$B'_2H_4FeCy_6$: white needles.—$B'_2H_3FeCy_6$ $4\frac{1}{2}$aq: yellow unstable crystals (Wurster a. Roser, *B.* 12, 1826).

Methylo-iodide C_6H_4Me.NMe_3I. Formed from o-toluidine and MeI (Thomsen). It is also a product obtained by heating di-methyl-aniline methylo-iodide at 220°–230° (Hofmann, *B.* 10, 1585). Needles.

Di-methyl-*m*-toluidine [3:1]C_6H_4Me.NMe_2. (208°) (N.; R. a. S.); (215°) (Wurster a. Riedel, *B.* 12, 1797). Formed from *m*-toluidine and MeI, or by distilling its methylo-iodide (Nölting). When dissolved in H_2SO_4, and treated with HNO_3 (S.G. 1·5), it yields $C_6H(NO_2)_3$Me.NMe.NO_2 (Van Romburgh, *R. T. C.* 3, 413).—$B'_2H_2PtCl_6$.—$B'_2H_4FeCy_6$2aq: white needles.—$B'_2H_3FeCy_6$ $1\frac{1}{2}$aq (Wurster a. Roser, *B.* 12, 1826).

Methylo-iodide B'MeI. Yields $(B'MeCl)_2PtCl_4$: yellow cubes.

Di-methyl-*p*-toluidine [4:1]C_6H_4Me.NMe_2. (208°) (R. a. S.; H.); (210°) (Van Romburgh). S.G. ·938. Formed, together with other products, by heating dimethylaniline methylo-iodide at 220°–230° (Hofmann, *B.* 5, 707). Formed also by heating its methylo-iodide with water and PbO and distilling the resulting C_6H_4Me.NMe_3OH (Hübner, Tolle, a. Athenstädt, *A.* 224, 337; *cf.* Thomsen, *B.* 10, 1586). Prepared by heating *p*-toluidine hydrobromide (or hydro-iodide) with rather more (5 p.c.) than two equivalents of methyl alcohol for eight hours at 150°, the yield being 95 p.c. of the theoretical (Reinhardt a. Staedel, *B.* 16, 29). Oil. Converted by fuming HNO_3 and H_2SO_4 into $C_6H(NO_2)_3$Me.NMe.NO_2 (Van Romburgh, *R. T. C.* 3, 404).—$B'_2H_2PtCl_6$.—$B'_2H_4FeCy_6$ aq: white powder.—$B'_2H_3FeCy_6$ $2\frac{1}{2}$aq: yellow crystals (Wurster a. Roser, *B.* 12, 1826).

Methylo-iodide C_6H_4Me.NMe_3I. Formed from *p*-toluidine and MeI. Converted by moist Ag_2O into C_6H_4Me.NMe_3OH. Yields $(C_6H_4Me.NMe_3Cl)_2PtCl_4$.

References.—Bromo-di-methyl-toluidine and Nitro-methyl-toluidine.

DI-METHYL-o-TOLUIDINE SULPHONIC ACID C_6H_3Me(NMe_2)SO_3H. Formed by sulphonating di-methyl-o-toluidine (Michler a. Sampaio, *B.* 14, 2167). Large prisms; v. sol. hot water; insol. alcohol.—BaA'_2: soluble plates.—CaA'_2: small nodules.—ZnA'_2: easily soluble needles.

METHYL-TOLUQUINOLINE *v.* Di-methyl-quinoline.

METHYL-TOLUQUINOXALINE *v.* Di-methyl-quinoxaline.

METHYL-TOLYLENE-DIAMINE *v.* Tolylene-methyl-diamine.

METHYL TOLYL KETONE *v.* Tolyl methyl ketone.

METHYL-TOLYL-NITROSAMINE *v.* *Nitrosamine* of Methyl-toluidine.

DI-METHYL-TOLYL-PHOSPHINE *v.* Tolyl-di-methyl-phosphine.

METHYL TRIDECYL KETONE $C_{15}H_{27}O$ *i.e.* CH_3.CO.$C_{13}H_{27}$. [39°]. (294°). S.G. (liquid) $\frac{39}{}$ ·8182. Formed by distilling a mixture of barium myristate and barium acetate (Krafft, *B.* 12, 1669; 15, 1724). Yields acetic and tridecoic acids on oxidation.

DI-METHYL-TRIDECYL-PYRIDINE $C_{20}H_{35}N$ *i.e.* $C_5NH_2Me_2(C_{13}H_{27})$. (216° at 13 mm.). Formed by distilling its dicarboxylic acid with soda-lime (Krafft a. Mai, *B.* 22, 1758). Oil.—$B'_2H_2PtCl_6$: yellow plates.

DI-METHYL-TRIDECYL-PYRIDINE DI-CARBOXYLIC ACID $C_5NMe_2(C_{13}H_{27})(CO_2H)_2$. Formed by saponifying its ether with alcoholic potash.—H_2A''HCl: crystalline powder; v. e. sol. alcohol.

Ethyl ether Et_2A''. (265° at 10 mm.). Formed from its dihydride by treatment of the alcoholic solution with nitrous acid (Krafft a. Mai, *B.* 22, 1758). Yellowish oil.—Et_2A''HCl: needles.

Di-methyl-tridecyl-pyridine dihydride di-carboxylic ether $C_5NMe_2(C_{13}H_{27})H_2(CO_2Et)_2$. [60°]. Formed by heating a mixture of myristic aldehyde, alcoholic NH_3, and acetoacetic ether (Krafft a. Mai, *B.* 22, 1757). Hard crystalline crusts.

METHYL-TROPIDINE *v.* Tropidine.

METHYL-TROPINE *v.* Tropine.

METHYL-UMBELLIC ACID *v.* Di-oxy-phenyl-crotonic acid.

METHYLUMBELLIFERON *v.* *Lactone* of di-oxy-phenyl-crotonic acid.

αβ-**Di-methyl-umbelliferon** $C_{11}H_{10}O_3$ *i.e.* $C_6H_3(OH)\left\langle\begin{array}{l}CMe{:}CMe\\ \quad | \\ O \text{—} CO\end{array}\right.$. *Lactone* of *di-oxy-phenyl-pentenoic acid.* [256°]. Formed by the action of H_2SO_4 on a mixture of methyl-aceto-acetic ether and resorcin (Pechmann a. Duisberg, *B.* 16, 2127). Colourless needles of high refractive power. Its dilute alkaline and H_2SO_4 solutions have a blue fluorescence.

Isomeride v. Lactone of DI-OXY-TOLYL-CROTONIC ACID.

METHYL UNDECYL KETONE *v.* METHYL HENDECYL KETONE.

METHYL-URACIL *v.* DI-OXY-METHYL-PYRIMIDINE.

METHYL-URAMIDO-ACETIC ACID *v.* METHYL-HYDANTOIC ACID.

m-**METHYL-URAMIDO-BENZOIC ACID** $C_9H_{10}N_2O_3$ *i.e.* $HMeN.CO.NH.C_6H_4.CO_2H$. Formed by the action of methylamine upon cyancarboxamido-benzoic acid $NC.CO.NH.C_6H_4.CO_2H$ (Griess, *B.* 18, 2415). White needles; sol. alcohol, v. sl. sol. water.—A'Ag: white plates.

METHYL-URAMINE. An old name for METHYL-GUANIDINE.

METHYL-UREA $C_2H_6N_2O$ *i.e.* $NH_2.CO.NHMe$. [102°]. Formed from methyl cyanate and ammonia, or by evaporating a mixture of potassium cyanate and methylamine sulphate (Wurtz, *C. R.* 32, 414). It is also a product of the action of HCl and $KClO_3$ on caffeïne (Fischer, *A.* 215, 257). It may be prepared by boiling its acetyl derivative with conc. HNO_3 (Hofmann, *B.* 14, 2734).

Properties.—Deliquescent prisms; v. e. sol. water and alcohol. Its aqueous solution is neutral to litmus, and yields with nitric acid a pp. of the nitrate $C_2H_6N_2OHNO_3$ [128°], which is converted by fuming nitric acid into methylamine and ammonium nitrate (Franchimont, *R. T. C.* 3, 220).

Nitrosamine $NH_2.CO.N(NO)Me$. [124°]. Formed by adding $NaNO_2$ to a solution of methyl-urea nitrate containing ice (Von Brüning, *B.* 21, 1810; *A.* 253, 6). Yellow plates or tables (from ether), v. sol. hot water, alcohol, and ether. Decomposed by long boiling with water. Exhibits Liebermann's reaction. On reducing with zinc-dust and HOAc it yields methyl-semi-carbazide $NH_2.CO.NMe.NH_2$ whence, by heating with conc. HClAq for 6 hours at 100°, methyl-hydrazine is got.

Acetyl derivative $NHAc.CO.NHMe$. [180°]. Formed from methyl-urea and Ac_2O. Formed by the action of boiling dilute NaOH on a mixture of bromo-acetamide ($CH_3.CO.NHBr$) and acetamide. This mixture is prepared by adding aqueous (10 p.c.) NaOH to acetamide (10 pts.) mixed with bromine (13·5 pts.) until the colour changes from red to yellow (Hofmann, *B.* 14, 2725; 15, 408). In this reaction methyl cyanate is perhaps first formed and then unites with acetamide. Monoclinic prisms (Haushofer, *J.* 1882, 365), sol. alcohol, ether, and hot water. Split up by alkalis into NH_3, CO_2, methylamine, and acetic acid. Boiling conc. HClAq forms acetic acid and methyl-urea.

s-**Di-methyl-urea** $C_3H_8N_2O$ *i.e.* $CO(NHMe)_2$. [102·5°]. (269°). Formed by the action of methylamine on methyl cyanate (Wurtz, *Rép. chim. pure*, 1862, 199). According to Wurtz, the same body when prepared by the action of cold water on methyl cyanate melts at 99·5° and boils between 273° and 288°. *s*-Di-methyl-urea crystallises easily, is v. sol. water and alcohol, and forms a hygroscopic nitrate $C_3H_8N_2OHNO_3$ [c. 65°] which is decomposed by fuming HNO_3 forming methylamine (Franchimont, *R. T. C.* 3, 222).

Cyano-acetyl derivative $C_6H_9N_3O_2$ *i.e.* $NHMe.CO.NMe.CO.CH_2Cy$. Formed from *s*-di-methyl-urea and cyano-acetyl chloride (Mulder, *B.* 12, 466). Crystals, not melted below 260°. Gives with bromine-water the compound $CO{<}\begin{array}{l}NMe.CO\\NMe.CO\end{array}{>}CBr_2$. Conc. HNO_3 forms, on warming, two purple-red compounds.

u-**Di-methyl-urea** $NMe_2.CO.NH_2$. [180°]. Formed by evaporating the mixed solutions of potassium cyanate and dimethylamine sulphate (Franchimont, *R. T. C.* 2, 122; 3, 222). Large hard crystals with sweet taste, sl. sol. alcohol and ether. Boiling Ac_2O forms NMe_2Ac and cyanuric acid. Aldehyde in the cold slowly forms $CH_3.CH(NH.CO.NMe_2)_2$ [160°]. Chloral forms $CCl_3.CH(OH).NH.CO.NMe_2$ [156°] and $C_5H_{11}Cl_3N_2O_3$ [74°] (Van der Zande, *R. T. C.* 8, 222). Nitrate $B'HNO_3$. [101°]. Very large crystals. Converted by fuming HNO_3 into di-methyl-nitramine.—Oxalate $B'H_2C_2O_4$ aq. Decomposes at 105°.—Picrate $B'C_6H_2(NO_2)_3OH$. [130°]. Decomposes on fusion (Van der Zande).

Tri-methyl-urea $C_4H_{10}N_2O$ *i.e.* $NMe_2.CO.NHMe$. [76°]. (232° cor.). Formed by mixing ethereal solutions of methyl cyanate and dimethylamine (Franchimont, *R. T. C.* 3, 226). Crystallises well from ether; v. sol. water and alcohol, sol. benzene. Fuming HNO_3 forms di-methyl-nitro-amine ($NMe_2.NO_2$) and methylamine.

Tetra-methyl-urea $C_5H_{12}N_2O$ *i.e.* $CO(NMe_2)_2$. (177° i. V.). S.G. $\frac{15}{}$ ·972). Prepared by passing dimethylamine into a solution of di-methyl-chloro-formamide $Cl.CONMe_2$ (derived from $COCl_2$ and NMe_2H) in benzene (Michler a. Escherich, *B.* 12, 1162; Franchimont, *R. T. C.* 3, 228). Oil, v. sol. alcohol and ether. With conc. HNO_3 (S.G. 1·5) it yields $NMe_2.NO_2$ and dimethylamine.

Reference.—CHLORO-METHYL-UREA.

METHYL-URETHANE *v.* METHYL CARBAMATE.

(*a*)-**METHYL-URIC ACID** $C_6H_6N_4O_3$ *i.e.* $CO{<}\begin{array}{l}NMe.CO.C.NH\\NH \text{——} C.NH\end{array}{>}CO$ or $CO{<}\begin{array}{l}NH.CO.C.NH\\NMe \text{—} C.NH\end{array}{>}CO$. S. ·4 at 100°. Formed by heating at 150° acid lead urate with MeI diluted with ether (Hill, *B.* 9, 370, 1090; *Am. S.* [3] 12, 428). Thin prisms, sl. sol. boiling water, insol. alcohol and ether. Sol. conc. H_2SO_4 and reppd. by water. Oxidised by alkaline $KMnO_4$ to methyl-allantoïn $C_4H_5MeN_4O_3$ [225°]. $KClO_3$ and HCl oxidise it to urea and methyl alloxan. By heating with HClAq it is split up into glycocoll, methylamine, CO_2, and NH_3 (Fischer, *B.* 17, 1776).

Salts.—K_2A'' 3aq. Ppd. by adding alcohol to its aqueous solution.—KHA''aq.—Na_2A''3aq.—$NaHA''$aq.—CaA'' 3aq.—BaA'' 4aq.—BaA'' $3\frac{1}{2}$aq: tufts of delicate needles.

Methyl-uric acid $C_5H_3MeN_4O_3$. Possibly identical with the preceding. Prepared by fusing urea (3 mols.) with methyl-amido-acetic acid (1 mol.), extracting the fusion with water, ppg. by ammoniacal $AgNO_3$ and magnesium mixture, digesting the pp. with an alkaline sulphide, filtering, acidifying, and evaporating to a small bulk (Horbaczewski, *M.* 6, 359). Formed also by heating methyl-hydantoïn with amyl allophanate or with biuret (Horbaczewski, *M.* 8, 584). Micaceous scales, sol. boiling water and alkalis, sl. sol. cold water, dilute acids, alcohol, and ether. Gives the murexide reaction. On heating with HClAq at 170° it gives a product (probably methylamine) which gives the carbamine reaction.

(β)-Methyl-uric acid $C_5H_3MeN_4O_3$ *i.e.* $\mathrm{CO}\left<\begin{array}{l}\mathrm{NH.CO.C.NMe}\\ \mathrm{NH——C.NH}\end{array}\right>\mathrm{CO}$. *Tri-oxy-methyl-purin.* S. ·05 at 100°.

Formation. — 1. By heating the di-methyl derivative of chloro-di-oxy-methyl-purin with HClAq at 130° (Fischer, *B.* 17, 332).—2. By heating di-chloro-oxy-methyl-purin with HClAq at 140° (Fischer, *B.* 17, 1777).—3. Occurs in small quantity, together with a much larger quantity of (α)-di-methyl-uric acid, by heating neutral lead urate with MeI at 100° (F.).

Properties.—Slender crystals. Sol. alkalis. Reduces ammoniacal $AgNO_3$ in the cold. Gives the murexide reaction. On heating with PCl_5 it yields di-chloro-oxy-methyl-purin. On oxidation with HNO_3 or with $KClO_3$ and HCl it gives methyl-urea and alloxan. Split up by heating with HClAq into CO_2, methylamine, NH_3, and glycocoll.

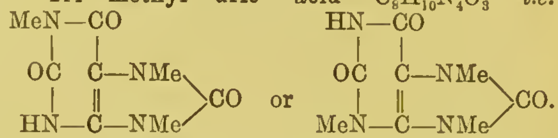
(α)-Di-methyl-uric acid $C_5H_2Me_2N_4O_3$ *i.e.* $C_2N_2HMeO_2:C_2:N_2HMeCO$. [above 340°]. S. ·5 at 100°; ·06 at 20°. Prepared by heating neutral lead urate with MeI in ether for 20 hours at 165° (Mabery a. Hill, *Am.* 2, 306; *P. Am. A.* 15, 256; *B.* 11, 1329; Fischer, *B.* 17, 1779). Slender monoclinic prisms (containing aq), sl. sol. water, sol. conc. H_2SO_4 and HClAq, insol. alcohol and ether. When heated with conc. HClAq at 170° it is resolved into CO_2, ammonia, NH_2Me, and glycocoll. Nitric acid oxidises it, forming methyl-alloxan and methyl-urea. HCl and $KClO_3$ form methyl-urea, methyl-alloxan, and a small quantity of a compound $C_5H_6N_2O_3$ [160°]. The ammonium salt is decomposed on boiling its solution with separation of the free acid (difference from (α)-methyl-uric acid).

S a l t s. — K_2A'' 4aq: silky needles, v. sol. water. — KHA'' 1½aq: needles, sol. water. — Na_2A'' 4½aq: needles, sol. water. —$NaHA''$ 2aq: small needles, sol. water. — BaA'' 3aq: flat prisms, m. sol. hot water.—$BaH_2A''_2$ 3aq.

(β)-Di-methyl-uric acid $\mathrm{CO}\left<\begin{array}{l}\mathrm{NH.CO.C.NMe}\\ \mathrm{NH——C.NMe}\end{array}\right>\mathrm{CO}$. *Tri-oxy-methyl-purin.* Formed by the action of H_2SO_4 at 140° on the di-ethoxy- compound obtained by treating di-chloro-oxy-di-methyl-purin with alcoholic NaOH. Formed also by heating di-chloro-oxy-di-methyl-purin with fuming HCl at 130° (Fischer, *B.* 17, 337, 1779). Colourless crystalline powder, v. sl. sol. water, alcohol, and ether. Melts at a very high temperature.

Reactions.—On heating with HCl it is split up into sarcosine, methylamine, CO_2, and NH_3. PCl_5 converts it back into di-chloro-oxy-di-methyl-purin. By $K_2Cr_2O_7$ and H_2SO_4 it is oxidised to cholestrophane. By oxidation with HNO_3 or $KClO_3$ and HCl it chiefly gives a body $C_7H_{10}N_4O_5$, which forms large colourless crystals [174°], v. sol. water, and decomposed on boiling with baryta-water into mesoxalic acid, urea, and probably di-methyl-urea.

Tri-methyl-uric acid $C_8H_{10}N_4O_3$ *i.e.*



[345°]. Formed by heating the lead salt of (β)-di-methyl-uric acid with methyl iodide (Fischer, *B.* 17, 1782). Fine white needles. Sublimable. Sol. hot water, sl. sol. alcohol and chloroform. Dissolves in alkalis. Gives the murexide reaction strongly. Is very unstable towards acids. $C_8H_9O_3N_4Ag$: fine white needles.

Tetra-methyl-uric acid $C_9H_{12}N_4O_3$ *i.e.* $\mathrm{CO}\left<\begin{array}{l}\mathrm{NMe.CO.C.NMe}\\ \mathrm{NMe——C.NMe}\end{array}\right>\mathrm{CO}$. [218°]. Formed by heating the silver salt of tri-methyl-uric acid with methyl iodide (Fischer, *B.* 17, 1784). Distils undecomposed. Fine white needles. V. sol. hot water, less sol. cold, sl. sol. ether. Has no acid properties. It is readily decomposed by alkalis, with evolution of methyl-amine. It gives the murexide reaction.

METHYL-UVIC ACID $C_8H_{10}O_3$ *i.e.* $\left.\begin{array}{l}\mathrm{CO_2H.CH\ .CHMe}\\ \quad\mathrm{CMe:CH}\end{array}\right>\mathrm{CO}$ or $\left.\begin{array}{l}\mathrm{CO_2H.CMe.CH_2}\\ \quad\mathrm{CMe:CH}\end{array}\right>\mathrm{CO}$. [98°]. Formed by heating methyl-methronic acid to 250° as long as CO_2 is evolved (Fittig, *A.* 250, 205). Needles (from water) or prisms (from other solvents); m. sol. hot, v. sl. sol. cold, water; v. sol. cold, v. e. sol. hot alcohol; v. sol. petroleum ether, $CHCl_3$, benzene, ether, and HOAc; volatile with steam. Yields on distillation CO_2 and oxy-di-methyl-pentamethenyl hydride.

S a l t s.—$(C_8H_9O_3)_2Ba$ 4aq: trimetric plates; $a:b:c$ = 0·9937:1:4·9021. — A'_2Ca 4aq: pearly plates, insol. alcohol.—$A'Ag$: small prisms (from water).

Ethyl ether A'Et. (219°). Colourless oil, heavier than water, volatile with steam.

METHYL-VALERIC ACID *v.* HEXOIC ACID.

METHYL-VALEROLACTONE *v.* *Lactone* of OXY-HEXOIC ACID.

METHYL-VANILLIN *v.* *Di-methyl derivative* of PROTOCATECHUIC ALDEHYDE.

DI-METHYL-DI-VANILLIN *v.* *Tetra-methyl derivative* of TETRA-OXY-DI-PHENYL DICARBOXYLIC ALDEHYDE.

DI-METHYL-VINYL-AMINE. *Methylo-hydroxide* $C_5H_{13}NO$ *i.e.* $NMe_3(C_2H_3)OH$. *Neurine.* Formed by the action of moist oxide of silver on di-methyl-bromo-vinyl methylo-bromide $NMe_3(CH_2.CH_2Br)Br$, the product of the union of trimethylamine with ethylene bromide (Hofmann, *C. R.* 47, 558; *Chem. Gaz.* 1858, 434; Baeyer, *A.* 140, 311). It is also a product of the decomposition of protagon by baryta (Liebreich, *B.* 2, 12), and of the putrefaction of flesh (Brieger, *B.* 16, 1190, 1406; 17, 516, 1137). It is extremely soluble in water, and is extracted from the solution by ether with great difficulty (Marino, *G.* 13, 441). Its solution is strongly alkaline, and fumes with HCl. On evaporating

its solution it decomposes with evolution of NMe_3. Its aqueous solution is poisonous, and antagonistic to atropine as regards the heart and glandular system (Cervello, *Arch. Ital. Biol.* 7, 232).

Methylo-chloride $^xNMe_3(C_2H_3)Cl$. Very deliquescent needles. — $(NMe_3(C_2H_3)Cl)_2PtCl_4$: yellow crystals, readily changing to neurine platinochloride $(NMe_3(C_2H_4OH)Cl)_2PtCl_4$. — $NMe_3(C_2H_3)AuCl_4$: yellow needles.

METHYL VINYL KETONE CARBOXYLIC ACID $CH_3.CO.CH:CH.CO_2H$. *β-Acetyl-acrylic acid.* [125°]. Formed by the action of aqueous sodium carbonate on β-bromo-acetyl-propionic acid $CH_3.CO.CHBr.CH_2.CO_2H$ in the cold (Wolff, *B.* 20, 425). Plates, v. sol. alcohol and ether, m. sol. cold water.—CaA'_2: nodules, v. sol. water.—ZnA'_2: amorphous.—AgA'_2: stellate groups of needles.

Phenyl-hydrazide $PhNH.N:CMe.CH_2.CH_2.CO_2H$. [157°]. Formed from the acid and phenyl-hydrazine (Decker, *B.* 21, 2937) or by saponifying its ether. Lemon-yellow needles, m. sol. hot water, v. sol. alcohol and ether.

Ethyl ether $^xEtA'$. *Phenyl hydrazide* $PhNH.N:CMe.CH_2.CH_2.CO_2Et$. [117°]. Formed from bromo-acetyl-propionic ether and phenyl-hydrazine (Bender, *B.* 21, 2493). Yellow spangles, sl. sol. cold, v. sol. hot alcohol. On reduction with tin and HClAq it yields methyl-indyl-acetic acid.

Isomeride *v.* TETRIO ACID.

METHYL-VIOLET. A violet dye obtained by the oxidation of di-methyl-aniline. It consists of a mixture of hexa- and penta-methyl-tri-amido-tri-phenyl carbinols (*q.v.*) (Fischer, *B.* 16, 706, 2904).

DI-METHYL-XANTHINE *v.* THEOBROMINE and THEOPHYLLINE.

Tri-methyl-xanthine *v.* CAFFEÏNE.

METHYL-XYLENE *v.* MESITYLENE and ψ-CUMENE.

METHYL-XYLIDINE $C_9H_{13}N$ *i.e.* $C_6H_3Me_2NHMe$. One of the products obtained by heating di-methyl-aniline hydro-iodide at 225° (Hofmann, *B.* 5, 712). Oil.

Di-methyl-xylidine $C_{10}H_{15}N$ *i.e.* $C_6H_3Me_2.NMe_2$. (196°). S.G. ·9293. Obtained by heating methyl-xylidine with MeI (Hofmann, *B.* 5, 712). Oil.

Di-methyl-xylidine $C_6H_3Me_2NMe_2$. (203°). Obtained by methylation of crude xylidine (H.). —B'MeI.

Di-methyl-xylidine $C_6H_3Me_2NMe_2$. [87°]. A by-product in the preparation of methyl-aniline (Sesemann, *B.* 6, 446). Long needles (from ligroïn).—B'EtBr.

Di-methyl-xylidine [1:3:4] $C_6H_3Me_2NMe_2$. (204°). Formed by heating xylidine hydrobromide with MeOH (Baur a. Staedel, *B.* 16, 32). Oil.—$B'_2H_2PtCl_6$: small yellow crystals.

METHYL XYLYL KETONE *v.* XYLYL METHYL KETONE.

METHYSTICIN $C_{15}H_{14}O_5$ (P.); $C_{16}H_{18}O_5$ (D.). [139°] (D.); [137°] (P.). Extracted by means of alcohol from Kawa root, the root of *Piper methysticum* (Gobley, *J. Ph.* [3] 37, 19; O'Rorke, *C. R.* 50, 498; Nölting a. Kopp, *Monit. Scient.* [3] 4, 9, 20; Cuzent, *An.* 1, 150; Davidoff, *J. R.* 19, 522; Pomeranz, *M.* 9, 863; 10, 785). White tasteless prismatic needles, sl. sol. hot water, ether, and ligroïn, v. sol. hot alcohol, benzene, and chloroform. Dissolves in NaOHAq, but on heating the solution methystic acid is formed. On fusion with KOH protocatechuic acid is formed. Boiling with KOHAq forms piperonal. Alkaline $KMnO_4$ oxidises it to piperonylic acid.

Acetyl derivative $C_{16}H_{16}Ac_2O_5$. [123°]

Benzoyl derivative $C_{16}H_{16}Bz_2O_5$. [148°].

Methystic acid $C_{14}H_{12}O_5$. [180°]. When 10 g. of methysticin are warmed with 6 p.c. NaOHAq 5 g. of methystic acid are formed. Methystic acid when heated at 180° evolves CO_2, and the product, after cooling, melts at 93°. $KMnO_4$ oxidises methystic acid to piperonal [37°] and piperonylic acid $C_8H_6O_4$ [227°]. Dilute mineral acids convert it into methysticol. Ac_2O has no action.

Methysticol $C_{13}H_{12}O_3$ *i.e.*

$CH_2{<}^{O}_{O}{>}C_6H_3(C_6H_7O)\left[\begin{smallmatrix}1 & \\ 2 & 4\end{smallmatrix}\right]$. [94°]. Formed by warming methysticin or methystic acid with dilute HClAq or H_2SO_4 (Pomeranz, *M.* 10, 792). Prisms; insol. alkalis, v. sol. alcohol and ether. Forms a phenyl-hydrazide melting at 143°. According to Davidoff methysticin is $C_{16}H_{18}O_5$ and is decomposed by alcoholic NH_3 into 'methysticin hydrate' $C_8H_{10}O_3$ and a compound $C_8H_{11}NO_2$ which crystallises from water in yellow needles. The 'methysticin hydrate' is also formed by the action of alcoholic KOH on methysticin. It melts at 159°, forms the crystalline salts $KC_8H_9O_3$ and $Ba(C_8H_9O_3)_2$, the ether $EtC_8H_9O_3$ [100°] and the benzoyl derivative $C_8H_9Bz_3O_3$ [122°].

METINULIN *v.* INULIN.

MICROCOSMIC SALT. Sodium-ammonium-hydrogen phosphate, $Na(NH_4)HPO_4.4H_2O$; *v.* PHOSPHORIC ACIDS AND PHOSPHATES.

MILK. Milk is the secretion of the mammary glands; to the naked eye it appears to be a white fluid, which in thin layers has a bluish tint. Its reaction is alkaline in herbivorous animals and in woman; acid in carnivorous animals. Its specific gravity varies greatly, averaging between 1·028 and 1·035. On microscopic examination milk is found to be an emulsion, consisting of a clear fluid which has a light straw colour, in which are suspended numerous minute fat globules of varying size, each inclosed in an envelope of casein. Numerous particles of casein and nuclein are also seen (Kehrer, *Arch. Gynaek.* 2, 1). The clear fluid in which these float contains proteids, lactose, and mineral salts in solution. During the first few days after parturition the milk contains a larger proportion of solid constituents, and is found microscopically to contain, besides the ordinary fat globules, a number of the secreting epithelium cells of the mammary gland of which the protoplasm has undergone fatty degeneration; this secretion has received the name *colostrum.* The name *uterine milk* is given to the whitish secretion of the uterine glands which is poured out from them during the early months of pregnancy in certain animals.

The following tables adapted from Charles's *Physiological Chemistry*, p. 383, after Gorup-Besanez, Liebermann, Gautier, &c., give quantitative statements of the constituents which occur in the milk of the commoner animals:—

Constituents	Woman Milk	Woman Colostrum	Ass	Cow	Goat	Sheep	Mare
Water	87·65	84·08	90·70	86·56	86·76	83·31	82·84
Solids	12·35	15·92	9·30	13·44	13·24	16·69	17·16
Proteids	3·07	3·23	1·70	4·08	4·23	5·73	1·64
Fats	3·91	5·78	1·55	4·03	4·48	6·05	6·87
Milk sugar	5·01	6·51	5·80	4·60	3·91	3·96	8·65
Mineral salts	0·17	0·35	0·50	0·73	0·62	0·68	

The Ash of Milk in 100 *parts.*

	Woman's Milk (Wildenstein)	Cow's Milk (Weber)	Cow's Milk (Haidlen)
Sodium	4·21	6·38	8·27
Potassium	31·59	24·71	15·42
Chlorine	19·06	14·39	16·96
Calcium	18·78	17·31	56·52
Magnesium	0·87	1·90	
Phosphoric acid	19·00	29·13	
Sulphuric acid	2·64	1·15	
Ferric oxide	0·10	0·33	0·62
Silica	trace	0·09	

The most abundant salts are thus the phosphates. The excess of potassium over sodium salts is the opposite to what obtains in blood plasma and most other fluids of the body. (See also Bunge, *Dissert.* Dorpat, 1874; *Zeit. Physiol. Chem.* 13, 399). The iron in milk appears to be combined with nuclein (Bunge).

Condensed Milk (*Cane Sugar added*).

Water	29 to 24
Solids	71 to 76
Casein	16 to 18
Milk sugar	8 to 18
Cane sugar	27 to 29
Ash	2 to 2·5
P_2O_5	0·2 to 0·7

Swiss Condensed Milk (*benzoic acid added—Fleischmann*).

Water	52·31	Milk sugar	17·43
Fat	13·09	Ash	2·78
Proteid	12·13	Benzoic acid	1·74

Gases of milk at 0° 41 metre pressure (Pflüger):

Carbonic acid	7·6	in 100 vols. of milk
Oxygen	0·1	„ „
Nitrogen	0·7	„ „

Certain preparations (Koumiss, Kephir) are now made from mare's and cow's milk, in which the alcoholic fermentation is allowed to take place, and which are valuable stimulants in cases of disease, especially of disordered digestion (for references on this subject *v.* Maly's *Jahrsber.* 14, 167).

The proteids of milk.—The most abundant is *casein.* This is coagulated by rennet, and the more soluble precursor in the milk of the curd should be more accurately called *caseinogen* (*v.* PROTEIDS). Albumin (*lact-albumin*) which is very similar to serum-albumin is also present. Other proteids have also been described in milk, but their presence is doubtful; thus peptone is described by Schmidt-Mulheim (*Pf.* 28, 287), by Dogiel (*Zeit. Physiol. Chem.* 9, 591), and by Biel (Maly's *Jahrsber.* 15, 193); hemi-albumose by J. Schmidt (Maly's *Jahrsber.* 14, 175). These proteids appear to be primary albumoses formed by the acidification and boiling employed to separate the casein and albumin (Neumeister, *Zeit. Biol.* 24, 271). True peptone is always absent (Neumeister, *loc. cit.*; Sebelien, *Zeit. Physiol. Chem.* 13, 135; Halliburton, *Journ. of Physiol.* 11, 449). Whey-proteid (Hammarsten), the lacto-protein of some observers, is a by-product of the action of rennet on caseinogen. Two other proteids, lacto-globulin, which is identical with paraglobulin (J. Sebelien, Maly's *Jahrsber.* 15, 184), and lacto-syntonin, which resembles acid albumin in its properties (J. Biel, *l.c.*), are also stated to occur in small quantities, but the evidence that they exist is not conclusive (Halliburton, *l.c.*). In koumiss the proteids are stated to consist of albumin, syntonin, and peptone (A. Dochmann, Maly's *Jahrsber.* 11, 190). In colostrum casein is absent, or nearly so, being replaced by globulin (Sebelien).

The fats of milk.—When milk stands, some of the fatty globules rise to the surface, and some of these are possibly freed from their proteid casing (Müller); this forms the layer of cream. Butter is the name generally given to the fat itself, which is separated from the milk globules by mechanical agitation (churning); a certain amount of casein is, however, generally present in butter, and about one-third of the fat of the milk remains in the butter-milk. The fats present are olein, much palmitin, much less stearin; and about two per cent. of the total fats consist of the triglycerides of butyric, caproic, and caprylic acids, with traces of myristic and arachidic acids. Cow's butter contains about 68 per cent. palmitin and stearin, 30 per cent. olein, and 2 per cent. the other fats just mentioned. Rancidity is due to the development of free fatty acids, acrolein, &c., and, according to Hagemann, of lactic acid from the lactose admixed with fat in the butter.

Lactose or milk sugar ($C_{12}H_{22}O_{11}$) may be obtained from milk by evaporation in rhombic crystals containing one molecule of water of crystallisation, which is given off at 140°. It dissolves in 6 parts of cold and 2·5 parts of boiling water. It is not so sweet as cane sugar; its specific rotation is $(\alpha)_D = 59·3°$. Dilute acids and hydrolytic ferments convert lactose into galactose, which is a glucose, and capable of undergoing the alcoholic fermentation, and which yields mucic acid when treated with nitric acid. Lactose reduces alkaline solutions of copper salts, and when oxidised yields mucic, saccharic, tartaric, and oxalic acid. Lactose does not itself undergo the alcoholic fermentation, but when much yeast is added fermentation occurs after some time, mannite being formed. In presence of casein, &c., it undergoes the lactic acid fermentation, and it is the occurrence of this to which the souring of milk is due.

Preservation of milk.—Many different antiseptics have been suggested for the preservation of milk, *e.g.* salicylic acid, ether, benzene, chloroform, borax, boroglyceride, &c. Preservation is, however, usually effected by evaporating the milk to a thick syrup and adding considerable quantities of cane sugar. (For recent papers on this subject *v.* A. Mayer, Maly's *Jahrsber.* 12, 168; P. Biedert, Jacobi, Dietzell, *ibid.* 169;

O. Loew, *ibid.* 171; Morgen a. Fleischmann, *ibid.* 13, 174; A. Baginsky, 175).

Alterations in milk.—Many drugs taken in medicinal doses appear in the milk, *e.g.* salts of arsenic, antimony, lead, mercury (?), zinc, &c.; also organic acids and alkaloids. In various diseases the proportion of solids to water and of the different solid constituents is altered; thus in osteo-malacia the lime-salts are increased. Blood and pus may occur in milk; a blue colour sometimes observed is due to the growth of a chromogenic bacterium (vibrio), which, however, appears to be different from that which produces the blue colour in pus (J. Reiset, *C. R.* 96, 682, 745). In tubercular diseases of cattle there is risk of contamination with tubercle bacilli; milk may also act as the carrier of other infections (scarlet fever, typhoid, &c.).

ANALYSIS OF MILK.

Qualitative.—The specific gravity, which is increased by the removal of the cream, and reaction are ascertained in the usual way; the milk may then be examined microscopically. Casein may be precipitated by acetic or hydrochloric acid, by saturation with magnesium sulphate, or by rennet coagulation. The precipitate contains also the fat which may be separated from the casein by ether. The filtrate contains the sugar, salts, and the other proteids of the milk, which may be identified by their usual tests. The butter is best obtained from milk by adding half its bulk of 10 p.c. caustic potash solution, and then shaking the mixture rapidly with twice its volume of ether; on evaporating the ethereal extract the fat is left as a residue. The milk globules may be separated from the rest of the milk by filtration through porcelain under pressure.

Quantitative.—*Solids.* To 10 grains of dry sand add 5 c.c. of milk, and dry at 100° to constant weight. The increase in weight gives the solids in 5 c.c. of milk. Below 10·5 p.c. of solids in cow's milk indicates dilution.

Butter. This may be estimated by weighing the amount of residue from an ethereal extract of milk to which an equal volume of 10 p.c. caustic potash has been added. The normal minimum for fats is about 2·75 p.c. (Cameron). There are also various optical methods which depend on the degree of opacity of milk, which varies directly as the number of globules present; galactoscopes have been invented by Donné and Vogel. (On the lacto-butyrometer, an instrument for estimating the fat by the ether method, *v.* Tollens a. Schmidt, Maly's *Jahrsber.* 8, 140; Kehrer, *ibid.* 11, 179; F. Soxhlet, 180; Egger, 181; M. Schmöger, 182.) *Cream.* This may be roughly estimated by allowing the cream to rise in a narrow graduated vessel; the thickness of the layer being read off at the end of 24 hours. Good milk should yield 10 to 15 p.c. of cream. *Proteids.* Pfeiffer's method is a good one; the casein is precipitated by acetic or hydrochloric acid, and freed from fat by ether; after filtering off the casein the albumin is precipitated in the filtrate by boiling, and after that has been removed the albumose is precipitated by tannin. It must, however, be remembered, as stated above, that albumose is an artificial product. Each of these precipitates is collected, dried, and weighed (Maly's *Jahrsber.* 13, 170; *v.* also Parr, *ibid.* 15, 185). J. Sebelien (*Zeit. Physiol. Chem.* 13, 135) estimates the proteids by the amount of nitrogen in the precipitates produced by various reagents. *Lactose.* The casein, fat, and albumin having been removed, the milk sugar is converted into dextrose by boiling with sulphuric acid, and this is estimated by Fehling's solution or by the polarimetric method.

[In addition to the papers already quoted abstracts of the most important of recent papers on milk analysis will be found in Maly's *Jahrsbericht* as follows: J. Forster, 11, 177; Giunti, 178; Weiske a. Kennepohl, 187; de Leon, 12, 151; Kraach, 155; Stenberg, 161; Emmerich, 165; Fleischmann a. Morgen, 166; Jörgensen, 167; F. Hofmann, 177; Liebermann, 13, 168; C. H. Wolff, 169; Schrodt a. Haussen, 14, 180; *v.* also Schmidt-Mulheim, *Pf.* 30, 602.] Fleischmann, *Das Molkereiwesen*, and Tatlock, *The Produce of the Dairy*, Glasgow, 1888, should be also consulted. W. D. H.

MILK SUGAR *v.* SUGAR.

MILLET OIL. Appears to contain an acid $C_{18}H_{32}O_3$. On fusion with potash oil of millet yields acetic and lauric acids. On distillation it yields an acid $C_9H_{16}O_2$ or $C_{10}H_{18}O_2$ (216°–220°). Oxidation by $KMnO_4$ forms an hexoic acid $C_6H_{12}O_2$, and two oxy-acids $C_{14}H_{26}(OH)_2O_2$ [60°], and oxy-hexoic acid [108°], which yields an acetyl derivative $C_6H_{11}(OAc).CO_2H$ [71°] (Kassner, *Ar. Ph.* [3] 25, 1081).

MILLON'S REAGENT. A solution of mercuric nitrate containing nitrous acid, prepared by dissolving mercury (1 pt.) in HNO_3 (1 pt.) diluted with water ($4\frac{1}{2}$ pts.). It gives a red coagulum when warmed with albumen (Millon, *A.* 72, 349).

MINERAL ACIDS. A term sometimes applied to acids formed of elements other than carbon. The term is chiefly applied to the stronger commonly used acids, sulphuric, nitric, and hydrochloric.

MINERALOGICAL CHEMISTRY. Mineralogical chemistry is that part of chemistry which relates to the mineral products of nature; it is also a part of mineralogy, the science which treats, not only of the chemical characters of these products, but also of their physical and geometrical characters, of their modes and places of occurrence, and of their classification.

Mineral products, as they are found in nature, frequently retain much the same character over a considerable extent of country and sometimes for a considerable depth; to such a product the term *rock* is applied, and to each kind of rock is given a special name. Mineral products are either simple or mixed. When simple they cannot be resolved, by mechanical or optical means, into matter presenting different characters; simple mineral products are briefly designated as *minerals.* Rocks are almost always mixed products. Generally the presence of different substances is obvious to the unaided eye, and the constituents can be readily separated from each other by mechanical means. From the rock termed *granite*, for example, may be got at least three kinds of matter: firstly, a substance yielding rhomboidal fragments when broken (*felspar*); secondly, a glassy substance yielding only irregular fractures

(*quartz*); and thirdly, a substance which may readily be split into very thin plates (*mica*). By no mechanical process can these substances be resolved into others having different characters; hence they are termed *minerals*; and as they present manifold differences from each other they have received distinctive names. Sometimes the composite nature of a rock is not evident until a slice, made sufficiently thin to be transparent, is examined with a microscope. Or, again, a rock, as for example *marble*, may consist wholly of a single kind of matter.

All simple minerals having the same essential characters are said to belong to the same *species*; those belonging to the same species may likewise have one or more unessential, yet more or less important, characters in common, and are then said to constitute a *variety* of that species.

It is the province of the mineralogist to discover what characters are presented by minerals, to name the characters, to determine their relative importance, to name the species and their varieties, to classify the species, and so on. Such a study of minerals must have been in progress since the earliest times. Even before 300 B.C. the study was so far advanced that minerals were classified as *metals* (*i.e.* those having a metallic lustre), *stones*, and *earths*; the characters then recognised as pertaining to *stones*, and used in their discrimination, were succinctly referred to by Theophrastus as follows:—

> 'There are in stones of different kinds many peculiar qualities, of which colour, transparency, brightness, density, hardness, and the like are frequent, though other more remarkable properties are not so common. But besides these qualities there are others; such as their acting upon other bodies, or being subject or not subject to be acted upon by them. Some are fusible, others will never liquefy in the fire; some may be calcined, others are incombustible; to which it may be added that in the action of fire on them they show also many other differences. Some, as amber, have an attractive quality. Others serve for the trial of metals, as the Lydian stone. But the most known and general properties of stones are their several fitnesses for the various kinds of work: some of them are proper for engraving on; others may be shaped by the turner's tools; others may be cut or sawn; some also there are which no iron instruments will touch, and others which can with difficulty, or scarcely at all, be cut by them.'

In this way it was possible even for the Ancients, without any knowledge of either crystalline form or chemical composition, to determine more or less satisfactorily the species met with in the mineral kingdom.

The definition and classification of species by means of what have been termed 'external characters' (such as crystalline form, cleavage, density, hardness, colour, lustre, &c.)—*i.e.* characters which can be determined without involving a total change of the characters of the mineral—had been found so far satisfactory that the external characters were used both for the definition and classification of the species by the best mineralogists even so lately as the early part of the present century. The most important of the external characters is now recognised to be the crystalline form. It was shown in the year 1772 that all the crystalline forms of the same substance, whether the substance is natural or artificial, are so closely related to each other that they are derivable by simple laws from a single form; and it has since been proved that the whole series of crystalline forms of the same substance can be defined by means of numerical values which fix the shape of one of its forms; hence the limitation of each species to specimens which can be referred to one fundamental crystalline form became a necessity (*v.* CRYSTALLISATION, vol. ii. p. 278).

The recognition of chemical elements and chemical compounds, and of the constancy of the proportion of the elements in each compound, the setting forth of the atomic theory and chemical formulæ, and the development of analytical methods, had great influence on the advance of mineralogy. When the specimens belonging to a species which had been defined by means of external characters were subjected to chemical analysis, it was discovered that in many cases there was a large variation in the proportion, and even in the nature, of the constituent chemical elements. For a time it was supposed that, while some substances have a great tendency to crystallise, others are comparatively inert; that, for example, the crystalline form of dolomite (carbonate of calcium and magnesium) is due entirely to the crystallising power of the carbonate of calcium, and that the carbonate of magnesium is either a mere inactive inclusion, or so feeble a crystalliser as to be completely overpowered by the carbonate of calcium. The explanation of these variations of chemical composition within species, as defined by means of the external characters, was eventually furnished by the principle of *Isomorphism* (*q. v.*); and it then became possible to define a species by means of a combination of only two characters —chemical composition and crystalline form. In other words, it was found that all specimens which can be referred to the same fundamental crystalline form and to the same chemical type have all other essential characters in common, though they may differ in the less important ones, such as colour or transparency. For example, if the forms of crystals can be referred to the same fundamental figure, the differences of crystalline development are themselves unessential; hence the substances popularly known as *dogtooth-spar* and *nailhead-spar*, which can be crystallographically referred to the same rhombohedron, and chemically are carbonate of calcium, are regarded as varieties of the species *calcite*, which includes all specimens having these two fundamental characters in common. Similarly, colour is another unessential character: the specimens belonging to the species *fluor*, for instance, show a remarkable variation in colour. In some cases a variety characterised by a particular colour receives a distinctive name; *emerald* and *aquamarine*, for example, are respectively dark-green and light bluish-green varieties of the species *beryl*. It is very seldom, however, that varieties are really worthy of being distinguished by special names, and in almost every species the transition from one variety to another is so gradual that it is often impracticable to decide on the single variety to which a specimen may be satisfactorily referred. On the other hand there are specimens which, though chemically carbonate of calcium, can all be referred to a single fundamental crystalline form quite distinct from that of

calcite. They are therefore regarded as belonging to a distinct species and are grouped together under the name of *aragonite.* That such a separation is a legitimate one is shown by the fact that the two species, as thus defined, differ in other important characters, such as cleavage, hardness, specific gravity, optical constants, &c. Hence the chemical compound calcium carbonate is said to be *dimorphous*; but, as already indicated, the difference between the two kinds of substance is much more than one of form. Titanic oxide, again, is met with in nature as three different kinds of substance, each presenting its own set of characters; they are necessarily to be regarded as distinct species, and have received the specific names *rutile*, *anatase*, and *brookite*: titanic oxide is said to be *trimorphous.* The variety of chemical composition among specimens regarded as belonging to a single mineral species, and which is explicable on the above-mentioned principle of isomorphism, is well illustrated by the results of analyses of specimens of *tetrahedrite* (or *grey copper ore*). The crystals of this mineral belong to the cubic system and are hemisymmetrically developed, being all closely related in figure to the regular tetrahedron; chemically they can be referred to the general formula $4R''S.R'''_2S_3$, where R″ includes chiefly Cu_2, Fe, Zn, Ag, and Hg, and R‴ includes Sb, As, and Bi. The composition shows the following variations: copper 15 to 42 p.c., iron 1 to 7, zinc 0 to 7, silver 0 to 31, mercury 0 to 17, antimony 12 to 30, arsenic 0 to 20, bismuth 0 to $1\frac{1}{2}$; a few of the varieties, those containing noteworthy proportions of silver or mercury, for instance, have been distinguished by special names. The difficulty of deciding whether a mineral product is to be regarded as a distinct species or as a variety of another species presents itself in the case of the specimens to which the name of *tennantite* has been given; crystallographically they show the same relationship to the regular tetrahedron which characterises the specimens of tetrahedrite, and chemically they are represented by the same general formula $4R''S.R'''_2S_3$; they are distinguished, however, by the absence of antimony (and bismuth): as in the chemical composition of the specimens belonging to the above crystallographic and chemical type there is thus a sudden transition from 12 p.c. of antimony (generally accompanied by more or less arsenic) to zero, the specimens of *tennantite* are generally regarded as entitled to rank as a distinct species. Similarly *aragonite*, *witherite*, *strontianite*, and *cerussite* belong to one chemical type $R''CO_3$, and are almost identical in their fundamental crystalline forms; for the several minerals R″ is essentially Ca, Ba, Sr, and Pb: they are regarded as distinct species because in nature there is found no gradual transition of chemical composition. On the other hand, the isomorphous rhombohedral carbonates belonging to the above chemical type $R''CO_3$, where R″ is Ca, Mg, Fe, or Mn, present such a gradual shading into each other, both chemically and physically, that a perfect definition of species is impossible. Another instructive illustration of this difficulty is furnished by the group of minerals to which the name *garnet* has been given. The garnets crystallise in the cubic system, and in their forms the dodecahedron is prominently developed; chemically they are represented by the general formula $3R''O.R'''_2O_3.3SiO_2$. They have in general very similar physical characters, though they differ considerably both in colour and specific gravity; they have in fact every claim to recognition as a natural family or group. But the differences of chemical composition are remarkable. R″ and R‴ are essentially, for *grossularite*, Ca and Al; for *pyrope*, Mg and Al; for *almandite*, Fe″ and Al; for *spessartite*, Mn and Al; for *andradite*, Ca and Fe‴; for *bredbergite*, Ca, Mg, and Fe‴; for *uvarovite*, Ca and Cr. As the above kinds of garnet are connected by various transitions, it may easily be imagined that the garnet group presents great difficulty as regards the definition of its species, and that it is possible to introduce a large number of unnecessary names into the science.

There are other natural groups or families, however, as for example, the *augite*, *hornblende*, *scapolite*, *felspar*, *mica*, *chlorite*, and *tourmaline* groups, in which the representation of the chemical composition of the whole group by a single chemical formula presents great difficulties. Indeed, the formulæ which are employed in mineral chemistry are at present for the most part empirical; constitutional formulæ, such as are employed in organic chemistry, are almost unknown. Much work must be done before we obtain a real insight into the structure of the more complex silicates. For attempts in this direction the student may refer to the following:—

Augites and *Hornblendes*: Tschermak's *Mineralogische Mittheilungen*, 1871. 17; *Neues J. M.* 1, 43.

Scapolites: *Sitz. W.* 1883 [1st part]. 1142.

Felspars: *ibid.* 1864 [1st part]. 566.

Micas: *ibid.* 1878 [1st part]. 5; *Am. S.* [3] 38, 384.

Clintonites: *Sitz. W.* 1878 [1st part]. 555.

Tourmalines: *P.* 139, 379, 547.

Silicates in general: *Z. K.* 17, 25.

Minerals are of interest to the chemist as the source of the various chemical elements, the characters of which, and of their combinations, it is his province to study. A few of these elements are found in the uncombined state, notably carbon, sulphur, arsenic, bismuth, copper, silver, gold, and platinum. Some are present in large proportion in numerous mineral species, the latter themselves plentifully dispersed through the earth's crust; others are found in few mineral species, and those only in small quantities and in few localities.

It is the province of the mineralogical chemist to determine the chemical composition of each species and variety, and to represent it by means of an empirical or constitutional formula. A considerable number of minerals are pure or nearly pure chemical compounds of simple constitution, and these are specially interesting to the chemist, as they often furnish him with beautifully crystallised specimens of compounds which, as laboratory products, are either amorphous or are obtained as minute crystals only with much expenditure of time and trouble; among such compounds we may especially note the sulphides of lead, zinc, copper, iron, antimony, and arsenic; the various sulpharsenites

and sulphantimonites; the oxides of aluminium, iron, titanium, silicon, and tin; various silicates; molybdate, tungstate, and chromate, of lead; tungstate of calcium; the sulphates and carbonates of calcium, strontium, barium, and lead; various phosphates, arsenates, and vanadates, of copper, lead, and calcium.

Time and energy are now rarely expended in the chemical analysis of a substance unless there is something extraordinary in its external characters; and it is by means of these characters that it is possible to describe for future recognition the substance of which an analysis has been made.

Mineralogical chemistry deals, too, with the classification of all the chemical compounds met with in the mineral kingdom; in fact, the arrangement in large groups is now generally based on chemical composition, though the definition of the species is made to rest also on the crystalline form. The system of classification now generally adopted is as follows:—

Division I. Native elements; metallic and non-metallic.

Division II. The compounds of metals with elements of the arsenic and sulphur groups, viz. arsenides, sulphides, arseno-sulphides, sulphosalts; and their analogues.

Division III. Chlorides; and their analogues.

Division IV. Compounds of oxygen: (*a*) oxides; (*b*) oxy-salts; namely, (1) carbonates, (2) silicates and titanates, (3) molybdates and tungstates, (4) chromates and sulphates, (5) borates, (6) nitrates, and (7) phosphates, arsenates, and vanadates.

For details *v.* Groth's *Tabellarische Uebersicht der einfachen Mineralien*; Braunschweig, 1889.

The mineralogical chemist observes the reactions of minerals with various reagents, both in the wet and dry way, and on a large or a microscopic scale, and by a classification of reactions he provides means for the determination of the species by chemical methods.

To the mineralogical chemist is further assigned the most important task of discovering the modes in which the various chemical compounds may be produced artificially, and the investigation of the processes and reactions by which these chemical compounds have been actually produced in nature. In this respect *pseudomorphs* (*i.e.* minerals presenting a form characteristic not of their own but of some other substance) are of great value. They are always results of chemical change, and are produced in various ways. Some are merely due to the investment of a substance afterwards removed from beneath the crust; these have been termed *epimorphs*. For example, hollow, well-defined scalenohedra of *limonite* (hydrated ferric oxide) are met with; they owe their form to crystals of calcite upon which the limonite has been deposited. In other cases the original mineral is altered throughout its mass, and suffers a loss of a chemical constituent, as when *galena* (sulphide of lead) is found with the form of *anglesite* (sulphate of lead). Or, again, there has been an addition of a chemical constituent; as when *chessylite* (a hydrated carbonate of copper) is found with the form of *cuprite* (oxide of copper). Or, again, there has been an exchange of chemical constituents; as when *galena* is found with the form of *pyromorphite* (phosphate and chloride of lead), or *calcite* with the form of *gypsum*. Sometimes there is a complete exchange of material without loss of form; as when copper is found with the form of aragonite. Pseudomorphs illustrate the decomposing influences to which many minerals have been subjected, and throw valuable light on the order of succession in which, and the conditions under which, particular minerals have been formed and deposited; and in furnishing sure proofs of conversions which we cannot hope to effect in the laboratory, they afford a knowledge of facts which can be arrived at in no other way.

The following works, relative to the artificial production of substances met with as minerals, may be consulted:—

Fuchs, *Die künstlich dargestellten Mineralien*, Haarlem, 1872.

Daubrée, *Études synthétiques de géologie expérimentale*, Paris, 1879.

Fouqué a. Lévy, *Synthèse des minéraux et des roches*, Paris, 1882.

Bourgeois, *Reproduction artificielle des Minéraux*, Paris, 1884. L. F.

MINT. The oil of spear mint (*Mentha viridis*) contains $C_{10}H_{14}O$ (225°), S.G. ·952, and a terpene (Gladstone, *J.* 1863, 548; *cf.* Kane, *A.* 32, 286).

Peppermint *v.* Menthol.

MOCHYLIC ALCOHOL $C_{26}H_{16}O$. [234°]. Present in bird-lime as mochyl palmitate $C_{42}H_{76}O_2$ (Divers a. Kawakita, *C. J.* 53, 274). Slender lustrous prisms; insol. water, v. sl. sol. petroleum-ether, v. sol. ether, m. sol. alcohol. Dissolves like birdlime in conc. H_2SO_4 with a red colour. Heated with palmitic acid in sealed tubes to 160° a substance very similar to birdlime is obtained. Yields on distillation a hydrocarbon $C_{26}H_{24}$.

MOLECULAR CONSTITUTION OF BODIES, THEORIES OF. The theory of the molecular constitution of matter now universally accepted was held long before any crucial proof was given of its necessity. For though such phenomena as the enormous changes in volume which take place when a gas condenses to a liquid point most strongly to some such view, they cannot be held to be conclusive, unless it is considered axiomatic that a perfectly homogeneous structure is incapable of dilatation or contraction. The first attempt to give more elaborate reasoning in favour of the molecular theory of the constitution of matter seems to have been made by Cauchy, and was founded upon the dispersion which light experiences when it passes through transparent bodies. Since the velocity of light when passing through such bodies depends upon the wave-length of the light, and also on the nature of the body, Cauchy argued, that since a velocity is not of the same dimensions as a length, the velocity cannot depend upon the wave-length absolutely, but must depend merely upon its ratio to some other length; now the only length available is one derived from the body itself, and since the dispersion does not depend upon the dimensions of the transparent body, this length must be one intrinsic to the body; the body therefore cannot be homogeneous and without structure or

there would be no such length available; the body must therefore be coarse-grained. This reasoning, however, is not quite conclusive, for light of different wave-lengths has different times of vibration, and the phenomenon of dispersion might be expected if there were any time connected with the structure of the body which could come into comparison with the time of vibration of the light. Dispersion proves that the transparent body is coarse-grained, either with respect to space or time, but does not prove that it is necessarily coarse-grained with regard to space on a scale comparable with the wave-length of light. In fact, in the theories which have been put forward to explain dispersion, this phenomenon is made to depend upon the ratio of the time of vibration of light to some time of vibration of the molecules of the system. A less ambiguous proof of the molecular structure of gases was given by Osborne Reynolds in his paper '*Some Dimensional Properties of Matter in the Gaseous State*' (*T.* 1879). This proof was founded on the phenomenon called the 'thermal effusion' of gases. This phenomenon is of the following kind:—If we have a vessel divided into two portions by a porous diaphragm, say of stucco or meerschaum, and the gas on one side of the diaphragm is kept at a different temperature from that on the other side, it is found that, in order to prevent the gas flowing from the cold to the hot side of the diaphragm, the pressure of the gas on the hot side must be greater than that on the cold side, and that the difference of pressure required to prevent the flow obeys different laws according as the gas is dense or rare. If the gas is dense, this difference of pressure varies inversely as the density of the gas, while if the gas is rare, the difference of pressure varies directly as the density. Reynolds found that the density of the gas at which the law changed from one form to the other depended upon the fineness of the pores of the diaphragm; the finer the pores, the greater was the density at which the law changed. Thus, since the law connecting the difference of pressure with the density depends upon the diameter of the pores of the diaphragm, there must be some length in the gas with which this diameter of the pores can come into comparison; the gas must therefore have structure, and since the density of the gas when the law changes is greater for small pores than for large ones, the structure of the gas must be finer at great densities than at low ones. The investigations of Sir William Thomson (*Popular Lectures and Addresses*), Loschmidt, and others, have gone further than this, and have not merely furnished proofs that matter has structure, but have given limits below which the coarse-grainedness of matter cannot lie. These investigations are founded on considerations about surface-tension, the difference of potential which occurs when two metals are put in metallic connexion, the amount of polarisation at the surface of an electrode and an electrolyte, the viscosity, the diffusion, and the conductivity for heat, of gases. It will be sufficient for us to show how one of these leads to a limit for the dimensions of molecular structure, and we will take the one depending on the surface-tension. The surface-tension of a film of liquid is not likely to alter until the thickness of the film falls below the distance at which one molecule ceases to exert an appreciable influence on another, for it is only the molecules within a film of this thickness which can exert any influence on those at the surface; so that if we can find a limit to the thickness of a film which possesses an unaltered surface-tension, we shall have a quantity comparable with the distance up to which one molecule exerts an appreciable effect on another. When a film is stretched, work is done on it against surface-tension, and this work is stored up in the film, so that if the surface-tension were the same for an infinitely thin film as for one of finite thickness, an infinite amount of work could be stored up in the film. But the greatest amount of energy which can be stored up in, say, a gram of water must be less than the amount required to separate the molecules to such a distance that they no longer exert any influence on each other; but this is exactly what is done when the water is vaporised, so that the greatest amount of energy which can be stored up in a gram of water is less than the amount required to convert it into steam. To convert one gram of water at 15° into steam requires the expenditure of $621 \times 4{\cdot}2 \times 10^7$ergs. If T be the surface-tension of water, and if the gram of water is stretched into a thin film whose thickness is x, the work done in stretching it is $\frac{2T}{x}$, but this is not all the energy which is communicated to the film, for, unless heat is supplied to the film as it stretches, it will cool; the amount of heat which must be supplied to the film, when measured in mechanical units, is about half the work done in stretching the film, so that the total energy communicated to the film is $\frac{3T}{x}$; this must be less than the work required to vaporise the film, so that $\frac{3T}{x}$ must be less than $536 \times 4{\cdot}2 \times 10^7$, or putting T at 15° equal to 74, x cannot be less than $8{\cdot}5 \times 10^{-9}$ cm., that is, a thickness of 10^{-8} cm. must be comparable with the range of molecular action of the water molecules.

Quincke (*P.* 137, 402) investigated the range of molecular forces, by finding the thickness of a silver film which when deposited on glass just began to alter the capillary ascent or depression of water in contact with the glass. The results of this, and other investigations with a similar object, are summarised in the following extract from a paper by Rücker (*C. J. Trans.* 1888. 260):—

Table of properties of thin films and of molecular magnitudes.

Thickness of film = 118×10^{-7} cm.

Superior limit to the radius of molecular action, deduced from Plateau's experiments (*Statique des Liquides*, 1873, i. 210) on the pressure of a soap-bubble, by using Maxwell's theory that the surface-tension first diminishes when the thickness of the film equals the range of molecular action, $96 \times 10^{-7} - 45 \times 10^{-7}$.

Between these limits the thickness of a film begins to be unstable, that is, the surface-tension

begins to diminish. Hence the radius of molecular action must be $< 96 \times 10^{-7}$ and $> 22 \times 10^{-7}$ cm.

50×10^{-7} cm.

Value of the range of molecular action deduced by Quincke (*P.* 137, 402) from experiments on capillary elevation.

12×10^{-7} cm.

Average thickness of black soap films, measured by two independent methods.

As the tension of a black film is equal to that of a thick film, the surface-tension, which begins to diminish at 50×10^{-7} cm., must increase again, and reach its original value at 12×10^{-7} cm. This is also about the thickness below which, according to O. Wiener (*W.* 31, 629), a thin silver plate will no longer produce the same effect on the phase of reflected light as a thick silver plate would do.

$10{\cdot}5 \times 10^{-7}$ cm.

Thickness of the permanent water-film observed by Bunsen (*W.* 24, 322) on unwashed glass at a temperature (23° C.) at which the vapour pressure of water is small.

4×10^{-7} to 3×10^{-7} cm.

Average distance from centre to nearest centre of molecules in gases under standard conditions, calculated by Meyer (*Die kinetische Theorie der Gase*).

3×10^{-7} cm.

Thickness of metal films required to polarise platinum completely (Oberbeck, *W.* 31, 331).

10^{-7} to 2×10^{-9} cm.

Thickness of electric double layer, according to Oberbeck and Falck (*W.* 21, 157).

2×10^{-8} cm.

Smallest thickness of silver which affects the phase of reflected light (Wiener, *l.c.*).

$1{\cdot}4 \times 10^{-8}$ to $1{\cdot}1 \times 10^{-8}$ cm.

Diameter of gaseous hydrogen molecule.

$7 \times 10^{-9} - 2 \times 10^{-9}$ cm.

This is given by combining (1) the specific inductive capacity and coefficient of viscosity; (2) the refractive index and coefficient of diffusion; (3) the law of expansion and the thermal conductivity.

Average distance between centre of molecules supposed arranged uniformly in liquids and solids according to Thomson.

2×10^{-9} cm.

Inferior limit to the diameter of a gaseous molecule according to Thomson. These results may be shortly summed up as follows:—

10^{-7} cm.		
118×1	Superior limit to range of molecular action.	Plateau. Maxwell.
96–45	Range of unstable thickness begins.	Reinold and Rücker.
59	Superior limit to range of molecular action.	Plateau.
50	Magnitude of range of molecular action.	Quincke.
12	Range of unstable thickness ends.	Reinold and Rücker.
12	Action of silver-film on phase of reflected light alters.	Wiener.
10·5	Thickness of permanent water-film on glass at 23°.	Bunsen.
4–3	Mean distance between centres of nearest molecules in gases at 760 mm. and 0° C.	O. Meyer.
3–1	Thickness of metal-films which polarise platinum.	Oberbeck.
1–0·02	Thickness of electric double layer.	Lippmann and Oberbeck.
·2	Smallest appreciable thickness of silver-film.	Wiener.
·14–·11	Diameter of gaseous hydrogen molecule.	Exner. O. Meyer. Van der Waals.
·07–·02	Mean distance between centres of nearest liquid molecules.	W. Thomson.
·02	Inferior limit to diameter of gaseous molecule.	W. Thomson.

Having obtained some idea of the coarseness of the structure of matter, we shall now consider various theories of that structure. In order to see what has been explained by these theories, and what remains to be explained, let us enumerate the most important properties of matter in that state of aggregation when the properties are the most simple, *i.e.* the state of a so-called 'perfect' gas.

1. The relation between pressure, density, and temperature is expressed by the laws of Boyle and Charles, $p = \kappa \rho \theta$, when p is the pressure, ρ the density, and θ the absolute temperature of the gas, and κ is a quantity which remains constant for the same gas. For different gases κ is inversely proportional to their combining weights. In all such gases there is the same number of molecules in unit volume, provided the pressure and temperature are the same.

2. The gases possess viscosity. The coefficient of viscosity (unless the density is very greatly reduced) is independent of the density, but depends upon the temperature. The most recent experiments show that the viscosity varies as the two-third power of the absolute temperature (Barus, *Bulletin of the U. S. Geological Survey*, No. 54, 1889).

3. The gases conduct heat with a facility depending on the temperature.

4. They diffuse into each other with a rapidity depending upon the density and the temperature.

5. They possess specific heats of various kinds, the ratio of the specific heat under constant pressure to that under constant volume being 1·4 for most gases.

6. They exhibit phenomena of the type of those which occur in the radiometer.

7. When they are raised to a high temperature they become luminous, and give out rays of definite periods, the periods being independent of the temperature. They absorb light of the same periods as those they give out when hot.

8. They possess very different electrical properties. For low differences of potential they insulate almost perfectly; but when the electric intensity is raised sufficiently a spark passes through them, and the electricity is discharged.

9. The various gases exhibit very different chemical properties.

According to the kinetic theory of gases a gas consists of a great number of small particles called molecules, moving about with great velocity in all directions, but continually either striking against each other, or coming so near together that they exert forces on each other which produce effects somewhat similar to those produced by the collision of two elastic balls. This theory has been shown by Maxwell and

Clausius (Maxwell's *Theory of Heat*; O. E. Meyer's *Die kinetische Theorie der Gase*) to be sufficient to explain all those properties of gases included under (1). These properties are independent of the nature of the molecule, and of the exact way in which two molecules act upon each other. They could be deduced equally well whether we supposed the molecules to be hard elastic spheres, or systems attracting or repelling each other when they come near together, or vortex rings. When we consider other properties besides those included in (1), we find the explanation less satisfactory. The theory gives an explanation of the viscosity, diffusion, and conduction of heat; but the exact way in which these properties vary with the temperature depends upon the nature of the action between the molecules. Two cases have been worked out by Maxwell. In the first case the molecules were supposed to be hard, perfectly elastic spheres, and which only acted upon other molecules when in collision with them. According to this hypothesis, the coefficient of viscosity would be proportional to the square root of the absolute temperature. The other case which has been worked out by Maxwell is that in which the molecules are regarded as systems repelling each other with forces which vary inversely as the fifth power of the distance between them. According to this hypothesis, the coefficient of viscosity would be proportional to the absolute temperature. The experiments of Barus (*l. c.*) and others show that the coefficient of viscosity obeys neither of these laws, but varies more quickly with the temperature than the result obtained on the first hypothesis, and more slowly than that obtained on the second. Neither of these theories of the action of one molecule on another can be the true one. Sutherland (*P. M.* 24, 113, 168), by considering the results of Thomson and Joule's experiments on the cooling of gases passing through a porous plug, arrives at the conclusion that the force between two molecules must be inversely as the fourth power of the distance between them. The value of the temperature-coefficient of the viscosity on this hypothesis has not, however, been worked out.

The fact that the ratio of the specific heat at constant pressure to the specific heat at constant volume is the same for the perfect gases with the same number of atoms in the molecule has not been explained by the kinetic theory, and in fact the results we should expect from the kinetic theory are so different from those actually observed that they constitute perhaps the gravest difficulty which the kinetic theory has yet encountered. The results to which the kinetic theory leads are easily found. Let T_m be the total kinetic energy of the molecules in unit mass, β the ratio of this to the energy due to the translatory motion of their centres of gravity, p the pressure, v the volume of unit mass, and θ the absolute temperature. Then $Tm = \frac{3}{2}\beta p v$, so that k the specific heat at constant volume will equal $\frac{3}{2}\frac{\beta p v}{\theta}$. If the pressure is kept constant, then, in addition to the energy spent in warming the gas, an amount of work—$p \times$ (change in volume for one degree)—is done; but when the pressure is constant the volume is proportional to the absolute temperature; so that the change in volume for one degree $= v/\theta$. Thus, if k_p be the specific heat at constant pressure, then

$$k_p = \frac{3}{2}\frac{\beta p v}{\theta} + \frac{p v}{\theta};$$

$$\text{so that } \frac{k_p}{k_v} = \frac{\frac{3}{2}\beta + 1}{\frac{3}{2}\beta}$$

or if the ratio of the specific heats be denoted by γ

$$\gamma = 1 + \frac{2}{3\beta}; \quad \beta - 1 = \frac{5 - 3\gamma}{3(\gamma - 1)}.$$

Now $\beta - 1$ is the ratio of the internal energy of the molecules to that due to the motion of translation of their centres of gravity, and we see from the preceding equation that this depends only upon the ratio of the two specific heats; the constancy of this ratio for different gases shows that the proportion which the vibratory energy bears to the energy of translation must be the same for all such gases, so that at the same temperature the vibratory energy of all these gases must be the same. Now the number of lines visible in the spectrum of the various gases is very different, and we should therefore expect the gases to have very different capacities for vibratory energy. The fact that it is not so seems to indicate that the vibratory energy is not due, at any rate at low temperatures, to those quicker modes of vibration which manifest themselves as light, but must be due to some other modes common to all gases. This mode in a diatomic gas may, possibly, be the motion of the atoms relatively to each other; and this view is strengthened by the fact that the ratio of the vibratory to the translatory energy increases with the number of atoms in the molecule. Thus, if we take Dulong's values of the ratio of the specific heats for hydrogen, carbon dioxide, nitrous oxide, and ethylene, the values of the ratio of the vibratory energy to the energy of translation are respectively ·75, 1·1, 1·1, and 2; thus, for these gases the ratios are very approximately proportional to the number of atoms in the molecule; and the result suggests that the vibratory energy at these low temperatures is that of the atoms in the molecule relatively to their common centre of gravity, and not of the quicker modes of vibration corresponding to the luminous rays. If experiments on the ratio of the specific heats could be made at temperatures high enough to produce luminosity of the gas, it is possible that the results might be different from those made at lower temperatures, and that they might be found to vary from gas to gas.

Theories of the Constitution of the Molecule. The kinetic theory of gases, as developed by Clausius and Maxwell, dealt chiefly with the behaviour of a large number of molecules, and said little about the constitution of individual molecules. Quite recently, however, Sir W. Thomson (*Lectures on Molecular Dynamics and the Wave Theory of Light*) and Lindemann (*Ueber Molekularphysik*; *Physikalisch. Gesellschaft*, Königsberg, 39 [1888]) have discussed the properties of a molecule consisting of a number of spherical

shells, one inside the other, each shell being connected to the one next it by an elastic spring. The external spherical shell is supposed to be acted on by the ether, or, what is the same thing, by a periodic force whose period is that of the vibrations which the ether is transmitting. We may say in passing that many of the results obtained do not depend upon this special view of the construction of the molecule, but would be true if we supposed the molecule to be a dynamical system whose configuration could be fixed by n co-ordinates, that is, a system possessing n degrees of freedom. The behaviour of such systems when light falls upon them is investigated in the papers above mentioned, and expressions are obtained for the refractive index of a medium consisting of molecules of this kind for light of any period. These expressions explain the dispersion of light, and the results deduced from them agree with those found by experiment; they also explain the anomalous dispersion of the rays whose periods nearly coincide with those which are absorbed by the medium—a subject which was investigated experimentally for several substances, especially a solution of fuchsine in alcohol, by Kundt and Christoffel—the periods of vibration of the glowing gas being the periods of vibration of the spherical shells which constitute the molecule. The nature of the molecules assumed in this theory imposes a limit to the amount of energy due to the relative motions of the shells; for it is evident that the amplitude of vibration of any shell cannot be greater than the difference between its radius and that of a neighbouring shell. Thus, on Lindemann's theory, the internal kinetic energy reaches a maximum, and when it has reached this maximum any further exposure to light must lead to an increase in the translatory energy, and thus to an increase in the temperature of the system made up of such molecules.

Lindemann explains the development of heat which occurs on chemical combination by the transference of the internal kinetic energy into translatory energy, the substances after combination possessing less internal energy than before, the heat being produced by a loss of kinetic energy, and not, as in the ordinary explanation, by a loss of the potential energy of separation. If this view is correct, however, the internal kinetic energy must in certain gases be enormously greater than the translatory energy; thus, for example, in the combination of hydrogen and oxygen enough heat is produced to raise the temperature of the mixture nearly 20,000° C.; and even assuming that after combination there is no internal kinetic energy, the internal kinetic energy before combination must be about 70 times the translatory energy. It is very difficult to see how this can be reconciled with the value found by experiment for the ratio of the specific heat at constant pressure to that at constant volume.

According to Lindemann, the electric properties of bodies are to be explained by internal kinetic energy due to vibrations which are too quick to be visible; in fact, roughly speaking, electricity is ultra-violet light. This view is open to many difficulties, one of which is that it would not lead us to expect the great difference that exists between the electrical properties of the atom and the molecule. A molecule seems to be almost electrically neutral; thus it is impossible to communicate a charge of electricity to the molecules of a gas, though when the molecule is split up into atoms it exhibits most energetic electrical properties. Karl Pearson (*Proc. London Math. Soc.*, 20, 38) has developed a theory in which the molecules are supposed to be made up of spheres vibrating in an uncompressible fluid; he obtains results similar to those of Sir W. Thomson and Lindemann. In fact, as we said before, many of these results do not depend upon the nature of the molecule, but would be true if we supposed the molecule to be a dynamical system possessing n degrees of freedom.

Evidence as to molecular structure afforded by the spectra of bodies.—If we consider the oscillations of a dynamical system possessing n degrees of freedom, we find that there are n periods of vibration given by the roots of a determinantal equation, and that the relation between these roots depends on the nature of the system; a system could be constructed having n periods of any given value. If, however, the system possesses an infinite number of degrees of freedom, there will be an infinite number of periods, but the periods will be connected by more or less simple relations. Thus, if the vibrating system were like a stretched string, the periods would be proportional to the natural numbers, while if it were like a bar, the periods would be proportional to the natural numbers for the longitudinal and torsional vibrations, and to the roots of the equation $\frac{1}{x}\left\{\epsilon^{\frac{1}{x}} + \epsilon^{-\frac{1}{x}}\right\} = \pm 2$ for the transversal vibrations. If the system were a circular membrane, the frequencies would be proportional to the roots of an equation formed by equating a Bessels function to zero. If the system were a uniform elastic sphere, the frequencies would be the roots of a complicated equation given by Chree in the *Transactions of the Cambridge Philosophical Society* (14, 316, 317). Other periods which have been worked out are those of circular vortex rings. The frequencies of the higher vibrations about the circular form are proportional to $\sqrt{n^2(n^2-1)}$, where n is a large natural number, and the vibrations about the circular cross section are proportional to the natural numbers (J. J. Thomson, *On the Motion of Vortex Rings*, 35, 74). Many investigations have been made with the object of finding whether or not there are simple harmonics—that is, frequencies proportional to the natural numbers—in the spectra of bodies. In the case of the spectrum of hydrogen, Johnstone Stoney finds that the wave-lengths 4102·37, 4862·11, 6563·93, which occur in this spectrum, are very accurately in the ratio $\frac{1}{32}$, $\frac{1}{27}$, $\frac{1}{20}$. Schuster, however, in his 'Report on the Genesis of Spectra' (*B. A. Reports*, 1882) says:

'Other writers, as, for instance, Soret (*P. M.* 1871. 464), have from time to time drawn attention to harmonic ratios in various spectra, and the author of this report has during the last ten years collected a large quantity of material bearing on the question. The results have, on

the whole, not been favourable to the theory of harmonic ratios. In any spectrum containing a large number of lines it is clear that, owing to accidental coincidences, we shall always be able to find ratios which agree very closely with the ratios of small integer numbers. It is only by means of a systematic investigation that we can find out whether these coincidences are due to any real cause. We must, by means of the theory of probabilities, calculate the number of the coincidences, which we might expect to find on the supposition that the lines are distributed at random throughout the whole range of the visible spectrum. If on calculating out all fractions which can be formed in a spectrum by any pair of lines the number of ratios agreeing within certain limits with ratios of integer numbers greatly exceeds the most probable number, we should have reason to suppose that the lines are not distributed at random, but that the law suggested by Messrs. Lecoq de Boisbaudran and Stoney is a true one.

'The results of a long investigation conducted in this manner tend to show that the number of harmonic ratios is, if anything, smaller than was to be expected on the hypothesis of no connexion.'

The simple harmonic ratio is not, perhaps, *à priori* the most probable relation between the periods. Balmer (*W.* 25, 80) has shown that the wave-lengths of a series of hydrogen lines are expressed by the formula $\frac{Cm^2}{m^2-4}$, where m is an integer. Hagenbach (*Verhand. d. Naturforsch. Ges. zu Basel*, 1886) has compared the results of this formula with Cornu's measurements of the wave-lengths of the hydrogen lines; the result of the comparison is given in the following table:—

$$\lambda = 3645{\cdot}42\frac{m^2}{m^2-4}$$

Line	m.	Calculated wave-length	Observed wave-length	Difference
$H\alpha$	3	6562·8	6563·1	+·3
$H\beta$	4	4860·6	4860·7	+·1
$H\gamma$	5	4339·8	4339·5	−·3
$H\delta$	6	4101·1	4101·2	+·1
$H\epsilon$	7	3969·5	3969·2	−·3
$H\zeta$	8	3888·4	3888·1	−·3
$H\eta$	9	3834·8	3834·9	+·1
$H\theta$	10	3797·3	3797·3	·0
$H\iota$	11	3770·0	3769·9	−·1
$H\kappa$	12	3749·6	3750·2	+·6
$H\lambda$	13	3733·8	3734·1	+·3
$H\mu$	14	3721·4	3721·1	−·3
$H\nu$	15	3711·4	3711·2	−·2

These results seem to show that the hydrogen molecule is a system possessing an infinite number of degrees of freedom, and not a finite number of rigid particles mutually attracting each other.

It is worthy of notice that when m is large the formula previously quoted for the frequency of vibrations of a circular vortex ring becomes $\lambda = \frac{Cn^2}{n^4-\frac{1}{2}}$ which is of the same type as Balmer's.

A very striking feature in the spectra of some elements is the recurrence in the spectra of certain groups of lines—for example, triplets in the magnesium, doublets in the sodium, spectrum—and the most promising way of finding whether there is anything corresponding to overtones in the spectrum would be the investigation of the relation between the frequencies of the lines in these groups as they recur in the spectrum. It is stated by Schuster that no simple harmonic relations exist between these groups. Deslandres (*C. R.* 104, 972) has shown that the periods of the recurring bands in the nitrogen spectrum are connected by a relation of the form An^2+B, where n is an integer.

The first explanation of the existence of these groups which suggests itself is that corresponding to a triplet we have three, to a doublet two, similar systems near together. Each of these systems, if free from the other's influence, would vibrate with the same period, but when placed so near together that they influence each other, the system of three will have three, and that of two will have two, nearly equal periods.

The theory of the oscillation of such systems shows that the gravest mode of the combined system will be lower, and the highest higher, than that of the original system. Thus in a triplet corresponding to each line of the original system, there will be three lines. If this view is correct, then any 'element' in whose spectrum doublets or triplets occur is capable of being split up into simpler systems, and the lines of the substance into which it is split up will be intermediate between those of the doublets or triplets. Thus, we should expect to find a tendency for these doublets to disappear as the temperature is raised. Though there does not seem much evidence to show that this tendency is widespread, it does appear to exist in the case of calcium, for in the drawing of the spectrum of this element given in Lockyer's *Studies in Spectrum Analysis* (191) there is in the violet end of the spectrum a doublet where the spark is taken without a jar in the circuit, but when a large jar is placed in the circuit the doublet is replaced by a single line intermediate to those of the doublet.

The widening of the lines of the spectrum of a gas when the pressure is increased might be explained on similar principles. A molecule when free from the influence of other molecules vibrates in certain definite periods, and shows sharp bright lines in its spectrum; when, however, it gets under the influence of another similar molecule its periods are slightly altered, and for each of the original periods we have two periods, the one graver and the other higher than the original period; the departure from the original period depending on the distance between the molecules. Thus, in the case of a gas so dense that the molecules influence each other, the molecules, instead of emitting light of a definite period, would emit light of different periods, some higher and some lower than the undisturbed one; thus, instead of a bright line in the spectrum, we should have a luminous band stretching across the original bright line.

Connexion between spectra of elements and those of their compounds.—One of the most interesting subjects in connexion with molecular theories, and one from which we may hope to gain great insight into molecular structure, is the connexion between the spectrum of a compound and the spectra of its constituents. Mitscherlich showed that compounds have emission-spectra of their own. A considerable amount of work bearing on the subject has been done by Gladstone and Dale, Abney and Festing, Kundt, and others, who have investigated the absorption-spectra of compounds. But, however important these researches are from other points of view,

they cannot be said to have as yet thrown much light on the structure of matter.

A relation between the lines in the spectrum of a compound and the lines in the spectra of its elements, based on a mathematical theory, which, however, does not seem yet to have been published, has been enunciated by Grünwald, who states (*P. M.* (6) 34, 354) :—

'Let a be a primary chemical element, which is chemically combined with other elements in a gaseous substance A, and occupies the volume $[a]$ in the unit volume of A. Let the substance A combine chemically with another gaseous substance B, to form a third C. In this combination let the element a pass into a different chemical condition a', giving up (or in exceptional circumstances taking up) a certain quantity of heat in order to permit the new compound to form, and in consequence chemically contracting (or exceptionally expanding). Let the volume which it occupies in the body C, after the new condition of chemical equilibrium has been established, be $[a']$, then the quotient $[a]:[a']$ is generally a very simple rational member in accordance with a known fundamental law of chemistry. If this is the case the wave-lengths λ of all the rays which belong to the element a in the line-spectrum of the free substance A, and are therefore radiated by it, are related to the wave-lengths λ' of the corresponding rays, which the same element emits in the new chemical condition a', in which it exists in the more complex substance A within the newly-formed compound C, as the corresponding volumes $[a]$ and $[a']$.'

This relation has been tested in the case of water vapour; as however both this substance and hydrogen have a good many lines in their spectra, it is not surprising that coincidences occur between the observed and calculated values of the wave-lengths of the lines in the water-vapour spectrum. We must, therefore, suspend our opinion as to the value of the relation given by Grünwald until the theoretical grounds on which it is based have been published. See also Ames (*N.* 40, 19).

In a binary compound, A B, we may suppose that the atoms A and B are dynamical systems, which in the molecule of the compound are near together, and that the proximity of A causes the periods of B to be slightly different from the periods when B is vibrating by the influence of other systems, and *vice versâ*. Then the theory of the vibrations of such a system shows that if p_1—p_2—p_n are the frequencies of A when free, q_1—q_n those of B; $\delta p_1 \ldots \delta p_n$, $\delta q_1 \ldots \delta q_n$, the increase in the frequencies p_1—, respectively, due to the proximity of the two systems; then

$$p_1 \delta p_1 = \frac{f_{11}^2}{p_1^2 - q_1^2} + \frac{f_{12}^2}{p_1^2 - q_2^2} + \ldots .$$

With similar expression for $\delta q_1 \ldots$ &c. The quantities $f_{11} \ldots$ are quantities depending on the proximity of the systems.

From this relation we see that the effect on the period, say p_1, of the first system of the existence of a period, say q_2, in the second, is to quicken the period of the first, if the first is quicker than the second, and to retard it, if it is slower than the second. If we observe the spectra, this result could be expressed by saying that the effect of the annexation was to make the line of B repel the lines of A. Thus on this theory the spectrum of the compound may be got by superposing the spectra of its constituents, A and B, and then supposing the lines of A to repel those of B, and the lines of B to repel those of A, the repulsion increasing with the proximity of the lines. Thus if we take two elements A and B, such that A and B have two lines nearly coincident, then in the compound A B these lines will be considerably displaced and the distance between them increased.

Arrangement of the atoms in the molecule on the supposition that the atoms are vortex rings. There is one theory of the structure of the molecule which is worth mentioning, as it affords a possibility of the explanation of that remarkable alternation of properties with atomic weight which is expressed by the periodic law. If we assume that a molecule is built up of a number of vortex rings placed close together, then a section of the molecule, by a plane through the centre at right angles to the planes of the ring, will consist of two groups, each consisting of a number of small circles. The arrangement of the circles in either group will be very much the same as the arrangement, when in steady motion, of the cross sections of the same number of uniform straight parallel vortex columns with circular sections. These, when in steady motion, arrange themselves in a definite way, which may easily be discovered without calculation, as the arrangement is very nearly the same as that of the same number of equal uniform parallel magnets under the attraction of a magnetic pole, some distance away from the nearer poles of the parallel magnets, and of opposite sign to these poles. These magnets will take up definite positions of equilibrium, under the action of their mutual repulsion and the external attraction. The figures of equilibrium of the magnet are given by Mayer (*N.* 18, 258) and Monckman (*Proc. Camb. Phil. Soc.* 6, 169). If we examine these figures, we see that as the number of magnets increase there is a tendency for certain peculiarities to recur, as, for example, the number of planes of symmetry, and the nature of the simpler groups of which we may imagine the more complex ones to be made up. Thus, if we imagine the molecules of all elements to be made up of the same primordial atom, and interpret increasing atomic weight to indicate an increase in the number of such atoms, then, on this view, as the number of atoms is continually increased, certain peculiarities in the structure will recur, which in all likelihood would be accompanied by a recurrence of some of the properties of the elements.

Electrical theory of molecular structure.— There is another view of molecular structure which is almost forced upon us by the laws of electrolysis; this is, that the forces between the atoms in the molecule are electrical in their origin. On this theory, the atoms in the molecule of a compound are supposed to be charged with definite quantities of electricity, the quantity of electricity on the atom being the same for all elements of the same valency, and being positive or negative, according as the element is electro- positive or electro- negative. The charge on an atom of a divalent element is assumed to be twice, and that on an atom of a trivalent element three times, the charge on the atom of a monovalent element (*v.* Von Helmholtz [*Faraday Lecture*], *C. J.* 39, 277). This view of the structure of the molecule at once explains Faraday's law of electro-chemical decomposition. It also explains the difference which exists between the electrical properties of the molecule and the atom; for in the molecule the positive and ne-

gative charges neutralise each other's effect at points outside the molecule; the free atom is, however, essentially charged and therefore capable of producing electrical effects. When we dissociate a gas into atoms, the dissociated gas, on this theory, consists of an equal number of electrically charged particles, some being charged with positive electricity, and an equal number (if the constituents of the molecule are of the same valency) charged with negative electricity. This collection of electrified particles would behave like a conductor of electricity, so that, if this theory of the structure of the molecule is correct, a gas whose molecules are dissociated by heat into atoms ought to be a conductor of electricity. J. J. Thomson (*P. M.* [6] 29, 358, 441) has recently made a series of experiments on the conduction of electricity through very hot gases, and has found that while some of these hot gases (hydriodic acid gas, for example) allow electricity to pass through them with ease, others (such as nitrogen) only allow it to do so with great difficulty; and it was found that whenever the electricity passed with ease through a hot gas, the dissociation of the gas could be detected by chemical means. These experiments are, therefore, in accordance with the result of this theory of molecular structure. On this view of molecular structure the 'bonds of affinity' of chemists have a distinct physical meaning, as they are the tubes of electrostatic force connecting the atoms.

A difficulty which arises on this theory, and one that seems to show that it requires modification, is the existence at low temperatures of what are called by chemists unsaturated compounds. For, according to this view of the structure of matter, an unsaturated compound is one in which there are not equal and opposite quantities of electricity in each molecule, so that the molecules of an unsaturated gas, being electrically equivalent to a number of positively and negatively charged particles, ought to behave like a conductor. But gases which are unsaturated at low temperatures, such as NO, behave at these temperatures with respect to electricity like saturated gases; they transmit electric induction. For example, a gold leaf electroscope will work perfectly well inside a glass vessel containing NO, and its leaves will be attracted by an electrified body outside the electroscope; and a current of electricity cannot be driven through a tube containing such gases by a battery containing only a small number of cells. We must therefore conclude that electrically such gases are saturated.

Maxwell, in the article on the 'Constitution of Bodies,' *Encyclopædia Britannica*, introduced the idea that in solids the molecules might arrange themselves in groups, some of which under the action of stresses might split up and form other stable groups in which the molecules are differently arranged, these new groups returning only slowly to their original configuration after the stresses are removed. This behaviour of the molecular groups shows itself in the 'elastic after effect' produced by torsion in metal wires and glass fibres. Ewing (*P. M.* [6] 30, 205) has lately applied the same idea to explain the behaviour of iron when magnetised, and has devised a model which illustrates very clearly the breaking up of the old groups and the formation of new ones. J. J. T.

MOLECULAR WEIGHTS. The article Atomic and molecular weights, in vol. i., describes the limits within which the term molecular weight may be applied with safety to solid and liquid bodies (*v.* especially pp. 347–350). Since that article was printed, an advance has been made in the methods by which the molecular weights of bodies which cannot be gasified without decomposition may be determined. This advance is based, for the most part, on the researches of Raoult. As the result of a long series of investigations into the lowering of the freezing-point of water and various other solvents, produced by dissolving therein quantities of various compounds proportional to the formula-weights, or reacting-weights, of these compounds, Raoult finds that such quantities of chemically similar compounds generally produce equal lowerings of the freezing-points of water and some other solvents (Raoult's Memoirs will be found in *A. Ch.*; *v.* especially [6] 8, 317).

Let P grams of a compound be dissolved in 100 g. of water or other solvent, and let the observed lowering of freezing-point of the solvent be C; then $\frac{C}{P}$ is called by Raoult the *coefficient of lowering of freezing-point* for the compound in question. Putting M as the reacting-weight, or formula-weight, of the compound, then $\frac{C}{P}M$ is called the *molecular lowering of freezing-point* for this compound.

Raoult finds that $\frac{C}{P}M$ is generally constant for all the members of a series of chemically similar compounds. Thus, Raoult gives the following values for $\frac{C}{P}M$, water being the solvent:—

19, for many organic compounds;
35, for salts of monovalent metals with monobasic acids;
40, for normal salts of monovalent metals with dibasic acids.

Raoult also gives the following values for $\frac{C}{P}M$, benzene being the solvent:—

49, for many organic compounds;
25, for the lower members of homologous series of alcohols.

Other values for $\frac{C}{P}M$ were found when other solvents, *e.g.* acetic acid, were used.

Another form in which Raoult's results may be put is the following:—$\frac{P}{C}$ = grams of dissolved body, in 100 g. solvent, that lower freezing-point of solvent 1°. Now $\frac{P}{C} \times e = M$; where e = constant determined experimentally for each series of chemically similar compounds, and for each solvent.

If the value of $\frac{C}{P}M$ is known for a group of compounds, or if the value of e is known in the

expression $\frac{P}{C} \times c = M$, it is possible to find the formula-weight of a member of this group. Thus, in the case of ether, the following data were obtained:—

(i) 4·47 g. ether were dissolved in 100 g. water; the freezing-point of the water was lowered by 1·05°; hence $\frac{C}{P} = \frac{1·05}{4·47} = ·23°$. But the value of $\frac{C}{P}M$ for organic compounds generally dissolved in water is 19; hence, for ether, $M = \frac{19}{·23} = 82$.

(ii) 2·721 g. ether were dissolved in 100 g. benzene; the freezing-point of the benzene was lowered by 1·826°; hence $\frac{P}{C} = 1·49$; *i.e.* 1·49 g. ether in 100 g. benzene lower the freezing-point by 1°. But the constant for such organic compounds as the ethers dissolved in benzene is 49; hence, for ether, $M = 1·49 \times 49 = 73$.

(iii) The value found for $\frac{C}{P}$ when ether was dissolved in acetic acid was ·529°. But the value of $\frac{C}{P}M$ for organic compounds generally dissolved in acetic acid is 39; hence, for ether, $M = \frac{39}{·529} = 74$.

The mean of these three results gives 76·6 for the formula-weight of ether; the molecular weight of ether-gas, determined by applying Avogadro's law, is 74.

The empirical law of Raoult—quantities of chemically similar compounds proportional to the reacting-weights, or formula-weights, of these compounds produce equal lowerings of the freezing-points of water and some other solvents—has been developed by van't Hoff, Arrhenius, and others (*v.* especially *Z. P. C.* 1, 481 [translation in *P. M.*, August 1888]; and *Z. P. C.* 1, 631; 2, 284, 491). If an aqueous solution of a substance is contained in a vessel the walls of which are permeable by water molecules but not by the molecules of the dissolved substance, and the vessel is immersed in water, water will enter the vessel, and the pressure on the walls will increase until equilibrium results, after which no more water will enter. The pressure on the walls of the vessel is called *osmotic pressure*. If the vessel were furnished with a movable piston, the same condition of equilibrium might be attained, without the entry of water into the vessel, by compressing the solution with a pressure equal to the osmotic pressure. With such an arrangement the concentration of the liquid could be altered by increasing or decreasing pressure by means of the piston; as the process is reversible, the second law of thermodynamics may be applied.

The experiments of de Vries (*Z. P. C.* 2, 415; 3, 103), Pfeffer (*Osmotische Untersuchungen* [Leipzig, 1887]), and others, show that the osmotic pressures of dilute aqueous solutions are proportional to the concentrations of these solutions. Now, to say that change of concentration of dilute solutions is proportional to the pressure exerted by the solutions, is equivalent to saying that Boyle's law holds good for dilute solutions. Moreover, the proportionality of concentration to osmotic pressure may be deduced theoretically. If we assume, as seems justifiable, that osmotic pressure is due to the impact of the molecules of the dissolved substance, then the number of impacts in unit time must be proportional to the number of molecules in unit volume (on this point *v.* L. Meyer, *Z. P. C.* 5, 23; and van't Hoff's reply, *Z. P. C.* 5, 174; *cf.* Bredig, *Z. P. C.* 4, 444). But this is the molecular conception of gaseous pressure. Hence, as in gases volume is inversely as pressure, the same proportionality should hold good in dilute aqueous solutions; in other words, Boyle's law should apply to these solutions. Van't Hoff then proceeds to deduce, by thermodynamical reasoning, that osmotic pressure is proportional to absolute temperature, concentration being constant. This conclusion is equivalent to saying that the law of Charles holds good for dilute aqueous solutions, inasmuch as concentration of solution corresponds with gaseous volume.

The experimental results of Pfeffer and of Soret (*A. Ch.* [5] 22, 293) are in keeping, on the whole, with the statement that the laws of Boyle and Charles hold good in dilute aqueous solutions.

Solutions which exert equal osmotic pressures are called *isotonic* solutions. Thermodynamical reasoning applied to these solutions leads to the conclusion that the osmotic pressure of a specified mass of a gasifiable substance in dilute solution is the same as the pressure exerted by the same mass of the same substance existing as a gas at the same temperature. If, then, osmotic pressure may be substituted for gaseous pressure, Avogadro's law may be extended to substances in dilute solution. This extension of the law of Avogadro is thus stated by van't Hoff. '*Equal volumes of different solutions, at the same temperature and osmotic pressure, contain equal numbers of molecules, which numbers are the same as would be contained in equal volumes of gases at the same temperature and pressure.*' This is van't Hoff's *law of osmotic pressure.* Various proofs of the accuracy of this law have been given.

To apply this law, it is necessary to find the mass of a substance present in a solution which is *isotonic* with another solution containing a known mass of a body of known molecular weight. The two solutions then contain equal numbers of molecules of the dissolved substances; and as the molecular weight of one substance is known, the molecular weight of the other can be found. There are many practical difficulties in determining whether or not two solutions are isotonic. Now van't Hoff has shown by thermodynamical reasoning (*Z. P. C.* 1, 496) that solutions of different bodies in the same solvent, having equal freezing-points, are isotonic at their freezing-points. Put into other words, this conclusion asserts that solutions which have equal freezing-points contain equal numbers of molecules in equal volumes; or, that solutions which contain equal numbers of molecules in equal volumes, and are therefore isotonic, have equal freezing-points. But this is the law of lowering of freezing-points em-

pirically established by Raoult. In place of tho somewhat vague term reacting-weight, or formula-weight, used in stating the law (*v. supra*), we are now justified in employing the more definite term molecular weight. This law, as developed by van't Hoff, asserts that the product of the lowering of the freezing-point of a 1 p.c. solution into the molecular weight of the dissolved body is a constant for different bodies dissolved in the same solvent. For solutions of most organic compounds in water, the constant is about 18·9.

Van't Hoff then proceeds to show that the molecular lowering of freezing-point of a dilute solution bears a simple relation to the latent heat of fusion of the solvent (for proof *v. Z.P.C.* 1, 496–7). This relation is expressed, for very dilute solutions, by the equation

$$t = \cdot 01976 \frac{T^2}{W},$$

where t = molecular lowering of freezing-point, already expressed as $\frac{C}{P}M$ (p. 417), T = freezing-point of solvent stated in absolute measure, and W = latent heat of fusion of solvent in gram-units (*cf.* Eykman, *Z. P. C.* 3, 203; and especially *ib. Z. P. C.* 4, 512). If this conclusion is granted, it follows that equal numbers of molecules of all bodies dissolved in the same solvent must lower the freezing-point to the same extent, provided the solutions are very dilute.

Let us take a case to exhibit the application of the law of molecular lowering of freezing-point in the form given to it by van't Hoff. Thymol is dissolved in phenol, and the lowering of the freezing-point of the phenol is observed. The constant for molecular lowering of freezing-point of phenol is first calculated by van't Hoff's formula: the freezing-point of the phenol used was 38°, in absolute measure this is 273° + 38° = 311°; the latent heat of fusion of the phenol was found to be 25; hence

$t = \cdot 0197 \frac{311^2}{625} = 76$. The solution of thymol used contained ·401 g. thymol in 7·559 g. phenol; the freezing-point was lowered by 2·49°; stating these results in parts of thymol per 100 of phenol, we find that 5·3 g. thymol dissolved in 100 g. phenol lowered the freezing-point through 2·49°. Then $\frac{5\cdot 3}{2\cdot 49} = 2\cdot 12$; *i.e.* 2·12 g. thymol in 100 g. phenol lowered the freezing-point through 1°. But this quantity, 2·12, is $\frac{1}{76}$th of the molecular weight of thymol; therefore molecular weight of thymol $= 2\cdot 12 \times 76 = 161$. The molecular weight calculated from the formula $C_{14}H_{10}O$ is 150.

In applying the law of molecular lowering of freezing-point it is necessary to work with dilute solutions. The freezing-point varies somewhat with concentration; in some cases this variation is very marked. Beckmann (*Z. P. C.* 2, 742) recommends that a series of observations should be made, concentration varying so that the lowering of freezing-point may range from c. ·2° to c. 2°. If possible, observations should be made with solutions in different solvents, care being taken to select solvents which do not react chemically, so far as is known, with the dissolved body, and the results should be checked by observations of the lowering of vapour-pressure of some solvent produced by dissolving in it the substance whose molecular weight is being determined (*v. infra*).

To sum up this part of the subject. Known weights of the substance, the molecular weight of which is to be determined, are dissolved in known weights of the solvent, so that the concentration of the solutions varies from, say, 1 to 5 or 6 p.c.; the freezing-point of each solution is determined. The freezing-point of the solvent is determined. Two methods of calculation may then be adopted :—

(i) The lowering of freezing-point, brought about by 1 g. of the substance dissolved in 100 g. of solvent, is calculated from each observation made; let this = A. The value of the constant expressing the molecular lowering of freezing-point of the solvent by the class of bodies to which the substance under examination belongs is known; let this be C. Then $\frac{C}{A}$ gives approximately the molecular weight of the substance.

(ii) The weight of the substance which would lower the freezing-point of the solvent by 1° is calculated from each observation made; let this be B. Then $B \times C$ gives approximately the molecular weight. (C has the same meaning as in (i).)

The values found for mol. w. from the different observations are compared; if the differences are small, the mean is taken; if there are marked differences, experiments are made with other solvents. It may be that the substance undergoes dissociation in all solvents, and that, therefore, the method is inapplicable (*v. infra*).

The molecular lowering of freezing-point of the solvent may be calculated by the use of van't Hoff's formula ($t = \cdot 01976\ \frac{T^2}{W}$), provided the latent heat of fusion of the solvent is known; the value thus found should agree with the constant determined by experiment.

The solvents commonly employed are water, benzene, phenol, and glacial acetic acid; naphthalene has also been used for some hydrocarbons; Eykman (*Z. P. C.* 4, 512) recommends urethane, phenyl propionic acid, the higher acids of the acetic series, stearin, and *p*-toluidine. Various modifications of Raoult's original apparatus have been devised; references to the papers in which the most important are described will be found at the end of this article.

There are many apparent exceptions to Raoult's law, and therefore to van't Hoff's law of osmotic pressure. These exceptions are explained by the hypothesis, pu tinto definite form by Arrhenius (*Z. P. C.* 1, 631), that bodies whose behaviour is not directly expressed by these laws are partially dissociated in solution. Here again there is a marked analogy between gases and dilute solutions; as the pressure of the vapour obtained by heating ammonium chloride is greater than the pressure calculated by Avogadro's law, on the assumption that the vapour consists of molecules of NH_4Cl, but as the observed pressure agrees with the calculated pressure when it is assumed that the vapour consists of equal numbers of molecules of NH_3 and HCl, so the apparently abnormal osmotic pres-

sures of many solutions are brought into agreement with van't Hoff's law by assuming that the bodies in these solutions are more or less dissociated into simpler molecules. If the molecular weight of a substance, as determined by observations of freezing-points, apparently decreases as dilution increases, it is likely that the substance is dissociated in the solution, and that the amount of dissociation increases as the quantity of solvent is increased. Substances may undergo dissociation in one solvent and not in another (for several carefully worked out examples, *v.* Beckmann, *Z. P. C.* 2, 715). Those substances, solutions of which show osmotic pressures agreeing with those calculated by van't Hoff's law from observations of the lowering of freezing-points of the solutions, are generally, if not always, non-electrolytes. The apparent exceptions to the law of van't Hoff occur chiefly, if not wholly, among electrolytes. The dissociation-hypothesis of Arrhenius regards such electrolytes as more or less dissociated into their ions when they are dissolved in water. A great deal of work has been done in developing and applying the hypothesis of electrolytic dissociation; an account of this work, and of the chief results, will be found in the article PHYSICAL METHODS, section *Electrical methods*.

Raoult has found that in many cases the lowerings of vapour-pressure produced by dissolving a comparatively non-volatile substance in a considerably more volatile liquid is related to the number of molecules of the dissolved body in 100 molecules of the solvent, provided the solution be very dilute (*Z. P. C.* 2, 353). Arrhenius has shown that this generalisation made by Raoult can be deduced from van't Hoff's law of osmotic pressures (*Z. P. C.* 3, 115). The generalisation has been placed on a thermodynamical basis by van't Hoff (*Z. P. C.* 1, 493) and Planck (*Z. P. C.* 1, 577). The law may be put in the following form. *At any specified temperature the ratio of lowering of vapour-pressure of a solvent, produced by dissolving a non-volatile body in it, to the vapour-pressure of the solvent, is equal to the ratio of the number of molecules of the dissolved body to the total number of molecules in the solution.* Let p = vapour-pressure of solvent, $p-p'$ = observed lowering of vapour-pressure, W= weight of dissolved body, W' = weight of solvent, m = molecular weight of dissolved body, and m' = molecular weight of solvent; then:

$$p-p' : p = \frac{W}{m} : \frac{W}{m} + \frac{W'}{m'}.$$

If W, W', p, p', and m' are known, m can be found. Suppose a grams of the substance are dissolved in 100 g. solvent; then:

$$m = \frac{m'.p.a}{100.p-p'}.$$

Among the solvents which have been used in applying this law to the determination of molecular weights are ether, alcohol, CS_2, and Hg. For descriptions of apparatus, and some of the data obtained, *v.* Raoult (*Z. P. C.* 2, 353); Walker (*Z. P. C.* 2, 602); Beckmann (*Z. P. C.* 4, 532); Ramsay (who determined mol. w. of several metals by using Hg as solvent) (*C. J.* 55, 521).

Raoult and others have found that the rise in the boiling-point of a liquid caused by dissolving a non-volatile substance therein bears a simple relation to the molecular weight of the dissolved substance. There is a constant which must be determined for each solvent which expresses the rise of b.p. caused by solution of 1 gram-molecule of substance in 100 grams of solvent; for ether this constant is 21° (Beckmann, *Z. P. C.* 3, 603). It is necessary then to find the weight of substance which, dissolved in 100 g. ether, raises the b.p. 1°; the product of this weight multiplied by 21 gives, approximately, the molecular weight of the dissolved substance. Thus Beckmann (*l.c.*) found that 2·153 g. aniline dissolved in 100 g. ether raised the b.p. of the ether ·484°; therefore 4·45 g. aniline would raise the b.p. 1°; but 4·45 × 21 = 93·4; the mol. w. of aniline is 93. Arrhenius contributes a note to Beckmann's paper (*Z. P. C.* 4, 550) in which he shows, by thermodynamical reasoning, that *the rise of boiling-point* (dT) *of a solvent, caused by dissolving n-gram molecules of another substance in* 100 *g. of the solvent, is directly proportional to the quantity dissolved* (n) *and the square of the b.p., and is indirectly proportional to the heat of vaporisation of* 1 *g. of the liquid, W.* Put into an equation this statement reads thus:—$dT = \frac{\cdot 02T^2}{W}.n.$ This equation is precisely similar to that found by van't Hoff (*v.* p. 419) for the molecular lowering of the freezing-point of a solvent; only in the present case the quantities T and W depend upon the boiling-point of the solvent. A description of apparatus suited for applying the law of *molecular raising of boiling-point* to molecular weight determinations will be found in Beckmann's paper, *Z. P. C.* 4, 543.

References.—Blagden, *T.* 58, 277; de Coppet, *A. Ch.* [4] 23, 366; 25, 502; 26, 98; Rudorff, *P.* 114, 63; 116, 55; 145, 599; Raoult, *A. Ch.* [5] 20, 217; 28, 133; [6] 2, 66, 93, 99, 115; 4, 401; 7, 289, 317; *Z. P. C.* 2, 488; Eykman, *Z. P. C.* 4, 497 (data bearing on question of series-constants, influence of concentration, nature of solvent, &c.).

The following memoirs bear chiefly on the similarities between the gaseous state and that of substances in dilute solutions:—van't Hoff, *Z. P. C.* 1, 481; 5, 175, 221; Arrhenius, *ibid.* 1, 631; 2, 284, 491; Ostwald, *ibid.* 2, 36, 270; Beckmann, *ibid.* 2, 734; Nernst, *ibid.* 2, 613; 4, 372; Planck, *ibid.* 1, 577; 2, 343; Bredig, *ibid.* 4, 444; Wiedemann, *ibid.* 2, 241, and Ostwald's reply p. 243; Pickering, *C. J.* 57, 331.

The following memoirs are on the application of van't Hoff's law and Raoult's method to special compounds:—von Klobukow, *Z. P. C.* 3, 351, 476 (shows that CHI_3 and morphine do not give the anomalous results which Raoult supposed they did); Eykman, *Z. P. C.* 2, 966 (morphine); Paterno a. Nasini, *B.* 21, 2153 (I); Loeb, *Z. P. C.* 2, 606 (I); Beckmann, *ibid.* 5, 76 (I, P, S); Paterno, *ibid.* 4, 457; Sabanejeff, *J. R.* 1889 [1] 515; abstract in *B.* 23, [*Ref.*] 87 (colloids); Brown a. Morris, *C. J.* 53, 610; 55, 462 (carbohydrates); Löw, *B.* 21, 271; 22, 470 (sugars); von Klobukow, *Z. P. C.* 5, 28 (sugars); Heycock a. Neville, *C. J.* 55, 666; 57, 376; Küster, *Z. P. C.* 5, 601 (isomorphous mixtures).

The following memoirs deal with relations between osmotic pressures, lowering of vapour-pressure and of freezing-point, and raising of boiling-point, of a solvent by substances dissolved therein :—Arrhenius, *Z.P.C.* 3, 115; van't Hoff, *ibid.* 1, 481; Planck, *ibid.* 1, 577; van't Hoff a. Reicher, *ibid.* 3, 198; Guldberg, *C.R.* 70, 1349; Beckmann, *Z.P.C.* 4, 532; Raoult, *C.R.* 110, 402; Raoult a. Recoura, *C.R.* 110, 402.

The following memoirs contain descriptions of apparatus :—Auwers, *B.* 21, 701; Hollemann, *B.* 21, 860; Hentschel, *Z.P.C.* 2, 306; Beckmann, *ibid.* 2, 638; 4, 543 (raising b.p.); Eykman, *ibid.* 2, 964; 3, 113; 4, 497; Fabinyi, *ibid.* 3, 38; von Klobukow, *ibid.* 4, 10; Raoult, *ibid.* 2, 353 (lowering vapour-pressures); Walker, *ibid.* 2, 602 (lowering vapour-pressures); Heycock a. Neville, *C.J.* 55, 666 (using Hg as solvent); Ramsay, *C.J.* 55, 521 (lowering vapour-pressure of Hg). M. M. P. M.

MOLYBDATES. *Salts of molybdic acid v.* MOLYBDENUM, ACIDS OF, p. 422.

MOLYBDENUM. Mo. At. w. 95·9. Mol. w. unknown. S.G. 8·56 (Long, *Am. S.* [2] 45, 131); 8·49 to 8·64 (Bucholz, *Nicholson's J.* 20, 121). Does not melt in O-H flame at temp. at which Pt melts (Debray, *A.* 108, 250). S.H. 5°–15° ·0659 (De la Rive a. Marcet, *A. Ch.* [2] 75, 113). Emission-spectrum (obtained by using electric spark) shows only a few lines, the most prominent in the blue and violet (*v.* Thalen, *A. Ch.* [4] 18, 242). S.V.S. c. 11·3.

Occurrence.—Never uncombined. The sulphide (*molybdenite*, or *molybdenum glance*), oxide (*molybdenum ochre*), molybdate of lead (*wulfenite*), and molybdate of cobalt (*pateraïte*), occur in small quantities in certain localities. Many iron-ores contain small quantities of Mo compounds (Braun, *Fr.* 6, 86; Wöhler, *Mineralanalyse* [Göttingen, 1861]). The residues from the copper smelting ovens at the Mansfeld works sometimes contain as much as 28 p.c. Mo (Heine, *J. pr.* 9, 176; *cf.* Stromeyer, *P.* 28, 551; Steinberg, *J. pr.* 18, 379; Genth, *J. pr.* 37, 193; Steinacker, *Ueber einige Molybdänverbindungen* [Göttingen, 1861] 22). An alloy of Mo and Pb, in plates 30 mm. long, was found in Utah by Silliman (*Am. S.* [3] 6, 128). According to Lockyer (*Pr.* 27, 279), Mo occurs in the sun.

Scheele in 1778 (*Opusc.* 1, 200) distinguished native Mo sulphide from galena. In 1782, Hjehn obtained the metal from the sulphide (*v. Crell. Ann.* for 1790, 1791, 1792, and 1794). For an historical account of this metal *v.* Svanberg a. Struve, *J. pr.* 44, 257. The name molybdenum was given from μολύβδαινα, or *molybdæna*, used by Dioscorides and Pliny to designate galena and other lead compounds.

Formation.—1. By reducing MoO_3 by H, K or Na, C, or KCN.—2. By reducing Mo chlorides by H at a high temperature.—3. By reducing acid K molybdate by C.—4. By electrolysing molten MoO_3, or $(NH_4)_2MoO_4$ in solution.

Preparation.—The starting-point is pure MoO_3 (*v. infra*).—1. MoO_3 is heated in a crucible in a stream of pure H (which must be passed over a long layer of red-hot Cu); the mass is transferred to a tube of unglazed porcelain, and very strongly heated in the H stream; finally the last traces of oxide are removed by gently warming in a stream of dry HCl as long as a white wool-like sublimate ($MoO_3.2HCl$) is formed (Liechti a. Kempe, *A.* 169, 344). The metal in contact with the porcelain tube is not pure (Debray, *C. R.* 56, 732; *cf.* Wöhler a. von Uslar, *A.* 94, 256; Rammelsberg, *P.* 127, 284).—2. MoO_3 is mixed with C and heated in a graphite-crucible, in the O-H flame; the product always contains a few per cents. of C (Debray, *C.R.* 46, 1098).—3. An intimate mixture of 1 pt. MoO_3 and $1\frac{1}{2}$ pts. KCN is placed in a crucible, the cover is luted on, the crucible is placed in another which is filled with C, and the whole is kept at white heat for 12 hours. By this method Loughlin (*Am. S.* [2] 45, 131) obtained metal with 98·7 p.c. Mo.

There are many methods for preparing MoO_3 from Mo ores. Finely powdered *molybdenite* (MoS_2) is roasted in an open porcelain vessel, with frequent stirring, until SO_2 ceases to be evolved; Brunner (*D. P. J.* 150, 672) recommends to mix the ore with its own weight of fine quartz-sand, previously washed with HClAq, and to heat in a flat Pt dish, to incipient redness, till the residue is citron-yellow when hot, and white when cold. The roasted ore is treated with NH_3Aq; to the solution are added a few drops of NH_4 sulphide, the ppd. CuS is removed, the filtrate is evaporated to dryness, the residue is dissolved in NH_3Aq, and the solution is evaporated to the crystallisation-point (Wöhler). Svanberg a. Struve (*J. pr.* 44, 264) add excess of K_2CO_3 to the ammoniacal solution of the roasted ore, separate ppd. Al_2O_3, evaporate to dryness, and strongly heat the residue in a Pt crucible; they treat with water, filter from CuO and Al_2O_3, evaporate to dryness, add S equal to double the weight of the residue, heat in a glass vessel on a sand-bath to full redness till excess of S is burnt off, wash with warm water (the last washings containing a little K_2CO_3) as long as the washings are coloured, and until the MoS_2 is perfectly black, and then roast the pure MoS_2 thus obtained, or oxidise it to MoO_3 by HNO_3Aq. Delffs (*A.* 106, 376) decomposes *molybdenite* by HNO_3Aq. Wittstein forms soluble sulphomolybdates by roasting with S, and decomposes by H_2SO_4Aq, finally roasting the sulphide to MoO_3 (*R. P.* [2] 73, 155; *cf.* Wicke, *A.* 45, 373; Wöhler, *ibid.* p. 374). *Molybdenite* may also be decomposed by calcining with alkali carbonates (*v.* Christl, *D. P. J.* 124, 398; Elbers, *A.* 83, 219); or by the use of H_2SO_4 (Elbers, *l.c.*).

Properties.—As prepared by reducing the chloride in H, Mo appears as dull silver-coloured, somewhat malleable, plates (Wöhler a. von Uslar, *A.* 94, 256). The metal obtained by reducing MoO_3 by H at very high temperatures is lustrous; if the reduction is effected at lower temperatures, an ashen-grey powder is obtained which becomes metal-like when rubbed. The metal obtained by Debray, which contained 4–5 p.c. C, was silver-white, and harder than topaz. The S.G. of Mo is given by Loughlin (*Am. S.* [2] 45, 131) as 8·56; this metal contained 98·7 p.c. Mo. Debray (*C. R.* 46, 1098) gives S.G. 8·6 for the metal obtained by reducing MoO_3 by C, and containing 4–5 p.c. C.

Mo, whether in powder or in pieces, is unchanged in ordinary air; when heated it becomes brown, then blue, then white, on the surface,

and at high temperatures it is burnt to MoO_3. It is oxidised by fusion with KNO_3, or slowly by KOH; also by HNO_3, or Cl water; it burns when heated in steam, evolving H. Mo is insol. in HClAq, dilute H_2SO_4Aq, and HFAq; it is not acted on by KOHAq. Mo combines directly with O, Cl, and Br, but not with I. The metal is infusible at white heat (Debray, *A*. 108, 250).

The atomic weight of Mo has been determined (1) by analysing, and determining V.D. of $MoCl_5$ (Liechti a. Kempe, *A*. 169, 344; Debray, *C. R.* 66, 732); (2) by determining S.H. of Mo (De la Rive a. Marcet, *A. Ch.* [2] 75, 113); (3) by determining Cl in MoO_2Cl_2 (H. Rose, *P*. 40, 400; Svanberg a. Struve, *A*. 68, 209); (4) by synthesis of Ag_2MoO_4 (Debray, *C. R.* 66, 732); (5) by analyses of $MoCl_2$ and $MoCl_4$ (L. a. K., *A*. 169, 344; *cf*. L. Meyer, *ibid*. p. 360); (6) by reducing MoO_3 in H (S. a. S., *J. pr.* 44, 301; Dumas, *A. Ch.* [3] 55, 143; Debray, *C. R.* 66, 732; Rammelsberg, *B*. 10, 1776); (7) by oxidising MoS_2 to MoO_3 (S. a. S., *A*. 68, 209); (8) by conversion of $MoCl_4$ and $MoCl_5$ to MoS_2 (L. a. K., *A*. 169, 344; *cf*. Meyer, *ibid*. p. 360). The atom of Mo is pentavalent in the gaseous molecule $MoCl_5$.

Mo is probably both metallic and non-metallic in its chemical relations. Few, if any, definite salts are known obtained by replacing the H of acids by Mo; but Mo_2O_3 and MoO_2 seem to dissolve in acids without evolution of O. The oxide MoO_3 is an anhydride; molybdic acid, H_2MoO_4, and molybdates, besides tri- tetra- *n*-molybdates, are known. MoO_3 also combines with some other anhydrides to form complex bodies which react as acids, *e.g.* $P_2O_5.20MoO_3.38H_2O$; $SiO_2.12MoO_3.26H_2O$. MoS_3 reacts as an acidic sulphide, forming sulphosalts $M^I{}_2MoS_4$. Several haloid compounds, and many oxyhaloid compounds, of Mo are known. Mo is closely related to Cr, W, and U, and is less closely related to S, Se, and Te. Mo occurs in Group VI. series 6; the following table exhibits the position of Mo relatively to the other members of the group:

Even series—

2	4	6	8	10	12
O = 16	Cr = 52	Mo = 96	—	W = 184	U = 240

Odd series—

3	5	7	9	11
S = 32	Se = 79	Te = 125	—	—

(*v*. Chromium group of elements, vol. ii. p. 168; *cf.* Classification, vol. ii. p. 207).

Reactions.—1. *Heated in air* or *oxygen*, Mo is burnt to oxide; if the temperature is sufficiently high, MoO_3 is formed.—2. Oxidised, to MoO_3, by *molten nitre*, and slowly by *molten potash*.—3. Heated in *steam*, blue oxide (? Mo_3O_8), and then MoO_3, is formed.—4. Pulverulent Mo is oxidised by rubbing with *silver oxide*, or *mercuric oxide*. 5. Oxidised by *nitric acid, conc. hot sulphuric acid*, or *chlorine water*.—6. Mo does not dissolve in *hydrochloric, hydrofluoric*, nor *dilute sulphuric, acid*; nor does it react with *potash solution*.

Combinations.—1. Mo combines with *chlorine* to form $MoCl_5$; and with *bromine* to form $MoBr_4$: it does not combine directly with I.—2. Heated in *oxygen*, Mo forms oxides, MoO_3 being the final product of the combination.

Detection and Estimation.—The greater number of the Mo compounds, including most of the molybdates of the alkaline earths and heavy metals, are insol. in water. Lower oxides, and also the sulphides, produce MoO_3 when heated in air; MoO_3 readily dissolves in alkali solutions. Insol. molybdates are brought into soluble forms by fusion with alkali carbonates. All Mo compounds may be changed to soluble alkali sulphomolybdates by fusion with Na_2CO_3 and S. Phosphomolybdates are readily soluble in NH_3Aq. Mo compounds impart a yellow colour to the borax bead when heated in the oxidising flame, the colour disappears on cooling; in the reducing flame, they give a dark-brown colour, the bead is opaque if excess of Mo compound is present. They give a clear green microcosmic salt bead in the reducing flame, and in the oxidising flame a bead which is greenish when hot and colourless when cold. In solution, Mo compounds give a brown-black pp. with H_2S, soluble in NH_4 sulphide; solutions of molybdates give blue-coloured compounds by the action of reducing agents. When MoO_3 or a molybdate is evaporated with conc. H_2SO_4, and then allowed to cool, the acid becomes deep blue in colour; this reaction distinguishes molybdates from tungstates; the blue colour does not appear if antimonic or stannic salts are present, unless the substance has been wetted with a few drops of phosphoric acid, and evaporated to dryness, before addition of H_2SO_4 (Schönn, *Fr*. 8, 379; Maschke, *Fr*. 12, 383). If Zn is put into solution of a molybdate, a few drops of conc. KCNSAq are added, and then enough HClAq or H_2SO_4Aq to cause slow evolution of H, a carmine-red colour is produced, even with $\frac{1}{800,000}$ part MoO_3; ether removes the coloured compound (Braun, *Fr*. 2, 36). Liquids containing molybdates yield deep-red solutions (sulphomolybdates) by boiling with yellow NH_4 sulphide (Braun, *Fr*. 6, 86).

Mo is estimated (1) as metal by reducing in H (Rammelsberg, *P*. 127, 281); (2) as MoO_3 by oxidising in air or by HNO_3Aq (v. d. Pfordten, *B*. 15, 1927); (3) as $PbMoO_4$ (Chatard, *B*. 4, 280; *v*. also Ullik, *A*. 144, 217); (4) by reduction with Zn and titration by means of standard $KMnO_4Aq$ (Werncke, *Fr*. 14, 1; v. d. Pfordten, *B*. 15, 1927); (5) by the reaction of MoO_3 with an acidified solution of KI, whereby I is set free and is determined by standard $Na_2S_2O_3Aq$ (Mauro a. Danesi, *Fr*. 20, 507).

Molybdenum, Acids of, and their salts. The oxide MoO_3 is slightly sol. in water; c. 500 parts cold water dissolve 1 part MoO_3. The solution reddens litmus. Several hydrates of MoO_3 have been isolated. $MoO_3.H_2O = H_2MoO_4$ was obtained by Ullik, and also by Vivier (*v. infra*); the hydrates $MoO_3.2H_2O$, $2MoO_3.H_2O$, $4MoO_3.H_2O$, $5MoO_3.H_2O$, and $8MoO_3.H_2O$, have also been prepared; some of these are soluble, and some are insoluble, in water. Several series of salts are known; these salts may be represented as derived from hydrates of MoO_3; in some cases the hypothetical hydrates have been isolated, and in other cases they have not been isolated. Besides reacting as the anhydride of more than one acid, MoO_3 reacts with some oxides more acidic than itself to form compounds, *e.g.* $MoO_3.SO_3$; it also combines with

certain acids—*e.g.* with HCl, H_3PO_4, H_3AsO_4—the compounds thus formed have acidic reactions and yield salts (*v.* ANTIMONO-MOLYBDATES, ARSENO-MOLYBDATES, PHOSPHO-MOLYBDATES, p. 425; *v.* also MOLYBDENUM TRIOXIDE, p. 432).'

MOLYBDIC ACIDS. 1. H_2MoO_4. The normal hydrate $MoO_3.H_2O$, or hydroxide $MoO_2(OH)_2$, was obtained by Ullik, but only once, by mixing $MgMoO_4$ with an equivalent of HNO_3Aq and allowing to stand (*A.* 153, 374). Vivier (*C. R.* 106, 601) obtained this compound by allowing a solution of NH_4 molybdate in HNO_3Aq to stand for some time, also by heating ordinary NH_4 molybdate solution with its own volume of water to 50°–60° for some days. H_2MoO_4 forms a mass of minute needles; it is quite insol. water.

2. $H_2Mo_2O_7$. The hydrate $2MoO_3.H_2O$ ($=MoO_2(OH)_2.MoO_3$) was obtained by Ullik (*A.* 144, 329) by the action of excess of H_2SO_4Aq on the Ba salt formed by adding $BaCl_2Aq$ to ordinary NH_4 molybdate solution, filtering, placing over H_2SO_4, and drying the gum-like residue over H_2SO_4 for some months, or at 100° (Ullik, *A.* 153, 373). $H_2Mo_2O_7$ is a gum-like amorphous solid, e. sol. water.

3. $H_2Mo_4O_{13}$, and $H_2Mo_8O_{25}$. The hydrates $4MoO_3.H_2O$ ($=MoO_2(OH)_2.3MoO_3$), and $8MoO_3.H_2O$ ($=MoO_2(OH)_2.7MoO_3$) are formed similarly to $2MoO_3.H_2O$, the drying being conducted at 120°, and 160°–170°, respectively (U., *l.c.*). These compounds are amorphous solids, e. sol. water. Sabanejeff (*J. R.* 1889 [1] 515; abstract in *B.* 23 (*Ref.*) 87) obtained a colloidal form of $H_2Mo_4O_{13}$, sl. sol. water, by drying for some weeks over H_2SO_4; the formula was determined by applying Raoult's law (*cf.* MOLECULAR WEIGHTS, p. 417). For other hydrates of MoO_3, viz. $MoO_3.2H_2O$ and $5MoO_3.H_2O$, *v.* HYDRATES OF MOLYBDENUM TRIOXIDE, p. 432.

Graham (*C. J.* 1864) obtained a soluble colloidal form of molybdic acid (he does not give the composition) by dialysing an aqueous solution of Na molybdate, to which excess of HClAq had been added, until the liquid in the dialyser was free from NaCl and HCl. Graham describes the solution of molybdic acid as 'yellow, astringent to the taste, acid to test paper, and possessed of much stability'; it decomposed Na_2CO_3 with evolution of CO_2; and became insol. when heated for some time with a strong acid.

Chloromolybdic acid $H_2MoO_3Cl_2$ ($=MoO(OH)_2Cl_2$). (*Molybdenum hydroxychloride*). This compound is obtained by passing HCl over MoO_3 at 150°–200° (Debray, *C. R.* 46, 1101). It forms a loose, white, crystalline, mass; c. sol. water; sublimed unchanged in HCl.

Thiomolybdic acid and *thiomolybdates*; *v.* MOLYBDENUM, THIOACIDS OF, AND THEIR SALTS, p. 434.

MOLYBDATES. A great many molybdates are known; they are more or less closely related to the chromates. The following classification is that given by Ullik (*W. A. B.* 60 [2] 295), and now generally adopted. R = divalent metal.

Monomolybdates, $RMoO_4$ or $RO.MoO_3$;	derived from H_2MoO_4 or $H_2O.MoO_3$.
Dimolybdates, RMo_2O_7 or $RO.2MoO_3$;	„ „ $H_2Mo_2O_7$ or $H_2O.2MoO_3$.
Trimolybdates, RMo_3O_{10} or $RO.3MoO_3$;	„ „ *hypothetical* $H_2Mo_3O_{10}$ or $H_2O.3MoO_3$.
Tetramolybdates, RMo_4O_{13} or $RO.4MoO_3$;	„ „ $H_2Mo_4O_{13}$ or $H_2O.4MoO_3$.
Octomolybdates, RMo_8O_{25} or $RO.8MoO_3$;	„ „ $H_2Mo_8O_{25}$ or $H_2O.8MoO_3$.
Decamolybdates, $RMo_{10}O_{31}$ or $RO.10MoO_3$;	„ „ *hypothetical* $H_2Mo_{10}O_{31}$ or $H_2O.10MoO_3$.
Tribasic heptamolybdates, $R_3Mo_7O_{24}$ or $3RO.7MoO_3$;	„ „ *hypothetical* $H_6Mo_7O_{24}$ or $3H_2O.7MoO_3$.

There are a few molybdates which do not belong to any of these classes, *e.g.* $5Al_2O_3.2MoO_3$, and $2BaO.5MoO_3$.

The alkali *monomolybdates* are produced by dissolving $MoO_3.xH_2O$, or MoO_3, in equivalent quantities of alkali, in solution or molten; they are easily sol. in water. The other salts of this series are generally insol. in water; they are produced by ppn. from the alkali salts, or, in crystals by fusing Na_2MoO_4 with NaCl and metallic chlorides (Schultze, *A.* 126, 55). The alkali *dimolybdates* are formed by fusing MoO_3 and alkali carbonates in the proper proportion, or by the action of MoO_3 on molten alkali nitrates (Ullik, *A.* 144, 214). The *trimolybdates* are formed by boiling metallic carbonates with considerable excess of MoO_3 and water, filtering, and allowing to evaporate in the air. These salts are generally easily sol. in hot water, but only slightly sol. in cold water; many of them exist both in crystalline and amorphous forms, the amorphous varieties are readily sol. in cold water (Ullik, *A.* 144, 227; 153, 376). The *tetramolybdates* may be obtained by rapidly evaporating very small quantities of the solutions which yield trimolybdates when allowed to evaporate slowly. They form amorphous, brittle, masses, which slowly decompose with formation of trimolybdates (Ullik, *A.* 144, 321). Crystallisable acid tetramolybdates are sometimes obtained by adding a fair excess of acid to solutions of mono- or dimolybdates; addition of a little acid to such solutions generally throws down trimolybdates. Very few octo- or *decamolybdates* have been prepared.

The following table presents the composition of the chief molybdates. The small figures after the formulæ refer to the list of memoirs given after this table:—

MOLYBDATES.

Monomolybdates, $RMoO_4$ or $RO.MoO_3$.

$(NH_4)_2MoO_4$ (also *infra*, Mg salts). (23, 27)
$5(NH_4)_2MoO_4.Mn_2Mo_6O_{21}.12aq.$ (22)
$BaMoO_4$. (1, 23)
$BeMoO_4.BeO_2H_2.6aq.$ (24)
$CaMoO_4$. (7)
$CoMoO_4$. (1, 39)
$CoMoO_4.2NH_3.aq.$ (33)
$3CuMoO_4.CuO_2H_2.4aq.$ (11)
$Fe_2(MoO_4)_3.MoO_3.7aq.$ (34, 1)
$Fe_2(MoO_4)_3.2MoO_3.16aq.$ (20)
$5Li_2MoO_4.2aq.$ (17, 26)
$MgMoO_4.5aq.$ (12, 21, 26)
$MgMoO_4.(NH_4)_2MoO_4.2aq.$ (12)
$MgMoO_4.K_2MoO_4.2aq.$ (12)
$MnMoO_4$ (*v. supra*, NH_4 salts; and *infra*, K salts). (1, 22, 39)
Hg_2MoO_4. (29)
$NiMoO_4.2NH_3.aq.$ (1, 33)
K_2MoO_4 (also *supra*, Mg salts). (23, 26, 34)
$2K_2MoO_4.Mn_2Mo_6O_{21}.12aq.$ (22)
$K_2MoO_4.2Na_2MoO_4.14aq.$ (15, 26)
$3Rb_2MoO_4.4MoO_3.4aq.$ (26, 31)
Ag_2MoO_4. (23)

$Ag_2MoO_4.4NH_3$. (35)
$2Ag_2MoO_4.3MoO_3$. (23)
$Na_2MoO_4.2aq$ (also *supra*, K salts). (23, 28, 36)
$SrMoO_4$. (1)
Tl_2MoO_4. (26, 37)
$3Tl_2MoO_4.5MoO_3$. (37)
$8Tl_2MoO_4.3MoO_3$. (37)
$ZnMoO_4$. (1, 39)

Dimolybdates, RMo_2O_7 or $RO.2MoO_3$ or $RMoO_4.MoO_3$.

$Al_2(Mo_2O_7)_3.3(NH_4)_2Mo_2O_7.20aq$. (18)
$Al_2(Mo_2O_7)_3.3K_2Mo_2O_7.20aq$. (28)
$Al_2(Mo_2O_7)_3.3Na_2Mo_2O_7.22aq$. (28)
$(NH_4)_2Mo_2O_7$ (also *supra*, Al salts, and *infra* Cr salts). (23)
$Cr_2(Mo_2O_7)_3.3(NH_4)_2Mo_2O_7.20aq$. (19)
$Cr_2(Mo_2O_7)_3.3K_2Mo_2O_7.20aq$. (19)
$Cr_2(Mo_2O_7)_3.3Na_2Mo_2O_7.21aq$. (19)
$Hg_2Mo_2O_7$. (29)
$Na_2Mo_2O_7$. (2)

Trimolybdates, RMo_3O_{10} or $RO.3MoO_3$ or $RMoO_4.2MoO_3$.

$(NH_4)_2Mo_3O_{10}.aq$. (25, 32)
$(NH_4.Na)Mo_3O_{10}.aq$. (38)
$BaMo_3O_{10}.3aq$. (23)
$CaMo_3O_{10}.6aq$. (7)
$CoMo_3O_{10}.10aq$. (11)
$2CuMo_3O_{10}.9aq$. (11)
$MgMo_3O_{10}.10aq$. (12)
$K_2Mo_3O_{10}.3aq$. (9, 23)
$Na_2Mo_3O_{10}.4aq$, and 7aq. (5, 23)
$(NaNH_4)Mo_3O_{10}.aq$. (38)
$ZnMo_3O_{10}.10aq$. (11)

Tetramolybdates, RMo_4O_{13} or $RO.4MoO_3$ or $RMoO_4.3MoO_3$.

$(NH_4)_2Mo_4O_{13}.aq$. (25)
$BaH_2(Mo_4O_{13})_2.17aq$. (6)
$CaMo_4O_{13}.9aq$. (7)
$CaH_2(Mo_4O_{13})_2.17aq$. (7)
$MgH_2(Mo_4O_{13})_2.19aq$. (12)
$KHMo_4O_{13}.6aq$. (10)
$NaHMo_4O_{13}.8aq$. (14)
$Na_2Mo_4O_{13}.6aq$. (3)
$ZnMo_4O_{13}.8aq$. (11)

Octomolybdates, RMo_8O_{25} or $RO.8MoO_3$ or $RMoO_4.7MoO_3$.

$Na_2Mo_8O_{25}.4aq$. (1a, 6)
$NaHMo_8O_{25}.4aq$. (1a, 6)

Decamolybdates, $RMo_{10}O_{31}$ or $RO.10MoO_3$ or $RMoO_4.9MoO_3$.

$Na_2Mo_{10}O_{31}.12aq$. (1a, 6)

Tribasic heptamolybdates (sometimes called *seven-thirds molybdates*), $R_3Mo_7O_{21}$ or $3RO.7MoO_3$ or $RMoO_4.2RO.6MoO_3$.

$(NH_4)_6Mo_7O_{24}.4aq$ (ordinary ammonium molybdate). (16, 23, 26, 27)
$Ba_3Mo_7O_{21}.9aq$. (23, 31)
$Mg_3Mo_7O_{21}.20aq$. (12)
$K_6Mo_7O_{21}.4aq$. (23, 26)
$Na_6Mo_7O_{21}.22aq$. (13, 26, 36)

Molybdates not included in foregoing classes.

$5Al_2O_3.2MoO_3$. (18, 28)
$4(NH_4)_2O.5MoO_3.aq$. (30)
$2BaO.5MoO_3.6aq$. (23)
$CuO.2(NH_4)_2O.5MoO_3.9aq$. (21)
$7(NH_4)_2O.2Na_2O.21MoO_3.15aq$. (26)
$7(NH_4)_2O.3Na_2O.25MoO_3.30aq$. (26)

For some other complex molybdates, *v.* Bärwald, *C. C.* 1885. 424 (Abstract in *C. J.* 50, 17).

Molybdates of Cd (1), Di (Frerichs a. Smith, *A.* 191, 355), La (F. a. F., *l.c.* p. 365), Pb (23), and Manross, *A.* 82, 358), and Sm (Clève, *Bl.* [2] 43, 170), have also been prepared.

Memoirs where accounts of the molybdates will be found:—(1.) Schultze, *A.* 126, 55. (1a.) Ullik, *W. A. B.* 60 [2], 295. (2.) Ullik, *A.* 144, 214. (3.) *Ibid. id.* 144, 321. (4.) *Ibid. id.* 144, 227; 153, 376. (5.) *Ibid. id.* 144, 223. (6.) *Ibid. id.* 144, 336. (7.) *Ibid. id.* 144, 231, 327, 334. (8.) *Ibid. id.* 144, 208. (9.) *Ibid. id.* 144, 230. (10.) *Ibid. id.* 144, 334. (11.) *Ibid. id.* 144, 232, 233. (12.) *Ibid. id.* 144, 345; 153, 368. (13.) *Ibid. id.* 144, 219. (14.) *Ibid. id.* 144, 233. (15.) *Ibid. id.* 144, 339. (16.) Rammelsberg, *P.* 127, 298. (17.) *Ibid. id.* 128, 311. (18.) Struve, *J. pr.* 61, 449. (19.) *Ibid. id.* 61, 457. (20.) *Ibid. id.* 61, 459. (21.) *Ibid. N. Petersb. Acad. Bull.* 12, 142. (22.) *Ibid. J. pr.* 61, 460 to 466. (23.) Svanberg a. Struve, *J. pr.* 44, 257. (24.) Atterberg, *J.* 1873. 258. (25.) Berlin, *J. pr.* 49, 445. (26.) Delafontaine, *J. pr.* 95, 136. (27.) Flückiger, *P.* 86, 594; *cf.* Wernicke, *Fr.* 14, 14. (28.) Gentele, *J. pr.* 81, 414. (29.) Hirzel, *J.* 1852. 419. (30.) Jean, *C. R.* 78, 1436. (31.) Jörgensen, *Gm.-K.* 2 [2] 217. (32.) Kämmerer, *J. pr.* [2] 6, 358. (33.) Sonnenschein, *J. pr.* 53, 340. (34.) Steinacker, *J.* 1861. 238. (35.) Widmann, *Bl.* [2] 20, 64. (36.) Zenker, *J. pr.* 58, 486. (37.) Flemming, *J.* 1868. 250. (38.) Mauro, *B.* 14, 1379. (39.) Coloriano, *Bl.* [2] 50, 451. For an account of the *crystalline forms* of many molybdates *v.* Zepharovich, *W. A. B.* 58 [2], 111.

To indicate the methods of preparation and properties of the molybdates, short descriptions are given of the NH_4 and Na salts; for the others, reference must be made to the original memoirs.

Ammonium molybdates. (1) *Monomolybdate*, $(NH_4)_2MoO_4$. Prepared by dissolving MoO_3 in excess of very conc. NH_3Aq, and ppg. by alcohol; obtained in small monoclinic crystals by spontaneous evaporation of the trimolybdate in conc. NH_3Aq. Effloresces in air, with loss of NH_3; with water, forms an acid salt. Forms double salts with $MgMoO_4$ and $Mn_2Mo_6O_{21}$. (2) *Dimolybdate*, $(NH_4)_2Mo_2O_7$. Prepared by evaporating the mother-liquor from which the monomolybdate has separated; a white crystalline powder. Forms double salts with $Al_2(Mo_2O_7)_3$ and $Cr_2(Mo_2O_7)_3$. (3) *Trimolybdate*, $(NH_4)_2Mo_3O_{10}.aq$. Prepared by slow decomposition of ordinary NH_4 molybdate solutions, at temperatures below 10°. Lustrous needles; easily sol. hot water, sl. sol. cold water. Forms a double salt with $Na_2Mo_3O_{10}$. (4) *Tetramolybdate*, $(NH_4)_2Mo_4O_{13}.aq$. Prepared by slowly decomposing solution of ordinary NH_4 molybdate by HClAq or HNO_3Aq; the solution eventually becomes filled with crystals of the tetra- salt, and the liquid is free from Mo. (5) *Tribasic heptamolybdate*, $(NH_4)_6Mo_7O_{24}.4aq$ $(=3(NH_4)_2O.7MoO_3.4aq)$. This is the *ordinary*

ammonium molybdate used as a reagent for phosphoric acid, &c. Crystallises from solution of MoO_3 in NH_3Aq, in large monoclinic prisms, unchanged in air. The same salt crystallises with 12aq from the mother-liquor.

Treatment of ammonium molybdate residues. Venator (*Ar. Ph.* [3] 23, 713) recommends to add enough $FeCl_3Aq$ to give a brownish colour to the solution; to ppt. phosphoric acid by NH_3Aq; to filter, and add $BaCl_2Aq$ whereby Ba molybdate and $BaSO_4$ are ppd. The pp. is thoroughly washed with hot water, and boiled for a long time with $(NH_4)_2SO_4Aq$; NH_4 molybdate separates from the filtrate on evaporation.

Sodium molybdates. (1) *Monomolybdate*, $Na_2MoO_4.2aq$. Prepared by fusing together equivalent quantities MoO_3 and Na_2CO_3, dissolving in water, and evaporating; also by dissolving MoO_3 in Na_2CO_3Aq; also by neutralising the solution of any of the other Na salts by Na_2CO_3. Small lustrous tablets; sol. water, solution has an alkaline reaction. Solutions evaporated under 6° give a salt with 10aq; these crystals effloresce to the salt with 2aq. Forms a double salt with K_2MoO_4. (2) *Dimolybdate*, $Na_2Mo_2O_7$. Prepared by fusing together MoO_3 and Na_2CO_3 in the proper proportion, and treating with a little cold water; also by adding MoO_3 to the equivalent quantity of molten $NaNO_3$ (only half of this is decomposed), and treating with cold water. Small lustrous needles; sol. with difficulty in water, hot or cold. Melts at incipient redness, and crystallises on cooling. An aqueous solution of this salt evaporated to a syrup yields crystals of $Na_2Mo_2O_7.aq$; easily sol. water. (3) *Trimolybdate*, $Na_2Mo_3O_{10}.7aq$. Prepared by saturating warm Na_2CO_3Aq with MoO_3, filtering, and allowing to evaporate spontaneously; also by adding excess of HNO_3Aq to a conc. solution of MoO_3 in Na_2CO_3Aq; also by adding acetic acid to solution of $Na_6Mo_7O_{24}.22aq$; also by spontaneous evaporation of solution of $NaHMo_4O_{13}.8aq$ after addition of 1 or 2 formula-weights of Na_2CO_3. A voluminous pp. consisting of fine needles. Small quantities of a hot conc. solution of this salt give $Na_2Mo_3O_{10}.4aq$ on rapid evaporation; amorphous mass, easily sol. water. Forms a double salt with $(NH_4)_2Mo_3O_{10}$. (4) *Tetramolybdates*; (*a*) *Normal salt*, $Na_2Mo_4O_{13}.6aq$. Prepared by adding the proper quantity of HClAq to Na_2MoO_4Aq, and evaporating; also by spontaneous evaporation of solution of $NaHMo_4O_{13}.8aq$, to which a little NaCl has been added. Easily sol. hot water, sl. sol. cold water. (*b*) *Acid salt*, $NaHMo_4O_{13}.8aq$. Prepared by adding the proper quantity of HClAq to Na_2MoO_4Aq. Large monoclinic crystals; sol. water, hot or cold. Melts below redness. (5) *Octomolybdates*; (*a*) *Normal salt*, $Na_2Mo_8O_{25}.4aq$. Prepared by digesting the acid salt with 1 formula-weight Na_2CO_3 in water. A white insol. powder. (*b*) *Acid salt*, $NaHMo_8O_{25}.4aq$. Prepared by adding excess of conc. HNO_3Aq to boiling Na_2MoO_4Aq. A white pp. (6) *Decamolybdate*, $Na_2Mo_{10}O_{31}.12aq$. Prepared by adding 2HClAq to Na_2MoO_4Aq, and evaporating on the steam-bath. Separates as a white, almost insol., crystalline powder. (7) *Tribasic heptamolybdate*, $Na_6Mo_7O_{24}.22aq$ ($=3Na_2O.7MoO_3.22aq$). Prepared by dissolving MoO_3 in the calculated quantity of Na_2CO_3 in water; also by mixing equivalent quantities of $Na_2Mo_3O_{10}$ and Na_2CO_3 in solution, and evaporating; also from a solution of MoO_3 in NaOHAq or Na_2CO_3Aq, by adding HNO_3Aq as long as the pp. of trimolybdate redissolves and until the liquid acquires an acid reaction. Large, lustrous, monoclinic prisms; easily sol. water; solution reacts acid. Melts when warmed, and crystallises on cooling; the molten salt is insol. water. There are also several *complex double sodium molybdates.*

ANTIMONO-, ARSENO-, FLUO-, PHOSPHO-, SILICO-, VANADO-, MOLYBDATES.

Antimonoso-molybdates. These salts are most simply regarded as compounds of Sb_2O_3 with MoO_3 and basic oxides; they are obtained by boiling SbOCl with an acid molybdate solution (Gibbs, *P. Am. A.* 21, 93).

Antimono-molybdates. Some of these salts, compounds of Sb_2O_5 with MoO_3 and basic oxides, are described by Gibbs (*P. Am. A.* 21, 105).

Arsenoso-molybdates. Described by Gibbs (*l.c.* 21, 81). The former salts are obtained by boiling As_2O_3 with conc. solutions of acid molybdates; the latter by oxidising the former in alkaline solution. (For composition of foregoing complex salts *v.* abstracts of Gibbs' papers in *C. J. Abstracts*, 1886. 426, 511; 1887. 113; *v.* also Pufahl, *B.* 17, 217; Debray, *C. R.* 78, 1408; Struve, *J. pr.* 58, 493.)

Arseno-molybdic acids. Compounds of H_3AsO_4 with MoO_3; *v.* Seyberth, *B.* 6, 391; Debray, *C. R.* 78, 1408; Struve, *J. pr.* 58, 493.

Regarding the relations of the antimono- and arseno- molybdates to the phospho- molybdates, *v. Phosphomolybdates*, p. 426.

Fluo-molybdates. A number of salts are obtained by dissolving molybdates in HFAq and evaporating; others are formed by dissolving metallic oxides along with MoO_3 in HFAq and evaporating; other salts are produced by dissolving hydrated MoO_2 along with metallic oxides in HFAq and evaporating; others by dissolving $MoCl_5$ in alkali fluorides. These salts may be regarded as *fluomolybdates*; most of them belong to one of the series $M^I_2MoO_2F_4$, $M^IMoO_2F_3$, or $M^I_2MoOF_5$; the first may be looked on as salts of the hypothetical acid $H_2MoO_2F_4$, derived from H_2MoO_4; the second may be looked on as salts of the hypothetical acid $HMoO_2F_3$, derived from $H_2Mo_2O_7$; and the third as salts of the hypothetical acid H_2MoOF_5, derived from the hypothetical $H_4Mo_2O_7$. The foregoing, and other, fluomolybdates may also be regarded as compounds of metallic fluorides with MoO_2F_2 and $MoOF_3$, respectively.

Fluomonomolybdates, $M^I_2MoO_2F_4$. These salts, which may also be represented as $2MF.MoO_2F_2$, are generally obtained by dissolving monomolybdates in HFAq; most of them are sol. water, and crystallise well. When carefully heated in air, many form molybdates, others give residues of metallic oxides (Delafontaine, *J.* 1867. 233). The chief fluomonomolybdates are the following. $(NH_4)_2MoO_2F_4.H_2O$; triclinic tables, by adding slight excess of HFAq to a strongly ammoniacal solution of ordinary NH_4 molybdate, and evaporating; when heated, H_2O and HF are evolved and blue oxide of Mo remains. $(NH_4)_2MoO_2F_4$; rhombic plates (Mauro, *Mem. R. Acad. dei Lincei* [4] 4, 481). $CoMoO_2F_4.6H_2O$; dark-red efflorescent crystals,

obtained by dissolving equivalent weights of CoO and MoO_3 in HFAq, and evaporating. $K_2MoO_2F_4.H_2O$; lustrous, triclinic crystals, obtained by dissolving K_2MoO_4 in HFAq, also by adding KF to MoO_3 dissolved in HFAq. Other salts of this series are $CdMoO_2F_4$, $NiMoO_2F_4.6H_2O$, $Rb_2MoO_2F_4.H_2O$, $2Na_2MoO_2F_4.H_2O$, $Tl_2MoO_2F_4.H_2O$, $ZnMoO_2F_4.6H_2O$.

Fluodimolybdates, $M^I{}_2Mo_2O_4F_6$ or $M^IMoO_2F_3$ (Delafontaine, *J.* 1867. 233). These salts may also be represented as $MF.MoO_2F_2$; they are obtained by dissolving dimolybdates in HFAq, or by treating the salts $M^I{}_2MoO_2F_4$ with HFAq. The chief salts of this series are $NH_4MoO_2F_3.H_2O$, and $KMoO_2F_3.H_2O$.

Fluomolybdates other than the foregoing. The salts $(NH_4)_3MoO_2F_5$ (or $MoO_2F_2.3NH_4F$) and $(NH_4)_4MoO_2F_6.(NH_4)_2MoO_4$ (or $MoO_2F_2.4NH_4F.(NH_4)_2MoO_4$) are described by Mauro (*Mem. R. Acad. dei Lincei* [4] 4, 481). The same chemist (*G.* 19, 179; *v.* also *B.* 15, 2509) describes the following salts:— $K_2MoOF_5.H_2O$ (or $MoOF_3.2KF.H_2O$); obtained by dissolving $MoCl_5$, or $MoO_2.xH_2O$, in conc. hot KFAq, and crystallising: $K_5Mo_3O_3F_{14}.H_2O$ (or $3MoOF_3.5KF.H_2O$), by dissolving the preceding salt in HFAq and evaporating: $(NH_4)_2MoOF_5$ (or $MoOF_3.2NH_4F$), by dissolving $MoO_2.xH_2O$ in HFAq, adding NH_3Aq till the green liquid becomes reddish, then adding HFAq till a green colour is produced again, and evaporating considerably at a moderate temperature: $(NH_4)_5Mo_3O_3F_{14}.H_2O$ (or $3MoOF_3.5NH_4F.H_2O$), by dissolving the preceding salt in warm HFAq and evaporating.

Phospho-molybdates. The phospho-molybdates have been examined by Berzelius, Svanberg a. Struve (*J. pr.* 44, 299), Debray (*Bl.* [2] 5, 404), Rammelsberg (*B.* 10, 1776), Finkener (*B.* 11, 1638), and especially by Wolcott Gibbs (*P. Am. A.* 17, 62; 18, 232; 21, 50). These salts are produced when phosphoric acid or a soluble phosphate is added to solution of a molybdate, with or without the presence of a free acid; also by fusing together phosphates and molybdates; by dissolving molybdates insoluble in water in phosphoric acid; by digesting MoO_3 with an alkaline phosphate; and by treating mixtures of insoluble phosphates and molybdates with a dilute acid. The phospho-molybdates of the fixed alkaline bases may be dehydrated by careful heating, but MoO_3 is generally partially volatilised. Solutions of these salts in NH_3Aq are decomposed by H_2S with formation of thio-molybdates.

The phospho-molybdates belong to the general form $mMoO_3.2P_2O_5.nR_2O.xaq$; m is always an even number varying from 10 to 48; n varies from 2 to 6, and is generally $=6$; n may, however, exceed 6, in one case $n=14$ when $R=Ag$; Gibbs); $R=$ basic metal usually Na, K, or NH_4; x is generally large, varying from 8 to 46. The chief sub-classes of these phospho-molybdates are the following (Gibbs):—

$10MoO_3.2P_2O_5.5R_2O.xaq$;	$R=NH_4$ and K, $x=7$ and 20.
$10MoO_3.2P_2O_5.6R_2O.xaq$;	$R=NH_4$, K, Ag, $x=14$; $R=Na$, $x=28$.
$32MoO_3.2P_2O_5.6R_2O.xaq$;	$R=NH_4$, $x=28$.
$36MoO_3.2P_2O_5.2R_2O.xaq$;	$R=Na$, x undetermined, >10.
$36MoO_3.2P_2O_5.4R_2O.xaq$;	$R=Na$, x ,, >8.
$44MoO_3.2P_2O_5.5R_2O.xaq$;	$R=K$, $x=22$.
$44MoO_3.2P_2O_5.6R_2O$;	$R=NH_4$.
$44MoO_3.2P_2O_5.6R_2O.xaq$;	$R=NH_4$, $x=18$ and 24.
$44MoO_3.2P_2O_5.6R_2O.xaq$;	$R=K$, $x=24$.
$44MoO_3.2P_2O_5.14R_2O.xaq$;	$R=Ag$, $x=28$.
$48MoO_3.2P_2O_5.2R_2O.xaq$;	$R=\frac{1}{2}Co_2(NH_3)_8(NO_2)_4O$, $x=46$.
$48MoO_3.2P_2O_5.4R_2O.xaq$;	$R=K$, $x=8$.

The only *phospho-molybdic acid* which has been isolated is $48MoO_3.2P_2O_5.6H_2O.xaq$; three hydrates are known in which $x=54$, 92, and 100 (Gibbs).

The salts with $6R_2O$ are regarded by Gibbs as normal salts; those with less than $6R_2O$ generally have acid reactions. To the *ordinary ammonium phospho-molybdate* — obtained by adding excess of a mineral acid to a solution containing MoO_3, P_2O_5, and an NH_4 salt — Gibbs assigns the composition $48MoO_3.2P_2O_5.5(NH_4)_2O.H_2O.16aq$ (*cf.* Svanberg a. Struve, *J. pr.* 44, 291; Nutzinger, *Pharmaceut. Vierteljahresschrift*, 4, 549; Sonnenschein, *J. pr.* 53, 342; Lipowitz, *P.* 109, 135; Seligsohn, *J. pr.* 67, 470; Hundeshagen, *Fr.* 28, 141, 172, who says that when dried above 130° the salt is $12MoO_3.(NH_4)_3PO_4$).

Gibbs (*l.c.*) describes four other series of phospho-molybdates:—

Metaphospho-molybdates, $mMoO_3.nRPO_3.pR_2O.xaq$.

Hypophospho-molybdates, $mMoO_3.nH_3PO_2.pR_2O.xaq$.

Phosphoroso-molybdates, $mMoO_3.nH_3PO_3.pR_2O.xaq$.

Phosphoroso-phospho- molybdates, $mMoO_3.nP_2O_5.n^1H_3PO_3.pR_2O.xaq$.

Metaphospho- molybdates, represented by $10MoO_3.4NH_4PO_3.3(NH_4)_2O.9aq$ and $14MoO_3.3Ba(PO_3)_2.BaO.55aq$ are converted by acids into orthophospho-molybdates (Gibbs, *P. Am. A.* 21, 116).

Hypophospho- molybdates are represented by $8MoO_3.2H_3PO_2 2(NH_4)_2O.2aq$; this salt was obtained by mixing NaH_2PO_2Aq with solution of $(NH_4)_6Mo_7O_{24}$, and adding HClAq (G., *P. Am. A.* 18, 232).

Phosphoroso- molybdates are represented by $24MoO_3.4H_3PO_3.4(NH_4)_2O.xaq$, in which $x=17$ and 25; obtained by adding H_3PO_3Aq (produced by adding water to PCl_3) to solution of $(NH_4)_6Mo_7O_{24}$ (G., *P. Am. A.* 18, 237; 21, 89).

Phosphoroso-phospho- molybdates are represented by $72MoO_3.3P_2O_5.2H_3PO_3.9(NH_4)_2O.38aq$; obtained by adding the product of the decomposition of PCl_3 by H_2O to solution of $10MoO_3.2P_2O_5.6(NH_4)_2O.14aq$ (G., *l.c.* 21, 96).

Note.—*Pyrophospho- tungstates* have been isolated, of the form $22WO_3.9P_2O_5.pR_2O$, $p=13$, 18, and 20; an *ortho-metaphospho- tungstate* has also been prepared,
$22WO_3.3(P_2O_5.3K_2O).6NaPO_3.2K_2O.2Na_2O.42aq$.

Corresponding molybdates have not yet been isolated.

Besides the foregoing phospho-molybdates, representatives of phosphovanado- and phosphostanno-molybdates have been prepared by Wolcott Gibbs.

Phosphovanado- molybdates are represented by $28MoO_3.2P_2O_5.16V_2O_5.16(NH_4)_2O.100aq$, and $48MoO_3.2P_2O_5.V_2O_5.7(NH_4)_2O.30aq$. These salts are obtained by digesting MoO_3 with solution of phosphovanadates, $mP_2O_5.nV_2O_5.pR_2O$; by heating solutions of vanado-molybdates, $mMoO_3.nV_2O_5.pR_2O$, with alkaline phosphates in the presence of acid; and by heating V_2O_5 with solution of an alkaline phospho-molybdate (Gibbs, *l.c.* 18, 253).

Phosphostanno molybdates; the salt $16MoO_3.3P_2O_5.4SnO_2.3(NH_4)_2O.28aq$ is obtained by pouring solution of $SnCl_4.2NH_4Cl$ into a hot solution of the acid NH_4 phospho-molybdate $10MoO_3.2P_2O_5.5(NH_4)_2O.7aq$ (Gibbs, *l.c.* 21, 120).

The arseno-molybdates already referred to (p. 425) belong to the series $mMoO_3.nAs_2O_3.pR_2O.xaq$ (*arsenoso- compounds*) where $m = 6$, 8, and 12, $n = 3$, 2, and 5, $p = 2$ and 3 ($R = NH_4, \frac{1}{2}Mn, \frac{1}{2}Ba$), and $x = 6$, 13, and 24 (Gibbs, *P. Am. A.* 21, 81). The *antimono-molybdates* (*v.* p. 425) belong to the series $17MoO_3.3Sb_2O_3.6(NH_4)_2O.21aq$ (*antimonoso-compounds*); and the series $7MoO_3.4Sb_2O_5.5(NH_4)_2O.12aq$ (*antimono- compounds*) (Gibbs, *P. Am. A.* 21, 93 a. 105).

Silico-molybdates. Alkali molybdate solutions produce yellow pps. when added to solutions of alkali silicates in presence of HNO_3 (Knop, *C. C.* 1857. 691, 861; Richter, *D. P. J.* 199, 183). According to Parmentier (*C. R.* 92, 1234) these pps. have the composition $13MoO_3.M^I_4SiO_4.xH_2O$. P. obtained the acid $12MoO_3.H_4SiO_4.24H_2O$ from the mercurous salt (*C. R.* 94, 213). This acid forms large yellow regular octahedra, melting at 45° and decomposing below 100°; easily soluble in water and dilute acids; decomposed by excess of NH_3Aq or alkali carbonates with separation of silica.

Vanado-molybdates. These salts belong to two series (Gibbs, *P. Am. A.* 18, 240 a. 264).

Vanadio-molybdates. These salts are represented by $6MoO_3.V_2O_5.2(NH_4)_2O.5aq$, $16MoO_3.2V_2O_5.5BaO.29aq$, and $18MoO_3.V_2O_5.8(NH_4)_2O.15aq$; they are obtained by digesting V_2O_5 (free from VO_2) with solutions of alkaline molybdates; by heating together solutions of alkaline vanadates and molybdates especially in presence of acid; by boiling solutions of alkaline vanadates or meta-vanadates (*e.g.* NH_4VO_3) with MoO_3; and by the decomposition of phosphovanadomolybdates (*v. supra*).

Vanadio-vanadico-molybdates. The representatives of this series which have been isolated are $28MoO_3.VO_2.4V_2O_5.11(NH_4)_2O.20aq$ and $30MoO_3.3VO_2.2V_2O_5.14BaO.48aq$. They are obtained by boiling VO_2 and V_2O_5 with an acid molybdate; by the partial reduction of vanadio-molybdates; and by digesting solutions of acid molybdates with solutions containing VO_2 and V_2O_5.

Alumino-, chromico-, ferrico-, and *mangano-molybdates* have been obtained by Struve (*Petersburg Acad. Bull.* 12, 142) and Parmentier (*C. R.* 98, 389). These salts are classed by Gibbs (*P. Am. A.* 21, 121) as belonging to the forms $10MoO_3.M_2O_3.2K_2O.15aq$, where $M = Al,Cr,Fe$; $12MoO_3.M_2O_3.6R_2O.xH_2O$, where $M = Al,Cr,Fe$, $R = NH_4$, K, or Na, and x is generally 20 to 22; and $16MoO_3.Mn_2O_3.5R_2O.12aq$ where $R = NH_4$ and K.

Molybdenum, alloys of. Mo alloys with several metals. With *aluminium*; a crystalline powder consisting of microscopic rhombic prisms, approximating in composition to $MoAl_4$, is obtained by melting together 1 pt. MoO_3 dissolved in HFAq and evaporated to dryness, 2 pts. cryolite, 2 pts. KCl.NaCl, and 1 pt. Al, and dissolving excess of Al from the regulus by NaOHAq (Wöhler a. Michel, *A.* 115, 102). With *iron*; grey, hard, brittle, alloys are obtained by directly fusing the metals together; by reducing $Fe_2O_3.4MoO_3$ in H at full red heat, an alloy of the composition Mo_2Fe is obtained (Steinacker, *Ueber einige Molybdänverbindungen* [Göttingen, 1861]). Alloys with Cu, Au, Pt, and Ag have been described. An alloy of Mo with *lead* was found in plates in Utah (Silliman, *Am. S.* [3] 6, 128).

Molybdenum, bromides of. Mo combines directly with Br to form three bromides $MoBr_2$, $MoBr_3$, and $MoBr_4$; no $MoBr_5$ corresponding with $MoCl_5$ has been isolated. When Br is passed over strongly heated Mo, an oxybromide is formed, then a greenish-grey sublimate of $MoBr_3$ near the heated part of the tube; the metal becomes yellow-red and is eventually converted into $MoBr_2$; between the $MoBr_2$ and $MoBr_3$, isolated lustrous black needles of $MoBr_4$ are formed. The only halogen compound of Mo which has been gasified, and the mol. w. of which is known in the gaseous state, is $MoCl_5$.

MOLYBDENUM DIBROMIDE, $MoBr_2(Mo_3Br_4.Br_2)$. (*Molybdous bromide*).

Preparation.—1. By passing Br vapour, much diluted by CO_2, over strongly heated Mo (Atterberg, *J.* 1872. 260).—2. By passing Br vapour over Mo at a moderate temperature; or over a heated mixture of MoO_2 and C, strongly heating the $MoBr_3$ thus produced, and treating the residue with water whereby unchanged Mo may be washed away (Blomstrand, *J. pr.* 82, 433).

Properties and Reactions.—A golden-yellow powder; unchanged by heat; insoluble in water and in all acids. *Concentrated alkali solutions* produce alkali bromide and $MoO.xH_2O$ (Blomstrand, *J. pr.* 77, 91). *Dilute alkali solutions* produce alkali bromide, and yellow solutions from which CO_2 ppts. $Mo_3Br_4(OH)_2.8H_2O$. This compound, known as *molybdenum bromohydroxide*, is prepared by slowly adding CO_2 to the solution of $MoBr_2$ in KOHAq, or by adding acetic acid and then passing in CO_2, or by decomposing the solution when hot by NH_4Cl (*v. Molybdenum bromohydroxide*). The reaction of $MoBr_2$ with KOHAq points to the formula $Mo_3Br_4.Br_2$ for the dibromide; the radicle Mo_3Br_4 combines with acid radicles to form salts; *v. Molybdenum bromohydroxide*, p. 428.

MOLYBDENUM TRIBROMIDE, $MoBr_3$ (*Molybdomolybdic bromide*). Obtained by passing Br vapour over gently heated Mo, or by heating a mixture of MoO_2 and C in Br vapour; any $MoBr_4$ and MoO_2Br_2 formed are removed by heating in the stream of Br, as these compounds are more volatile than $MoBr_3$ (Blomstrand, *J. pr.* 82, 433).

Forms a blackish-green mass of small interlaced needles. Sublimes with difficulty; at bright red heat gives $MoBr_2$ and Br. Unchanged by water; insoluble in conc. HClAq and cold dilute HNO_3Aq. Slowly acted on by dilute alkali solutions; decomposed by boiling alkali solution with ppn. of black $Mo_2O_3.3H_2O$ (Blomstrand, *l.c.*).

MOLYBDENUM TETRABROMIDE, $MoBr_4$ (*Molybdic bromide*). Formed in small quantity by heating Mo in Br; appears as single, black, lustrous, needles. Easily decomposed by heat to $MoBr_2$ and Br, the temperatures at which it is formed and decomposed being not very different. Fusible and volatile, forming brown vapours. Deliquescent; soluble in water, forming a brown-yellow solution from which alkalis ppt. rusty-brown $MoO_2.xH_2O$ (Blomstrand, *J. pr.* 82, 433).

Molybdenum, bromochlorides of. $Mo_3Br_4Cl_2.3H_2O$ and $Mo_3Cl_4Br_2.3H_2O$. Produced by adding HClAq to a solution of $MoBr_2$ in KOHAq, and by adding HBrAq to $MoCl_2$ in KOHAq respectively; *cf. Molybdenum bromohydroxide, infra*; and *Molybdenum chlorohydroxide*, p. 430.

Molybdenum, bromochlorohydroxide of. $Mo_3Cl_4.BrOH.xH_2O$; obtained by adding water to an alcoholic solution of $Mo_3Cl_4.Br_2.3H_2O$; *cf. Molybdenum chlorohydroxide.*

Molybdenum, bromofluoride of. $Mo_3Br_4F_2.3H_2O$. Produced by adding HFAq to solution of $MoBr_2$ in KOHAq; *cf. Molybdenum bromohydroxide.*

Molybdenum, bromohydroxide of. $Mo_3Br_4(OH)_2$. Prepared by dissolving $MoBr_2$ in KOHAq, and passing in CO_2 or adding acetic acid, or by adding NH_4Cl to a hot solution of $MoBr_2$ in KOHAq (Blomstrand, *J. pr.* 82, 433; *cf.* Atterberg, *J.* 1872. 260). The yellow crystalline pp., consisting of $Mo_3Br_4(OH)_2.8H_2O$, is dried at 100° or *in vacuo* over H_2SO_4: by placing the pp. over H_2SO_4 the dihydrate $Mo_3Br_4(OH)_2.2H_2O$ is produced.

$Mo_3Br_4(OH)_2$ is a red powder; sol. in KOHAq; this solution probably contains $Mo_3Br_4)OK)_2$. Addition of acids to this solution generally ppts. a compound of the acid radicle with the group Mo_3Br_4; thus HClAq ppts. $Mo_3Br_4.Cl_2.3H_2O$, HBrAq ppts. $Mo_3Br_4.Br_2.3H_2O$, HFAq ppts. $Mo_3Br_4.F_2.3H_2O$, and HIAq ppts. the double compound $(Mo_3Br_4.I_2)_2.Mo_3Br_4(OH)_2.8H_2O$. H_2SO_4Aq ppts. $Mo_3Br_4.SO_4.3H_2O$. $K_2Cr_2O_7$Aq ppts. black $Mo_3Br_4.CrO_4.2H_2O$. Addition of NH_4 molybdate and acetic acid ppts. the molybdate $Mo_3Br_4.MoO_4.2H_2O$. H_3PO_4Aq, $H_2C_2O_4$Aq, and HNO_3Aq also yield pps.; that by HNO_3Aq dissolves in excess of the acid. Acetic acid and CO_2 reppt. the hydroxide from its solutions in alkalis. The haloid compounds of the radicle Mo_3Br_4 are yellow solids insol. in excess of the haloid acids; they are decomposed by boiling water giving $Mo_3Br_4(OH)_2.xH_2O$. The sulphate is yellow, and is sol. in excess of H_2SO_4Aq; this solution gives no pp. with $AgNO_3$Aq; addition of HClAq ppts. $Mo_3Br_4.Cl_2.3H_2O$.

The compound $MO_3Br_4(OH)_2.8H_2O$ might be represented as an oxybromide of Mo, viz. as $Mo_3OBr_4.9H_2O$; but the production of $Mo_3Br_4(OH)_2$ by drying the hydrate, and the reactions of this compound with acids, are better expressed by representing the compound as a compound of the radicle Mo_3Br_4 than as an oxybromide: a corresponding chlorohydroxide, $Mo_3Cl_4(OH)_2$, exists (*v.* p. 430).

Molybdenum, bromo-iodide of, $Mo_3Br_4I_2$. This compound is only known in combination with $Mo_3Br_4(OH)_2$; the compound has the composition $(Mo_3Br_4.I_2)_2.Mo_3Br_4(OH)_2.8H_2O$, and is produced by adding HIAq to a solution of $Mo_3Br_4(OH)_2$ in KOHAq; *cf. Molybdenum bromohydroxide, supra.*

Molybdenum, chlorides of. $MoCl_5$ is formed when Mo is heated in Cl free from O; by heating $MoCl_5$ in H, $MoCl_3$ is produced; and $MoCl_3$ produces $MoCl_2$ and $MoCl_4$ when heated in CO_2. The formula $MoCl_5$ represents the molecular composition of the gaseous pentachloride; the mol. w. of none of the other chlorides in the gaseous state has been determined.

MOLYBDENUM DICHLORIDE $MoCl_2$(?$Mo_3Cl_4.Cl_2$) (*Molybdous chloride*).

Formation.—1. By heating $MoCl_3$ in an indifferent gas (Blomstrand, *J. pr.* 77, 95; Liechti a. Kempe, *A.* 169, 344).—2. By heating Mo with HgCl.—3. By carefully heating Mo in Cl largely diluted with CO_2.

Preparation.—$MoCl_3$, as pure as possible, is placed in several porcelain boats, which are heated to dull redness in a glass tube, while a slow stream of perfectly dry CO_2, free from air, is passed through the tube; the contents of the first boat are not quite pure $MoCl_2$, but may be purified by gently warming with very dilute HNO_3Aq (Liechti a. Kempe, *A.* 169, 344).

Properties and Reactions.—An amorphous dull yellow powder; unchanged in air, but when heated forms Mo_2O_3 and then MoO_3; volatilised with difficulty; insol. water; dissolves in alcohol and ether (L. a. K., *l.c.*). Dissolves in HClAq and crystallises from this solution as $MoCl_2.H_2O$, $MoCl_2.2H_2O$, or $2MoCl_2.3H_2O$ (Blomstrand, *J. pr.* 77, 95; *v. infra, Combinations*, No. 1). Very slightly sol. in HNO_3Aq; dissolved by H_2SO_4Aq; soluble in NH_3Aq, on boiling a brown powder containing N is ppd. Decomposed by hot conc. alkali solutions with ppn. of $MoO.xH_2O$. Dissolved by dilute alkali solutions to form a yellow liquid from which CO_2 or dilute acetic acid ppts. $Mo_3Cl_4.(OH)_2.xH_2O$; *v. infra Molybdenum chlorohydroxide.* This reaction suggests the formula $Mo_3Cl_4.Cl_2$ for the dichloride (*cf. Combinations*, No. 2); the radicle Mo_3Cl_4 combines with acid radicles to form salts; *v. Molybdenum chlorohydroxide.*

Combinations.—1. With *water* to form the hydrates $MoCl_2.H_2O$, $MoCl_2.2H_2O$, and $2MoCl_2.3H_2O$ (or $Mo_3Cl_4.Cl_2.3H_2O$, $Mo_3Cl_4.Cl_2.6H_2O$, and $(Mo_3Cl_4.Cl_2)_2.9H_2O$). The first of these hydrates is formed by dissolving $MoCl_2$ in rather dilute HClAq and allowing to stand; it forms thin yellow plates, insol. water. The second hydrate is formed by warming a solution of $MoCl_2$ in HClAq on a water-bath, or by slowly diluting a conc. solution; it forms long thin prisms, sol. water, alcohol, and ether. Dilute solutions of this hydrate deposit $Mo_3Cl_4(OH)_2.xH_2O$. The third hydrate is formed by dissolving $MoCl_2$ in hot HClAq and allowing to cool; it forms lustrous needles, insol. water, decomposed by hot water, decomposed by heat with loss of H_2O, Cl, and HCl (Blomstrand, *J. pr.* 77, 95).—2. With the *alkali haloid salts* to form compounds of the type $2MX.Mo_3Cl_4.X_2.2H_2O$

where $M = NH_4$ or K, and X = Cl, Br, or I (Blomstrand, *l.c.*). Obtained by adding excess of haloid acid, HX, to solutions of $MoCl_2$ in KOHAq or NH_4OHAq, and evaporating. These compounds are decomposed by water, with solution of KX, or NH_4X, and ppn. of $Mo_3Cl_4.X_2.3H_2O$. From solutions of these compounds $AgNO_3Aq$ ppts. only half of the halogen present; thus 4Br is ppd. from $Mo_3Cl_4.Br_2.2KBr$, and 4Cl from $Mo_3Cl_4.Cl_2.2KCl$. These compounds are not decomposed by H_2S in presence of acids, nor by K_4FeCy_6Aq.

Molybdenum trichloride, $MoCl_3$ (*Molybdo-molybdic chloride*).

Formation.—1. By passing vapour of $MoCl_5$ over heated Mo (Berzelius).—2. By heating $MoCl_5$, by means of an ordinary spirit-lamp, in a stream of H (Blomstrand, *J. pr.* 71, 449).—3. By passing CO_2 charged with $MoCl_5$ through a tube heated in one spot; $MoCl_3$ remains behind the heated place as a thick crystalline crust (Blomstrand, *l.c.*).

Preparation.—$MoCl_5$ is prepared in a hard glass tube, narrowed at intervals so as to form 3 or 4 divisions (*v. Molybdenum pentachloride, Preparation*); the greater part of the $MoCl_5$ is in the second division, while a little is in the first division. Pure dry H is passed through the tube for some time, the second division of the tube is then heated until the $MoCl_5$ begins to sublime into the third division; the temperature of the third division is kept at 250°, at which temperature reduction to $MoCl_3$ proceeds. When reduction is complete (known by the change of colour of black $MoCl_5$ into red $MoCl_3$), the H is replaced by a stream of dry CO_2, and the small quantity of $MoCl_5$ in the first division of the tube is sublimed over the $MoCl_3$ which is not yet quite pure (Liechti a. Kempe, *A.* 169, 344).

Properties and Reactions.—A dark brownish-red solid, resembling amorphous P. Unchanged in air. Heated in a tube drawn to a fine opening, $MoCl_5$ forms as a red crystalline sublimate; heated in air, gives a white woolly sublimate, then brownish-red, and finally dark blue, vapours, while impure $MoCl_2$ remains (L. a. K., *l.c.*). Decomposes at red heat into $MoCl_2$ and $MoCl_4$. Insol. water and HClAq; sol. in hot HNO_3Aq, also in conc. H_2SO_4 forming a deep-blue liquid (L. a. K., *l.c.*). Decomposed by boiling water; also by KOHAq or NaOHAq, with ppn. of $Mo_2O_3.3H_2O$; warm NH_3Aq produces a brown powder which contains N. A compound of KCl with $MoCl_3$ was obtained by Berzelius by the action of K-amalgam on MoO_2 dissolved in HClAq.

Molybdenum tetrachloride, $MoCl_4$ (*Molybdic chloride*).

Preparation.—$MoCl_3$ is placed in a porcelain boat and heated to dull redness, in a long tube of hard glass, in a very slow stream of pure, air-free, CO_2; $MoCl_2$ remains in the boat, and $MoCl_4$ sublimes, and is carried forward some distance by the CO_2 (Liechti a. Kempe, *A.* 169, 344).

Properties.—A brown semi-crystalline solid; the vapour is intensely yellow. Deliquescent; dissolves in water with hissing sound, the solution shows the reactions of salts of MoO_2. Somewhat sol. in alcohol and ether; dissolved by H_2SO_4Aq with evolution of HCl; sol. in conc. HNO_3Aq.

Reactions.—1. Kept in contact with *air*, oxychlorides are produced.—2. *Heated in air*, MoO_2Cl_2 and $MoO_3.2HCl$ are formed.—3. Heated in *carbon dioxide*, forms $MoCl_5$ and $MoCl_3$; at a higher temperature the $MoCl_3$ is decomposed to $MoCl_4$ and $MoCl_2$.

Combinations.—1. With *phosphorus pentachloride* to form $MoCl_4.2PCl_5$; a bluish amorphous solid, obtained by the reaction of PCl_5 with $MoCl_5$ or MoO_2Cl_2. When this compound is heated, $MoCl_4.PCl_5$ is produced; a metal-like lustrous solid, soluble in water to form a black liquid (Cronander, *Bl.* [2] 19, 500).—2. With *ammonium chloride* to form $3MoCl_4.2NH_4Cl.6H_2O$; obtained by saturating NH_4ClAq with $MoCl_5$, filtering from NH_4Cl which separates, and allowing to crystallise: forms green, deliquescent octahedra (Blomstrand, *J. pr.* 71, 449).

Molybdenum pentachloride, $MoCl_5$. Mol. w. 272·75. V.D. at 350° = 137. This chloride was supposed by Berzelius, also by Blomstrand, to be tetrachloride; its composition was determined by Debray (*C. R.* 66, 732).

Formation.—1. By gently heating Mo or MoS_2 in Cl.—2. By strongly heating in Cl a mixture of MoO_2 and C.

Preparation.—A tube of hard glass is narrowed at intervals so that 4 or 5 divisions are formed; a porcelain boat containing Mo is placed in the tube, and the Mo is heated in a stream of dry HCl so long as any white woolly sublimate of $MoO_3.2HCl$ is formed; this sublimate is driven out of the tube by warming in the stream of HCl. After cooling, dry air-free Cl is passed through the tube for at least an hour, to ensure the removal of every trace of air, and the Mo is then gently heated in the stream of Cl. $MoCl_5$ is formed and deposited immediately in front of the porcelain boat; by careful heating while the stream of Cl passes, the $MoCl_5$ can be sublimed into the different divisions of the tube, each of which is then sealed off (Liechti a. Kempe, *A.* 169, 344).

Properties.—A black, crystalline, lustrous mass; a shade of greenish colour indicates presence of oxychloride (L. a. K., *l.c.*). Melts at 194°, and boils at 268° (Debray, *C. R.* 66, 732). The vapour is dark red. V.D. at 350° = 137 (Debray, *l.c.*; Rieth, *B.* 3, 668). May be sublimed unchanged in Cl or CO_2. Decomposed by heating in air with production of MoO_2Cl_2. Fumes in air, and deliquesces to a brown liquid. Dissolves in water with decomposition; solution in a little water is brown, but becomes colourless on dilution. Sol. in alcohol and ether, forming green liquids. Sol. in H_2SO_4Aq and HNO_3Aq.

Reactions.—1. Heated in *air* forms MoO_2Cl_2; same change results by exposure to air.—2. Reacts towards some *organic compounds* as a carrier of chlorine, *e.g.* CCl_4 and S_2Cl_2 are produced by passing Cl into CS_2 mixed with $MoCl_5$ (Aronheim, *B.* 9, 1788).—3. Heated with *ammonia* or *ammonium chloride* produces compounds of Mo with N and H (*v. Molybdenum, nitride of*, p. 430).

Combinations.—With *phosphoryl chloride*, to form $MoCl_5.POCl_3$; large dark-green crystals, melting at 125°–127°, and boiling at 170° with separation into its constituents (Piutti, *B.* 12, 1326). This compound is formed by heating PCl_5 with MoO_3, in the ratio $3PCl_5.MoO_3$, to 170° in a sealed tube, pouring off the brown liquid

from the crystals, washing the latter with CS_2 and drying them in a stream of CO_2.

Molybdenum, chlorobromides of, $Mo_3Br_4Cl_2.3H_2O$ and $Mo_3Cl_4Br_2.3H_2O$. Produced by adding HClAq to a solution of $MoBr_2$ in KOHAq, and by adding HBrAq to a solution of $MoCl_2$ in KOHAq respectively (*cf. Molybdenum bromohydroxide*, p. 428, and *Molybdenum chlorohydroxide, infra*).

Molybdenum, chlorobromohydroxide of. $Mo_3Cl_4.BrOH.2H_2O$; obtained by adding water to an alcoholic solution of $Mo_3Cl_4.Br_2.2H_2O$ (*v.* next article).

Molybdenum, chlorohydroxide of. $Mo_3Cl_4(OH)_2.2H_2O$. Prepared by dissolving $MoCl_2$ in KOHAq, and neutralising by acetic acid; the *octohydrate* $Mo_3Cl_4(OH)_2.8H_2O$ is obtained by adding CO_2, or NH_4Cl, in place of acetic acid. The dihydrate a light-yellow amorphous powder; insol. water and alcohol; when freshly ppd. and washed with cold water it dissolves readily in acids, but on boiling the solution in HNO_3Aq or H_2SO_4Aq the hydrate is reppd., and is now quite insoluble in acids. The octohydrate forms yellow lustrous crystals (Blomstrand, *J. pr.* 77, 95).

By adding HBrAq or HIAq to $MoCl_2$, or $Mo_3Cl_4(OH)_2.xH_2O$, warming, and allowing to cool, the compounds $Mo_3Cl_4.Br_2.3H_2O$ and $Mo_3Cl_4.I_2.3H_2O$ are obtained, and by evaporating the mother-liquor from the second of these, on the water-bath, the compound $Mo_3Cl_4.I_2.6H_2O$ is produced. These haloid compounds of the radicle Mo_3Cl_4 are yellowish-red crystals, soluble in alcohol, crystallisable from dilute HBrAq and HIAq respectively. Addition of water to the alcoholic solution of $Mo_3Cl_4.Br_2.3H_2O$ ppts. $Mo_3Cl_4.BrOH.2H_2O$ (Blomstrand, *l.c.*).

The compounds $Mo_3Cl_4(OH)_2.2H_2O$ and $Mo_3Cl_4(OH)_2.8H_2O$ might be represented as oxybromides of Mo, viz. as $Mo_3OCl_4.3H_2O$ and $Mo_3OCl_4.9H_2O$; but the reactions of these compounds with HBrAq and HIAq, and the composition and properties of the salts $2KX.Mo_3Cl_4.X_2.xH_2O$ (*v. Molybdenum dichloride*), are better expressed by representing them as hydrated hydroxides of the radicle Mo_3Cl_4 than as hydrated oxybromides: a corresponding bromohydroxide, $Mo_3Br_4(OH)_2$, exists (*v.* p. 428).

Molybdenum, chloro-iodides of. $Mo_3Cl_4.I_2.xH_2O$; $x = 3$ and 6. Obtained by adding HIAq to $MoCl_2$ or to $Mo_3Cl_4(OH)_2.xH_2O$ (*cf.* preceding article).

Molybdenum, fluorides of. No fluoride of Mo has been isolated. Solutions of $Mo_2O_3.xH_2O$, $MoO_2.xH_2O$, and $MoO_3.xH_2O$, in HFAq may contain the corresponding fluorides (Berzelius). The first of these solutions is purple, on evaporation a purple-coloured varnish is obtained; addition of KF, NH_4F, or NaF, to this solution, and evaporation, ppts. rose-coloured powders which may be double compounds of alkali fluoride and MoF_3. Solution of $MoO_2.xH_2O$ in HFAq is rose-red, but goes colourless on addition of much HFAq; on evaporation it yields a crystalline solid which dissolves in water; KF ppts. a reddish-brown solid. Solution of MoO_3 in HFAq is colourless, on evaporation it yields a yellow syrup; addition of KF produces $2KF.MoO_2F_2.H_2O(=K_2MoO_2F_4.H_2O)$; (*cf. Fluomolybdates* under *Molybdates*, p. 425).

Molybdenum, fluobromide of. $Mo_3Br_4F_2.3H_2O$; prepared by adding HFAq to solution of $Mo_3Br_4(OH)_2$ or $MoBr_2$ in KOHAq: *cf. Molybdenum, bromohydroxide of*, p. 428.

Molybdenum, haloid compounds of. The haloid compounds of Mo which have been isolated are $MoBr_2$, $MoBr_3$, $MoBr_4$, $MoCl_2$, $MoCl_3$, $MoCl_4$, and $MoCl_5$; the three bromides are formed by the direct union of Mo and Br; $MoCl_5$ is produced by heating Mo in Cl, $MoCl_3$ is obtained by partial reduction (by H) of $MoCl_5$, and $MoCl_2$ and $MoCl_4$ are the products of the decomposition by heat of $MoCl_3$. The only one of these compounds whose molecular weight is known in the gaseous state is $MoCl_5$. The reactions of the dibromide and dichloride leave little doubt that the molecular formulæ of these compounds are not less than Mo_3X_6; these compounds react as $Mo_3X_4.X_2$; the radicles Mo_3X_4 combine with acid radicles to form salts such as $Mo_3Br_4.SO_4$ and $MO_3Cl_4.Br_2$. These radicles Mo_3X_4 also combine with alkali haloid compounds to form $2MY.Mo_3X_4.Y_2.xH_2O$ where M = alkali metal and Y = halogen.

No fluoride or iodide of Mo has been isolated with certainty.

Molybdenum, hydroxides or hydrated oxides of; *v. Molybdenum, oxides of*, p. 431; also *Molybdic acids*, p. 423.

Molybdenum, hydroxychlorides of; $Mo(OH)_2Cl_2$ *v. Chloromolybdic acid*, p. 423; $Mo_3Cl_4(OH)_2$ *v. Molybdenum, chlorohydroxide of, supra.*

Molybdenum, hydroxybromide of; $Mo_3Br_4(OH)_2$, *v. Molybdenum, bromohydroxide of*, p. 428.

Molybdenum, iodides of. None has been isolated with certainty. A solution of $MoO_2.xH_2O$ in HIAq gives a crystalline solid on evaporation; this solid is sol. water, on heating it gives MoO_2 and HI (Berzelius).

Molybdenum, iodobromide of. $Mo_3Br_4I_2$. Known only in combination with $Mo_3Br_4(OH)_2$, as $(Mo_3Br_4I_2)_2.Mo_3Br_4(OH)_2.8H_2O$; which is produced by adding HIAq to a solution of $Mo_3Br_4(OH)_2$ in KOHAq; *cf. Molybdenum, bromohydroxide of*, p. 428.

Molybdenum, iodochloride of. $Mo_3Cl_4I_2.xH_2O$, $x = 3$ and 6. Obtained by adding HIAq to $MoCl_2$ or $Mo_3Cl_4(OH)_2.xH_2O$; *cf. Molybdenum, chlorohydroxide of, supra.*

Molybdenum, nitride of. Mo_3N_2, or (?) Mo_5N_3. A greyish-black powder, obtained by passing dry NH_3 over $MoCl_5$ heated to full redness (Uhrlaub, *P.* 101, 605). Heated to whiteness in NH_3, Mo is produced.

Compounds of Molybdenum with Nitrogen and Hydrogen. These compounds are produced by heating $MoCl_5$ or MoO_3 in NH_3, also by heating NH_4Cl with $MoCl_5$. $MoCl_5$ melts when heated in dry NH_3, NH_4Cl volatilises, and on continued warming a blackish mass remains, which when powdered, quickly washed with water, and dried over H_2SO_4, has the composition $Mo_5N_{10}H_4$ (Uhrlaub, *P.* 101, 605). Wöhler (*A.* 108, 258) regarded this compound as $4MoN_2.Mo(NH_2)_2$. By heating to incipient redness, a body of the composition $Mo_6N_{10}H_4$ is produced (Uhrlaub, *l.c.*). Both these compounds are black powders; heated in air they burn to MoO_3 and give off NH_3; with molten KOH they evolve NH_3, and with NaClOAq

they evolve N (Uhrlaub, *l.c.*). By heating to a temperature slightly above that at which NH_4Cl is sublimed, Tuttle obtained $Mo_3N_4H_4$ (*A.* 101, 285). These compounds are all reduced to Mo by very strongly heating in NH_3. According to Tuttle (*l.c.*), purple coloured to black crystals are obtained by heating MoO_3 to redness in NH_3, and these crystals consist of MoO_2, Mo nitride, and Mo amide.

Molybdenum, oxides and hydrated oxides of. The three oxides MoO_2, Mo_2O_3, and MoO_3 have been isolated; there also exist one or more oxides with more O than Mo_2O_3 and less than MoO_3; a hydrate of the monoxide (MoO) was obtained by Blomstrand, but little is known concerning it. The oxides Mo_2O_3 and MoO_2 are basic; they dissolve in acids to form salts, but little is known with certainty regarding these salts. MoO_3 is acidic, it is the anhydride of molybdic acid H_2MoO_4, and several other acidic hydrates of MoO_3 are known; *v. Molybdenum, acids of*, p. 423. MoO_3 also combines with some acids, *e.g.* HCl, and acidic radicles, *e.g.* SO_3. The mol. w. of none of the oxides is known with certainty, as none has been gasified.

Hydrated molybdous oxide, $MoO.xH_2O$. By treating $MoBr_2$ with conc. KOHAq, Blomstrand obtained a black hydrate of MoO (*J. pr.* 77, 91). This compound has been examined only slightly.

Molybdenum sesquioxide, Mo_2O_3 (*Molybdo-molybdic oxide*). This oxide was regarded by Berzelius as the protoxide; its composition was determined correctly by Blomstrand (*J. pr.* 71, 454; *cf.* Svanberg a. Struve, *J. pr.* 44, 257).

Formation.—1. By heating MoO_3 to redness for some time in a stream of H (S. a. S., *l.c.*).—2. By long-continued digestion of MoO_3 with Zn and HClAq; the product oxidises readily in air (Berzelius).—3. By decomposing $MoCl_3$ by KOHAq, washing the pp. of $Mo_2O_3.3H_2O$ with cold water, pressing between paper, drying over H_2SO_4, and heating *in vacuo* (Blomstrand, *J. pr.* 71, 455).

Preparation.—$Mo_2O_3.3H_2O$ is obtained by one of the following methods; it is dried over H_2SO_4, and heated to a moderate temperature, *in vacuo*, or out of contact with air (if heated in air it is oxidised to MoO_2). To obtain $Mo_2O_3.3H_2O$, HClAq is added to a conc. solution of a molybdate till the pp. which forms is re-dissolved, this solution is digested with Zn until the colour changes from blue to red-brown and finally to black (Blomstrand, *J. pr.* 71, 455; Rammelsberg, *P.* 127, 284; Werncke, *Fr.* 14, 1; Pisani, *Fr.* 4, 420; Macagno, *B.* 8, 258; *cf.* O. von der Pfordten, *B.* 15, 1925). Addition of NH_3Aq to this black solution ppts. $Mn_2O_3.3H_2O$; care should be taken to ppt. as little $ZnO.H_2O$ as possible along with the $Mo_2O_3.3H_2O$ (the $ZnO.H_2O$ begins to come down when most of the $Mo_2O_3.3H_2O$ is ppd.). The pp. is washed with water containing a little HCl, to remove $ZnO.H_2O$, then with pure cold water (Blomstrand, *l.c.*), and is then pressed between paper. $Mo_2O_3.3H_2O$ is also obtained by reducing the HCl solution of a molybdate by K-amalgam containing very little K, and then ppg. by NH_3Aq (Berzelius); also by adding NH_3Aq to the solution obtained by boiling HClAq and Cu with $PbMoO_4$ (von Kobell, *J. pr.* 41, 158; *cf.* Hirzel, *J.* 1850. 309), or with MoO_3Aq (Rammelsberg, *P.* 127, 281).

Properties and Reactions.—A black solid. As obtained by reducing MoO_3 with Zn and HClAq (*v. Formation* No. 2), Mo_2O_3 is brass-yellow and shows the same crystalline form as the MoO_3 from which it is prepared; this variety of Mo_2O_3 oxidises in air more rapidly than the black variety obtained by heating the hydrate. Heated in air, burns to MoO_2. Insol. acids.

Hydrate of molybdenum sesquioxide, $Mo_2O_3.3H_2O$. A black solid obtained as described under *Molybdenum sesquioxide, Preparation.* The moist hydrate oxidises by exposure to air. Dissolves slowly in acids to form purple solutions, which are opaque but become transparent and greyish-brown when much diluted. By evaporation, dark-grey or black, non-crystallisable, salts are obtained; these salts have not been examined at all satisfactorily; a phosphate, nitrate, borate, and several sulphates were obtained by Berzelius (*P.* 6, 331, 369).

Molybdenum dioxide, MoO_2 (*Molybdic oxide*). By strongly heating NH_4 molybdate, in a closed crucible, Bucholz obtained a dark metal-like mass which he regarded as Mo dioxide (*Scher. J.* 9, 485), but Uhrlaub (*P.* 101, 605) and Tuttle (*A.* 101, 285) showed that this substance contains N and H.

Formation.—1. By reducing MoO_3 or Hg_2MoO_4 (H. Rose, *P.* 75, 319) by heating in H (Svanberg a. Struve, *J. pr.* 44, 257; Rammelsberg, *P.* 127, 281).—2. By melting $Na_2Mo_3O_{10}$ with $\frac{1}{3}$ its weight of Zn, added in small pieces, and repeatedly washing the cold mass first with warm conc. KOHAq and then with warm HClAq; the product usually contains a little MoO_3 (Ullik, *A.* 144, 227).—3. By strongly heating $Na_2Mo_3O_{10}$ in H, and removing Na_2MoO_4 produced by very dilute KOHAq (S. a. S., *l.c.*) (? $Na_2Mo_3O_{10} + 2H_2 = Na_2MoO_4 + 2H_2O + 2MoO_2$).

Preparation.—A mixture of 1 part MoO_3, 1 part K_2CO_3, and $\frac{1}{2}$ part H_3BO_3, is very strongly heated in a Pt crucible; the crystals of MoO_2 found in the mass on cooling are washed with H_2O, then with dilute NH_3Aq, and then with dilute HClAq (Mauro a. Panebianco, *G.* 11, 501; *cf.* Muthmann, *A.* 238, 108).

Properties and Reactions.—A dark-brown powder, appearing somewhat purple in direct sunlight. Obtained by fusing MoO_3 with K_2CO_3 and H_3BO_3 (*v. Preparation*), MoO_2 forms copper-red to greyish, metal-like, very lustrous prisms; S.G. 6·44 at 10° (M. a. P., *l.c.*). Unacted on by alkali solution, HClAq or HFAq; oxidised to MoO_3 by HNO_3Aq, or by heating in air; heated in Cl forms MoO_2Cl_2. Slightly soluble in conc. H_2SO_4, and cream of tartar solution.

Hydrate of molybdenum dioxide, $MoO_2.xH_2O$. Obtained by adding NH_3Aq to solution of $MoCl_5$, washing the pp. with NH_4ClAq, then with alcohol, pressing between paper, and drying *in vacuo* over H_2SO_4. The solution of $MoCl_5$ may be prepared by digesting a conc. solution of MoO_3 in HClAq with powdered Mo or with Cu (in absence of air) till all is dissolved (Rammelsberg, *P.* 127, 281; *cf.* Hirzel, *J.* 1850. 309).

$MoO_2.xH_2O$ is reddish-brown to nearly black; it closely resembles $Fe_2O_3.3H_2O$. Slightly soluble in water, forming a reddish-yellow liquid, which reddens litmus, and from which salts (*e.g.* NH_4Cl) reppt. the hydrate. This solution gela-

latinises after long standing, and dries to a brown-black, insoluble, hydrate (Berzelius, *Lehrbuch*). Moist $MoO_2.xH_2O$ oxidises superficially in air, forming the blue oxide. Heated *in vacuo* MoO_2 is produced. $MoO_2.xH_2O$ is insoluble in caustic alkali solution, but dissolves in alkaline carbonates and bicarbonates; these solutions reppt. the hydrate on boiling, by standing in air molybdates are formed (Berzelius).

$MoO_2.xH_2O$ dissolves in acids to form salts. These salts are generally purple-red to black; only a few are crystallisable; their solutions oxidise in air; alkalis ppt. $MoO_2.xH_2O$ from these solutions. The same salts may be prepared by digesting MoO_3 and Mo with acids till the colour is reddish-brown. Berzelius (*P.* 4, 153; 6, 331, 369; 7, 261) prepared some of the salts of MoO_2, but they have not been examined satisfactorily. By mixing MoO_2 in HClAq with NH_4 molybdate, Rammelsberg obtained a crystalline salt $(NH_4)_2O.2MoO_2.4MoO_3.9H_2O$ (*P.* 127, 281).

Molybdenum trioxide, MoO_3 (*Molybdic anhydride*). This oxide was obtained by Scheele in 1778 soon after he had distinguished native Mo sulphide from galena.

Occurrence.—As *molybdenum ochre* in small quantities in a few localities.

Formation.—1. By heating Mo, or any of the lower oxides, for some time in air.—2. By prolonged heating of the lower oxides in steam (Regnault, *A. Ch.* 62, 356).—3. By roasting MoS_2 in air, or oxidising it by HNO_3Aq (*v. Molybdenum, Preparation*, p. 421).—4. From NH_4 molybdate, by evaporating with excess of HNO_3 and washing the residue with water (Brunner, *D. P. J.* 150, 372); also by heating in thin layers spread out in a flat porcelain dish (Ullik, *A.* 144, 205).

Preparation.—Impure MoO_3 is dissolved in NH_3Aq, H_3PO_4 is removed by ppn. with $MgCl_2Aq$, the filtrate is evaporated, the crystals of NH_4 molybdate which separate are heated with excess of HNO_3Aq, and the residual MoO_3 is washed with water. (For details as to preparation of MoO_3 from Mo ores *v.* Molybdenum, *Preparation*, p. 421.)

Properties.—A white, light, porous, solid; when thrown into water it separates into small, thin, lustrous, scales. S.G. 4·39 at 21° (Schafarik, *J. pr.* 90, 12). Strongly heated in an open vessel, sublimes in colourless, transparent, rhombic needles (Nordenskjöld, *P.* 112, 160). Melts at red heat. Soluble in 500 parts cold water (Bucholz, *Scher. J.* 9, 485), in 960 parts hot water (Hatchett, *T.* 1795. 323). The solution reddens litmus, tastes metallic (Wittstein, *J.* 1860. 159; Müller, *J. pr.* 80, 119). Soluble in acids; but scarcely soluble after being strongly heated. Dissolves in alkali, alkaline carbonate, and cream of tartar solutions.

Reactions.—1. By heating in *hydrogen* MoO_3 is reduced to MoO_2, Mo_2O_3, or Mo, according to the temperature employed.—2. Reduced to Mo by treating with *potassium* or *sodium*.—3. Reduced to Mo_2O_3 by digesting with *hydrochloric acid and zinc* or *copper*, &c.; also by *potassium-amalgam*.—4. Reduced to the blue oxide (*v.* p. 433) by *a little hydrogen sulphide* (excess of H_2S produces black Mo sulphide), also by *solution of sulphur dioxide, hydrogen iodide solution, boiling hydrochloric acid, nitric oxide*, or *stannous chloride*.—5. Heated with *ammonia*, compounds of Mo with N, and with N and H, are produced (*v. Molybdenum, nitride of*, p. 430).—6. Heated with *sulphur*, MoS_2 is produced.—7. Oxychlorides, along with molybdates, oxybromides, or oxyfluorides are formed by heating MoO_3 with *metallic chlorides, bromides*, or *fluorides* (Schulze, *J. pr.* [2] 21, 440).—8. Various reduction products result by heating with *potassium iodide* (Schulze, *l.c.*).—9. *Hydrogen chloride* produces $MoO_3.2HCl$ ($=MoO(OH)_2Cl_2$; *v. Chloromolybdic acid*, p. 423).—10. *Hydrofluoric acid* probably produces MoO_2F_2 (*v. Molybdenum, oxyfluoride of*, p. 423).—11. Dissolves in fairly conc. *sulphuric acid*; on evaporation, crystals of $MoO_3.SO_3$ separate (*v. infra, Combinations*, No. 3). Hot dilute H_2SO_4Aq, saturated with MoO_3, gelatinises on cooling.—12. Reacts with *alkalis* to form molybdates, R_2MoO_4, &c. (*v.* p. 423).—13. Oxychloride, MoO_2Cl_2, is formed by heating in *chlorine* (H. Rose, *P.* 75, 319).—14. Oxychlorides are produced by heating with *phosphorus tri-* or *penta-chloride* (Michaelis, *J.* 1871. 249; Schiff, *A.* 102, 116).

Combinations.—1. With *water* to form various acidic hydrates (*v. Molybdic acids*, p. 423; also *infra, Hydrates of molybdenum trioxide*).—2. With *hydrogen chloride* to form $MoO_3.2HCl$. This compound is produced as a white, loose, sublimate, by heating MoO_3 in HCl to 150°–200°; it is easily soluble in water, and can be sublimed unchanged in HCl (Debray, *C. R.* 46, 1101). This compound may be regarded as an acid and called *chloromolybdic acid*; $MoO(OH)_2Cl_2$ (*v.* p. 423).—3. With *sulphur trioxide* to form $MoO_3.SO_3$, and with SO_3 and H_2O to form $MoO_3.3SO_3.2H_2O$. $MoO_3.SO_3$ was obtained by Schultz-Sellac (*B.* 4, 14) by evaporating a solution of MoO_3 in fairly conc. H_2SO_4; it forms lustrous, transparent, deliquescent crystals, which lose SO_3 when heated. $MoO_3.3SO_3.2H_2O$ was obtained by Anderson (*J. B.* 22, 161) by adding excess of H_2SO_4Aq to $BaMoO_4$, filtering, and evaporating.—4. Combines with the *oxides of phosphorus, arsenic, antimony, vanadium, and silicon*, in presence of basic oxides, to form salts of complex acids; *v. Antimono-*, &c., *molybdates*, pp. 425 *et seq.*—5. With *ammonium fluoride* to form $MoO_3.2NH_4F$ (? NH_4 salt of $MoO(OH)_2F_2$); obtained in lustrous, light yellow, octahedral crystals, by adding NH_3Aq to an aqueous solution of $MoO_2F_2.3NH_4F$ (this salt is obtained by evaporating a solution of NH_4 molybdate in excess of NH_4FAq acidified by HFAq) (Mauro, *Mem. R. Acad. dei Lincei*, [4] 4, 481).

Hydrates of molybdenum trioxide. Six compounds $xMoO_3.yH_2O$ have been isolated. Four of these have been described under *Molybdic acids* (p. 423); the remaining two are described here.

Monomolybdic dihydrate, $MoO_3.2H_2O$. A yellow, crystalline, solid. Slowly separates from a solution of 15 grs. ordinary NH_4 molybdate in 1000 c.c. water mixed with 1000 c.c. HNO_3Aq S.G. 1·16; may be washed with cold water; sol. in water and acids; solution reddens litmus and turns turmeric brown; conc. HNO_3Aq separates MoO_3 (Millingk, *Gm.-K.* 2 [2], 170).

Octomolybdic monohydrate, $8MoO_3.H_2O$. Obtained by ppg. solution of or-

dinary NH_4 molybdate by $BaCl_2Aq$, decomposing the Ba salt by exactly the equivalent quantity of dilute boiling H_2SO_4Aq, filtering, evaporating over H_2SO_4, and drying at 160°–170° (Ullik, *A.* 144, 329; 153, 373). Soluble in water.

OXIDES OF MOLYBDENUM OTHER THAN THE DI-, SESQUI- AND TRI- OXIDE. Several oxides appear to exist intermediate between MoO_2 and MoO_3; their compositions are not yet settled. Some of them form hydrates of which some are soluble and some insoluble in water. The substance known as 'blue oxide of molybdenum,' formed by the action of reducing agents on acid solutions of MoO_3, is probably Mo_3O_8.

References.—Mo_5O_{14}; by heating lower oxides in air (Berzelius, *P.* 6, 331, 369). Mo_2O_5; by heating $(NH_4)_2O.2MoO_2.4MoO_3.9H_2O$ (Rammelsberg, *P.* 127, 281). Mo_3O_8; by heating NH_4 molybdate with MoO_3 (Berlin, *J. pr.* 49, 447; Uhrlaub, *P.* 101, 605); also by electrolysis of molten MoO_3 (Wöhler a. Baff, *A.* 110, 275). Mo_4O_{11}; by heating MoO_3 with KI (Schulze, *J. pr.* [2] 21, 440). $Mo_2O_5.3H_2O$; by adding NH_4 molybdate or MoO_3, to MoO_2 in HClAq (Berzelius, Rammelsberg, *l.c.*). Regarding properties of the blue products obtained by reducing acid solutions of MoO_3, *v.* Schiff, *A.* 120,47; Maschke, *Fr.* 12, 384; Berzelius, *Gm.-K.* 2 [2], 164; O. von der Pfordten, *B.* 15, 1925. Fairley (*C. J.* 31, 142) obtained indications of an oxide of Mo with more O than MoO_3, by adding H_2O_2Aq to MoO_3 dissolved in excess of alkali solution.

Molybdenum, oxybromide of. MoO_2Br_2. Obtained by passing Br vapour over heated MoO_2; by melting MoO_3 with H_3BO_3, powdering, and then heating with KBr; by the reaction of MoO_3 on many metallic bromides (Schulze, *J. pr.* [2] 21, 442). Yellow crystals; may be sublimed; deliquescent and soluble in water. The compound $Mo_3Br_4(OH)_2.8H_2O$ may be represented as an oxybromide $Mo_3OBr_4.9H_2O$, but is better regarded as hydrated *bromohydroxide* (*q. v.*, p. 428).

Molybdenum, oxychlorides of. Many oxychlorides of Mo exist. They are produced by the reaction of Mo oxides with Cl, Mo chlorides with O, and PCl_5 and metallic chlorides with MoO_3.

I. *Green oxychloride.* $Mo_9O_8Cl_{32}$, more probably $MoOCl_4$ (Blomstrand, *J. pr.* 71, 459; Püttbach, *A.* 201, 123). By heating a mixture of Mo and MoO_2 in air-free Cl; and in many other ways. Melts and sublimes below 100°. Soluble in water. Reduced by H at high temperatures; Püttbach (*l.c.*) describes $Mo_3O_3Cl_7$ as a product of this reduction.

II. *Yellow-white oxychloride.* MoO_2Cl_2. By passing Cl over heated MoO_2, or MoO_3 (H. Rose, *P.* 75, 319); by heating Mo chlorides in presence of O (Blomstrand, *l.c.*); and in many other ways (*v.* Schulze, *J. pr.* [2] 21, 441; Michaelis, *J.* 1871. 249; Schiff, *A.* 102, 216; Püttbach, *l.c.*). Melts at a high temperature when heated under pressure; at ordinary pressure sublimes without melting; soluble in water and alcohol.

III. *Violet oxychloride.* $Mo_2O_3Cl_6$; perhaps $MoOCl_3$ (Blomstrand, *l.c.*). Produced along with the green oxychloride, than which it is much less easily volatilised. Dark violet-red crystals; deliquescent.

IV. *Brown oxychloride.* $Mo_2O_3Cl_5$ (Blomstrand, *l.c.*). Produced, along with MoO_2Cl_2, by heating Mo_2O_3 in dry Cl; purified by sublimation in H. Forms large dark-brown crystals; melts easily; deliquescent and soluble in water. Püttbach (*l.c.*) describes a brown oxychloride, $Mo_2O_3Cl_4$, obtained in the preparation of $MoOCl_4$; also a red oxychloride, $Mo_3O_5Cl_8$, obtained by heating the violet compound in CO_2.

The compound $Mo_3Cl_4(OH)_2.2H_2O$ may be represented as an oxychloride, $Mo_3OCl_4.3H_2O$, but its reactions are more those of *chlorohydroxide* (*q. v.*). $MoO_3.2HCl$, which might be represented as $MoO_2Cl_2.H_2O$, is described as *chloromolybdic acid* (*q.v.*).

Molybdenum, oxyfluoride of. MoO_2F_2. Produced by heating MoO_3 with metallic fluorides, as a blue-white amorphous sublimate (Schulze, *J. pr.* [2] 21, 442). A number of compounds are known which may be regarded as double compounds of MoO_2F_2 with alkali fluorides; others may be regarded as double compounds of $MoOF_3$ with alkali fluorides; these are described as *fluomolybdates* (p. 425).

Molybdenum, phosphide of. Mo_3P_2. A grey crystalline powder; S.G. 6·17; oxidised by heating in air; with conc. HNO_3Aq forms H_3PO_4 and MoO_3; heated in Cl forms $MoCl_5$ and PCl_5; reduces Cu solutions with ppn. of Cu. Produced by heating a mixture of 1 pt. MoO_3 with 2 pts. glacial phosphoric acid to a high temperature for some time, and washing with HClAq and then with NaOHAq (Wöhler a. Rautenberg, *A.* 109, 374).

Molybdenum, salts of. Little is known with certainty of the salts obtained by replacing H of oxyacids by Mo. MoO_2 and Mo_2O_3 dissolve in acids to form salts, but accurate analyses and description of those salts are lacking (*v. Molybdenum dioxide* and *sesquioxide*, p. 431). MoO_3 combines with SO_3 to form $MoO.SO_3$ and with HCl to form $MoO_3.2HCl$, but those compounds are probably rather acids than salts (*v. Molybdenum trioxide*, p. 432). The radicles Mo_3Br_4 and Mo_3Cl_4 combine with certain acidic radicles to form salts (*v. Molybdenum bromohydroxide*, and *chlorohydroxide*, pp. 428, 430).

Molybdenum, selenide of. $MoSe_3$. Obtained, but not free from a greyish-blue substance which is produced along with it, by saturating acid NH_4 molybdate with H_2Se gas (Uelsmann, *A.* 116, 125).

Molybdenum, sulphides of. Three are known; MoS_2, MoS_3, and MoS_4. As none has been gasified the molecular weight of none is known with certainty. MoS_3 and MoS_4, and probably also MoS_2, are all acidic towards the alkali sulphides.

MOLYBDENUM DISULPHIDE, MoS_2. Occurs native, as *molybdenite*; S.G. 4·138 to 4·569. Prepared by heating to redness a mixture of 1 pt. MoO_3 and 2 pts. S, in a crucible, till excess of S is burnt off, and washing the residue with warm water as long as the washings are coloured (Svanberg a. Struve, *J. pr.* 44, 261). According to Carnot (*Bl.* [2] 32, 164) compounds of Mo generally yield MoS_2 when heated in a stream of dry H_2S. A black, lustrous powder; insol. water; sol. conc. H_2SO_4, with evolution of SO_2, and production of a blue liquid. Forms MoO_3 when roasted in air, or heated with conc.

HNO_3Aq; readily attacked by Cl, more slowly by Br; not acted on by aqueous alkali but after fusion with alkali dissolves in water (? with formation of a thio- salt). Slowly reacts with steam at high temperatures (Regnault, *A. Ch.* 62, 385). Reduced to Mo by strongly heating in H (O. von der Pfordten, *B.* 17, 731).

Molybdenum trisulphide, MoS_3. (*Thiomolybdic anhydride.*) Obtained by passing H_2S into solution of a molybdate until decomposition is complete, *i.e.* till all molybdate is changed to a thiomolybdate, adding dilute HClAq in slight excess, warming gently (Atterberg, *J.* 1873. 258), washing, and drying at a moderate temperature. A black powder; red-brown when moist. Goes to MoS_2 when heated. E. sol. alkali sulphide solutions; slowly dissolved by alkali or alkali hydrosulphide solution; the solutions thus obtained contain *thiomolybdates*, $M^I_2MoS_4$ (*v.* Thiomolybdic acids and their salts, *infra*). MoS_3 is reduced to Mo by heating in H (O. von der Pfordten, *B.* 17, 731).

Molybdenum tetrasulphide, MoS_4. Prepared by fusing a mixture of 2 pts. MoO_3 and 1 pt. K_2CO_3, powdering, boiling with water, filtering, diluting, saturating with H_2S, washing the pp. with cold and then with hot water, then treating with HClAq, and heating the chocolate-brown powder thus obtained to 140° in a stream of H_2S (Krüss, *B.* 16, 2044). Also obtained by heating MoS_3 to 100° in H_2S (K., *l.c.*). Also by boiling MoS_3 with K_2MoS_4Aq, washing the pp. of MoS_2 and K_2MoS_5 with cold water, dissolving in boiling water, and adding acid to this solution (Berzelius). MoS_4 is a cinnamon-brown powder; partially oxidised in moist air. With basic sulphides forms *perthiomolybdates* $M^I_2MoS_5$ (*v.* Thiomolybdic acids and their salts, *infra*).

Molybdenum, sulpho-acids of; *v. Molybdenum, thio-acids of, and their salts.*

Molybdenum, thio- acids of, and their salts. A number of molybdates are known in which O is partly or wholly replaced by S. These salts may be divided into two classes; those containing both O and S, these may be called *oxy-thiomolybdates*; and those containing only S, these may be called *thiomolybdates*. The latter salts are classed as thiomolybdates, derived from MoS_3; and perthiomolybdates, derived from MoS_4. The only thio- acid of Mo which has been isolated with certainty is H_2MoS_5.

Perthiomolybdic acid, H_2MoS_5. A red pp. obtained by adding a weak acid to K_2MoS_5 (which separates during the preparation of MoS_4), washing with cold water, and drying over H_2SO_4 (Krüss, *A.* 225, 1). Insol. water, alcohol, and ether. Sol. warm NaOHAq; not acted on by NH_3Aq; evolves H_2S slowly when boiled with conc. HClAq.

Oxy-monothiomolybdates, $M^I_2MoO_3S$. The Na salt is prepared by melting pure MoO_3 with dry Na_2CO_3 till CO_2 is all expelled, powdering the $Na_2Mo_3O_{10}$ thus obtained, dissolving in freshly-prepared NaHSAq, withdrawing the reddish heavy oil which separates, washing the crystals which are formed by allowing this oil to stand, with alcohol, ether, CS_2, and then again with alcohol and ether, and drying over H_2SO_4 (Krüss, *A.* 225, 1). A hygroscopic salt; sol. water.

Oxy-dithiomolybdates, $M^I_2MoO_2S_2$. The NH_4 salt is prepared, as golden-yellow needles, by passing H_2S into NH_4 molybdate dissolved in NH_3Aq, at c. 0° (Krüss, *l.c.*). The K salt is also described by Krüss (*l.c.*).

Oxy-pyrodithiomolybdates, $M^I_2Mo_2O_4S_3$ ($=2M_2MoO_2S_2-M_2S$). The salts of this series at present known are acid salts. The NH_4 salt, $NH_4HMo_2O_4S_3$, is prepared, as a reddish-yellow pp., by adding NH_4HS drop by drop to NH_4 molybdate at c. 90°, filtering after addition of NH_4Cl, washing with alcohol, and drying over H_2SO_4. Corresponding K and Na salts are described by Krüss (*l.c.*).

Tetrabasic dioxy-dithiomolybdates. The salt $K_2O.3K_2S.2MoO_3.2MoS_3$ ($=K_8Mo_4S_9O_7$) was obtained by Krüss (*l.c.*) by adding alcohol to a solution of $K_2Mo_3O_{10}$, repeatedly shaking the oil which forms with alcohol, separating the black flaky crystals from the yellow crystals and the brownish-red powder, all of which are produced on standing, washing and drying.

Thiomolybdates, $M^I_2MoS_4$. These salts are derived from the hypothetical thiomolybdic acid H_2MoS_4, of which acid MoS_3 is the anhydride. The soluble thiomolybdates are obtained by directly combining MoS_3 with basic sulphides, also by passing H_2S into conc. solutions of the corresponding molybdates; the insoluble thiomolybdates are obtained by ppg. salt-solutions by soluble thiomolybdates. The soluble thiomolybdates may generally be crystallised; the crystals show fluorescence, green in reflected, red in transmitted, light. Solutions of these salts are red. The thiomolybdates as a class are decomposed by heat, giving a mixture of sulphide of the basic metal and MoS_2; the K salt is only partly decomposed at white heat. Conc. solutions are stable in presence of excess of MoS_3; when diluted, and especially in presence of free alkali, the solutions become turbid with formation of thiosulphates and thiomolybdates richer in S than the original salts. Boiled in absence of air, the solutions evolve H_2S and form MoS_2 and perthiomolybdates, $M^I_2MoS_5$ (Berzelius, *P.* 7, 261; Krüss, *A.* 225, 1; *cf.* Bodenstab, *J. pr.* 78, 186).

Potassium thiomolybdate, K_2MoS_4. Prepared by gradually heating, finally to a high temperature, a mixture of equal parts K_2CO_3 and S, with a little C, and a large excess of MoS_2, dissolving in water, filtering, and crystallising (Hirzel, *J.* 1850. 319). Krüss (*l.c.*) obtained this salt by dissolving 5 g. K_2MoO_4 in 16 c.c. water, adding 50 c.c. KOHAq, S.G. 1·46, and saturating with H_2S. Red, rhombic, crystals, with greenish fluorescence. Sol. water; acetic acid ppts. $K_2Mo_2S_7$.

The other thiomolybdates which have been examined, more or less fully, are the salts of NH_4, Ba, Cd, Ca, Ce, Cr, Co, Cu, Au, Fe, Li, Mg, Mn, Hg, Ag, Na, Sr, Sn, U, and Zn.

Perthiomolybdates, $M^I_2MoS_5$. The soluble salts of this class are formed by boiling thiomolybdates M_2MoS_4 with MoS_3; the insoluble salts by ppg. salt-solutions by soluble perthiomolybdates. The perthiomolybdates are generally dark red; solutions of the alkali salts give

a pp. of MoS_4 on addition of acids (Berzelius, *P.* 7, 261).

Potassium perthiomolybdate, K_2MoS_5. Prepared by saturating an acid K molybdate solution with H_2S (a mixture of K_2MoS_4 and MoS_3 is thus produced), boiling for some hours in a retort, cooling, collecting the pp. of K_2MoS_5 mixed with MoS_2, washing with water till the washings give a flocculent dark-red pp. on addition of HClAq, extracting with boiling water, and evaporating the solution. Also by heating dilute K_2MoS_4Aq with excess of MoS_3 nearly to 100° till the liquid is nearly dry. Also by reacting on MoS_4 with KHSAq. A red mass, resembling an extract; on one occasion Berzelius obtained ruby-red crystalline granules. Insol. cold water, sol. hot water. Scarcely acted on by cold HClAq or KOHAq.

The other perthiomolybdates examined, more or less fully, are the salts of NH_4, Ba, Bi, Ca, Au, Fe, Hg, Ag, Na, Sr, and Sn.

Tribasic dithiomolybdates. Krüss (*A.*225, 1) obtained the salt $K_6Mo_2S_9$ ($=3K_2S.2MoS_3 = K_2MoS_4.MoS_3.2K_2S$) by passing H_2S into K_2MoO_4Aq containing KOHAq, S.G. > 1·46 (*cf. Potassium thiomolybdate, supra*). Small reddish-orange rhombic crystals; sol. water, insol. alcohol and ether. Decomposes slowly in air, giving K_2MoS_4. M. M. P. M.

MONARDA OIL. The essential oil of *Monarda punctata*, which smells like thyme, contains thymol $C_{10}H_{14}O$ [48°] and a terpene (Arppe, *A.* 58, 41).

MONO-. This prefix is very seldom used in this dictionary. Compounds whose names begin with mono- are described under the name to which mono- has been prefixed.

MORIN or **MORIC ACID** $C_{13}H_8O_6$ aq (B. a. H.); $C_{15}H_{10}O_7$ aq (from alcohol); $C_{15}H_{10}O_7$ 2aq (from water) (L.). S. ·025 at 20°; ·094 at 100°. Occurs in old fustic (*Morus tinctoria*) to which it imparts its dyeing properties (Wagner, *J. pr.* 51, 82; Hlasiwetz a. Pfaundler, *J. pr.* 90, 445; 94, 65; *A.* 127, 352; Löwe, *Z.* 1875, 117; *Fr.* 14, 119; Benedikt a. Hazura, *M.* 5, 165, 667).

Preparation.—1. Deposited as calcium salt from an infusion of the wood on cooling. This deposit is extracted with alcohol, water is added to the alcoholic extract when calcium morate is ppd. while maclurin remains in solution. The calcium salt is then decomposed by oxalic acid (Wagner).—2. The deposit is washed, heated with very dilute HClAq, freed from $CaCl_2$ by washing, and repeatedly dissolved in alcohol and ppd. by water (H. a. P.; B. a. H.).

Properties.—Needles, v. sl. sol. water, v. sol. alcohol, m. sol. ether, insol. CS_2. The solutions are deep yellow. Blackens at 300°. Conc. H_2SO_4 dissolves it, without change, forming a brownish-yellow solution. Its alkaline solutions are deep yellow. Its solution does not ppt. gelatin. It stains the skin yellow. $FeCl_3$ colours the alcoholic solution deep olive-green. It reduces Fehling's solution on warming and ammoniacal $AgNO_3$ in the cold. Its alcoholic solution exhibits green fluorescence on the addition of an aluminium salt (Goppelsröder, *J. pr.* 101, 406; 104, 10; *Z.* [2] 4, 154, 607). Morin yields resorcin on dry distillation.

Reactions.—1. *Sodium-amalgam* turns the alkaline solution indigo blue and finally yellow, the solution then containing phloroglucin.—2. *Potash-fusion* yields phloroglucin and resorcin. 3. *Nitric acid* in HOAc oxidises it to (4, 2, 1)-di-oxy-benzoic acid.—4. *Bromine* added to its alcoholic solution forms ethyl-tetra-bromo-morin $C_{15}H_5EtBr_4O_7$ 4aq which is ppd. on adding water and melts at 135°. Tin and HCl convert this ether into tetra-bromo-morin $C_{15}H_6Br_4O_7$ $2\frac{1}{2}$aq which becomes anhydrous at 110° and then melts at 258°. It dyes silk and wool yellow without a mordant.

Salts.—$KC_{12}H_9O_6$: yellow needles (from K_2CO_3Aq).—$Ca(C_{12}H_9O_6)_2$: yellow precipitate $Ba(C_{12}H_9O_6)_2$: red-brown powder.—$Zn(C_{12}H_9O_6)_2$: lemon-yellow needles, insol. water, sol. alkalis.—$PbC_{15}H_{12}O_9$: egg-yellow pp.—$Pb_2C_{15}H_{10}O_9$: (L.).

Morin sulphonic acid $C_{15}H_9O_7.SO_3H$ 2aq. Formed by heating morin with conc. H_2SO_4. Golden-brown powder, sl. sol. cold, v. sol. hot, water.—$K_2C_{15}H_8SO_{10}$ $\frac{1}{2}$aq: golden needles. —$BaC_{15}H_8SO_{10}$. Golden flocculent pp., converted by nitric acid into tri-nitro-phloroglucin.

Isomorin. Formed by adding sodium-amalgam to an alcoholic solution of morin containing HCl until the solution is deep-purple, and then evaporating (H. a. P.). Purple-red prisms. When heated alone or in alcoholic solution, or more quickly by treatment with alkalis, it is reconverted into ordinary morin. Its solution mixed with dilute alum is dichroïc.

Paramorin. $C_{12}H_8O_5$. Obtained, together with a larger quantity of resorcin, by distilling morin mixed with sand (Benedikt, *B.* 8, 606). Yellowish, woolly needles (from ether). Tasteless. May be sublimed. Reduces Fehling's solution. V. sol. hot water and ether (unlike morin). It dissolves unchanged in conc. H_2SO_4. Alkalis form a yellow solution. Unlike morin, its alcoholic solution is not ppd. by $Pb(OAc)_2$.

MORINDIN $C_{28}H_{30}O_{15}$ (A.). [245°] (Stein). Extracted by alcohol from the root of various species of *morinda* used as a dye ('Suranji') in India (Anderson, *Tr. E.* 16 [6], 435; *A.* 71, 216). Slender lustrous orange needles; when heated it gives off orange vapours which condense to red needles of morindone. It is insol. ether, v. sl. sol. cold water and alcohol, sol. aqueous KOH and conc. H_2SO_4 forming reddish-violet solutions. Gives a red lake with alum, and a cobalt-blue pp. with baryta-water. Morindin resembles ruberythric acid $C_{26}H_{28}O_{14}$ (Rochleder, *Sitz. B.* 7, 806; Stenhouse, *C. J.* 17, 333) but differs from it in being insoluble in ether and in the behaviour of the red alkaline solution on boiling, for this becomes deep purple in the case of ruberythric acid, but does not change in that of morindin (Stein, *J. pr.* 97, 234; Thorpe a. Greenall, *C. J.* 51, 52; 53, 171).

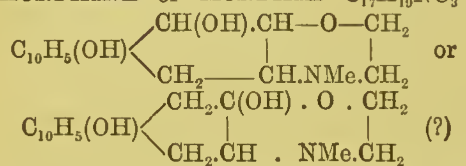
Morindone $C_{15}H_{10}O_5$. *Tri-oxy-methyl-anthraquinone* (?). Formed together with glucose by boiling morindin with dilute mineral acids. Red needles, resembling alizarin. Insol. water, v. sol. alcohol and ether. Its solution in potash is reddish-purple, but fades on standing (unlike alizarin). Conc. H_2SO_4 gives a dark-blue solution (alizarin gives an orange solution). $FeCl_3$ gives a green colour. On distillation with zinc-dust it yields methyl-anthracene.

MORINGIC ACID. An acid supposed by Walter to exist as a glyceride in oil of ben (from

Moringa aptera) but shown by Zaleski (*B.* 7, 1013) to be oleïc acid.

MORITANNIC ACID $C_{15}H_{12}O_7$ (?) If, after the aqueous extract of fustic has deposited morin, the filtrate be shaken with EtOAc, the acetic ether evaporated, and the residue dissolved in cold water and ppd. by NaCl, brown amorphous moritannic acid separates first, followed by maclurin (Löwe, *Fr.* 14, 127). V. sol. water. The solution is ppd. by albumen, gelatin, and alkaloids. $FeCl_3$ gives a brownish-black pp. Alcoholic lead acetate gives a pp. $(C_{15}H_{12}O_7)_2 5PbO$.

MORPHINE or **MORPHIA** $C_{17}H_{19}NO_3$ *i.e.*



(Knorr, *B.* 22, 1117). Mol. w. 285. [230°] (Hesse, *Ph.* [3] 18, 801). S.G. 1·32 (Schröder, *B.* 13, 1074). S. ·01 at 10°; ·04 at 40°; ·22 at 100° (Chastaing, *Bl.* [2] 37, 477). S. (absolute alcohol) 1·132 at 10·6°; 8·623 at 78°. S. (alcohol of 90 p.c.) ·377 at 10·6°; 2·991 at 78°. S. (amyl alcohol) ·268 at 11°; 2·247 at 78° (Florio, *G.* 13, 496). S. (ether) ·023 at 10° (F.). S. (chloroform) ·04 at 9·4°; 1·235 at 56° (F.). S. (amyl alcohol) ·26 in the cold (Kubly, *J.* 1866, 823). The solubility of crystallised morphine in boiling liquids is given by Prescott (*Ph.* [3] 6, 404) as follows: S. (ether) ·0163; S. (chloroform) ·023; S. (amyl alcohol) 1·1; S. (benzene) ·0112. The solubility of amorphous morphine in boiling liquids is given by Prescott as S. (ether) ·0473; S. (chloroform) ·0506. The solubility of freshly ppd. morphine in boiling solutions is given by Prescott as: S. (ether) ·094; S. (chloroform) ·116; S. (amyl alcohol) 1·1; S. (benzene) ·05. According to Burg (*Fr.* 19, 222), the solubility of morphine in pure chloroform is ·01, and in a mixture of 9 pts. chloroform and 1 pt. alcohol it is ·9. $[\alpha]_D$ (in a 2 p.c. solution containing 2 mols. NaOH) $= -70·23°$ (Hesse, *A.* 176, 190). $[\alpha]_D$ (in a solution of the hydrochloride) $= -100·67° - 1·14p$, where p = percentage of salt present (Hesse; Grimbert, *J. Ph.* [5] 16, 295).

Occurs in opium, being known in an impure state as *Magisterium opii* in the seventeenth century, and was first isolated in 1816 by Sertürner (*Gilb. Ann.* 55, 61; 57, 192; 59, 50). Dott (*Pr. E.* 12, 189) found in a sample of opium that half the morphine was present as meconate and half as sulphate. It also occurs in *Eschscholtzia californica* (Baudet a. Adrian, *C. C.* 1889, 197), and in hops.

Preparation.—1. Opium is macerated with water at 38°, the extract evaporated with $CaCO_3$ to a small bulk, and then mixed with $CaCl_2$. The liquid is filtered from ppd. calcium meconate and evaporated. It first deposits calcium meconate, and afterwards a mixture of the hydrochlorides of morphine and codeïne. These crystals are dissolved in water and treated with ammonia, which ppts. morphine, leaving codeïne in solution (Robiquet a. Gregory, *A.* 5, 87; 7, 261).—2. The aqueous extract of opium is boiled with lime, and the filtrate boiled with NH_4Cl, which ppts. morphine (Mohr, *A.* 35, 120).

Properties.—Small trimetric prisms (containing aq), v. sl. sol. water, alcohol, and ether. It has a very bitter taste, and is a powerful narcotic poison. It dissolves readily to the extent of one equivalent in aqueous KOH, lime, baryta, and NaOH, but scarcely at all in ammonia and alkaline carbonates. It readily dissolves in acids. It is lævorotatory. It loses its water of crystallisation at 100° (Dott, *Ph.* [3] 18, 701), and begins to sublime at 150° in dots (Blyth).

Reactions.—1. Very readily *oxidised*, thus ·014 p.c. of the base is sufficient to liberate iodine from iodic acid (Serullas, *B. J.* 11, 238). Morphine is oxidised by alkaline K_3FeCy_6 to pseudomorphine $C_{34}H_{36}N_2O_6$ (Hesse, *A.* 235, 229), and the same substance is formed by the action of nitrous acid on morphine (Schützenberger, *A.* 108, 346; *Bl.* 4, 176), and by allowing morphine to stand in aqueous NH_3 exposed to the air (Polstorff, *B.* 13, 86). Morphine slowly reduces silver nitrate in the cold.—2. On oxidation with alkaline $KMnO_4$ it yields an acid, apparently pyridine tricarboxylic acid (Barth a. Weidel, *M.* 4, 700).—3. *Potash-fusion* yields protocatechuic acid (B. a. M.) and methylamine (Wertheim, *A.* 73, 208). Alcoholic potash at 180° forms methyl-ethyl-amine (Skraup a. Wiegmann, *M.* 10, 110).—4. *Nitrous acid* forms nitroso-morphine, pseudomorphine, and a base $C_{17}H_{21}NO_5$.—5. *Nitric acid*, diluted with ($1\frac{1}{2}$ mols. of) water, forms at 100° an acid $C_{10}H_9NO_9$, which can be converted by conc. HNO_3 into picric acid, and which yields methylamine when heated with KOH (Chastaing, *C. R.* 94, 44; *J. Ph.* [5] 4, 338).—6. Converted into codeïne by heating with NaOEt and MeI, the yield being small owing to the formation of morphine methylo-iodide (Grimaux, *A. Ch.* [5] 27, 273; Dott, *Ph.* [3] 12, 1009).—7. On distillation with *zinc-dust* it yields pyridine, NH_3, pyrrole, and a base which may be quinoline, as chief products, together with 4 p.c. of phenanthrene and $\frac{1}{2}$ p.c. of phenanthraquinoline (Gerichten a. Schrötter, *A.* 210, 396).—8. When evaporated with dilute H_2SO_4 till white fumes appear, morphine yields a residue turned brown by alkalis. Morphine (1 pt.), heated with H_2SO_4 ($1\frac{1}{2}$ pts.) and oxalic acid (2 pts.), at 120° forms a product which, on diluting with water, leaves a yellowish-white amorphous body undissolved. This substance, $C_{14}H_{17}NO_4$, is soluble in hot water and in alkalis. It turns green in air, and its alkaline solution turns red in air. The reddened alkaline solution gives with HCl a blue pp., 'morphine blue,' $C_{13}H_{11}NO_2$, which can be crystallised from ether. Malonic and succinic acids behave like oxalic acids, forming the compounds $C_{15}H_{19}NO_5$ and $C_{16}H_{21}NO_6$. All these formulæ should perhaps be doubled (Chastaing a. Barillot, *C. R.* 105, 941, 1012).—9. Heating with *oxalic acid* forms trimorphine.—10. Heating with conc. HCl yields apomorphine (Matthiessen a. Wright, *Pr.* 17, 455, 460), and the bases $C_{34}H_{39}ClN_2O_6$, $C_{34}H_{37}ClN_2O_5$, $C_{34}H_{36}ClN_2O_4$, and $C_{136}H_{151}Cl_2N_8O_{24}$.—11. With $Cl.CH_2.OAc$ and H_2SO_4 it gives an intense violet colour, and after dilution with water and addition of NH_3, an amorphous yellow base, possibly $CH_2(C_{17}H_{18}NO_3)_2$, which gives a violet colour with H_2SO_4 (Grimaux, *C. R.* 93, 217).—12. Aqueous *alloxan* and SO_2 form $C_4H_2N_2O_4C_{17}H_{19}NO_3H_2SO_3$ (Pellizzari, *A.* 248, 151).—13. *Bleaching-powder*, acting on a solution

of morphine hydrochloride, forms $C_{17}H_{16}Cl_3NO_{10}$, a crystalline body (Mayer, *B.* 4, 121).

Colour-tests.—1. Liberates iodine from iodic acid solution. The brown colour is increased by adding ammonia (Lefert, *J. Ph.* [3] 40, 97). If a layer of very dilute ammonia be poured upon a very dilute solution of morphine containing iodic acid and starch, a brown ring below a blue ring will appear at the junction of the liquids (Dupré, *C. N.* 8, 267).—2. *Chloride of gold* colours the solution blue, being reduced to gold.—3. $KMnO_4$ is reduced, becoming green.—4. *Ferric salts* give a blue colour, destroyed by acids, by heat, and by alcohol (Robinet a. Pelletier, *A.* 5, 172).—5. $FeCl_3$, added to a previously heated solution of morphia in H_2SO_4, gives a deep-red colour, changing to dirty green (Husemann, *A.* 128, 305). According to Lindo (*C. N.* 37, 158), morphine, gently warmed with H_2SO_4 and $FeCl_3$, gives an indigo-blue colour.—6. A solution of *molybdic acid* in conc. H_2SO_4 gives, with solid morphine, a violet colour, changing through blue to dirty green (Fröhde, *Fr.* 5, 214).—7. A solution obtained by adding ammonia to cupric sulphate till the pp. cupric hydrate is just redissolved is coloured green by salts of morphine (Nadier, *Fr.* 13, 235; Lindo, *Fr.* 19, 359).—8. Nitric acid gives an orange-red colour, gradually changing to yellow.—9. H_2SO_4, containing a little nitric acid, gives a violet-red solution (Erdmann, *A.* 120, 188; Husemann, *A.* 128, 305).—10. When morphine is boiled with aqueous phosphorous or hypophosphorous acid, and conc. H_2SO_4 is added, the liquid becomes reddish-violet. On now adding a little nitric acid the solution becomes yellowish, and on warming with copper it assumes a splendid blue colour (Dragendorff, *J.* 1864, 727).—11. $KClO_4$ (free from chlorate), added to morphine mixed with H_2SO_4, gives a dark-brown colour (Grove, *Fr.* 13, 324; Siebold, *ibid.*).—12. Conc. H_2SO_4, followed by water and some oxidising agent (iodic acid, K_3FeCy_6, $K_2Cr_2O_7$, KNO_3, MnO_2, or PbO_2), best in the solid state, gives a deep-red colour on gentle warming (Lindo, *C. N.* 36, 228; Dott, *C. N.* 36, 255).—13. A mixture of K_3FeCy_6, ferric chloride, and HCl is coloured blue. This reagent may be used to detect morphine in quinine salts (Kieffer, *A.* 103, 271; Hager, *Fr.* 12, 220; Armitage, *Ph.* 18, 761). According to Hesse (*Ph.* 18, 801), the blue colour is due to pseudomorphine, not to Prussian blue.—14. Chlorine-water and ammonia give a red colour in a 1 p.c. solution (Flückiger, *Ar. Ph.* [3] 1, 117).—15. Aqueous $K_2Cr_2O_7$ gives a dirty-brown pp. (Plugge, *Ar. Ph.* [3] 25, 793).—16. Conc. H_2SO_4, containing a little K_3AsO_4, gives on warming a blue-violet colour, changing to dark brown-red. Water turns this green, and chloroform on shaking with it becomes violet, while ether becomes violet-red, the liquid below it being brown (Tattersall, *C. N.* 41, 63; Donath, *J. pr.* [2] 33, 563).—17. H_2SO_4 and a little $KClO_3$ gives in the cold a grass-green colour, the edge of the liquid being pale-rose colour (Vitali, *B.* 14, 1583).—18. A mixture of morphine (1 pt.) and powdered sugar (7 pts.) turns purple on addition of a drop of H_2SO_4, the mass gradually changing in colour through bluish-green to yellow (Schneider, *J.* 1872, 747).—19. If morphine is heated with H_2SO_4 at 200°, and the mass poured into water, the liquid becomes blue. If chloroform be shaken with this liquid it acquires a blue colour, while if ether be used the ethereal layer becomes purple (Jorisson, *Fr.* 20, 422).—20. On warming morphine with H_2SO_4 and sodium phosphate a violet colour appears (Vulpius, *Ar. Ph.* [3] 25, 256).

Estimation in Opium.—Opium (200 pts.) is exhausted with warm water and the extract evaporated to a thin syrup, mixed with alcohol (40 pts. of S.G. ·82), ether (380 pts.), and ammonia (45 pts. of S.G. ·935). The mixture is occasionally shaken, and after 18 hours it is filtered and washed with alcohol-ether. The pp. is dried, digested with benzene, dried, and weighed. After weighing the base may be titrated with standard HCl (Teschemacher a. Smith, *C. N.* 57, 93, 103, 244; Flückiger, *J.* 1885, 1962; *Ar. Ph.* [3] 27, 721; Venturini, *G.* 16, 239; Stillwell, *Am.* 8, 307; R. Williams, *C. N.* 57, 134).

Another method consists in exhausting 7 g. of opium with 110 c.c. of water and 4 g. of slaked lime. 50 c.c. of the filtrate are mixed with 5 c.c. of 95 p.c. alcohol, 25 c.c. of ether, and 3 g. of NH_4Cl. After standing for 12 hours the ether is filtered off, and another 10 c.c. of ether added. The entire liquid is then filtered and the morphine collected on the filter determined by direct weighing or by titration (Goebel, *Chem. Zeit.* 11, 508). The morphine may also be extracted from the opium by baryta-water and ppd. by CO_2 (Von Perger, *J. pr.* [2] 29, 97). Indeed, a great many processes for estimating morphine in opium have, from time to time, been proposed (Guillermond, *J. Ph.* [3] 16, 17; [4] 6, 102; Riegel, *Jahrb. pr. Pharm.* 23, 202; Guibourt, *J. Ph.* [3] 41, 97, 177; F. Mayer, *Am. J. Pharm.* 35, 28; Arnoldi, *Russ. Zeit. Pharm.* 1873, 641; Lynn, *Amer. J. Pharm.* [4] 6, 358; *C. J.* 34, 612; Flewry, *J. Ph.* [4] 6, 99; Schachtrupp, *Fr.* 7, 284, 509; Merck, *A.* 18, 79; 21, 202; 24, 46; Stein, *Ar. Ph.* [2] 148, 150; *C. J.* 25, 180; J. T. Miller, *Ph.* [3] 2, 465; *C. J.* 25, 181; Reveil, *Monit. Scient.* 13, 312; *J.* 1871, 821; Kremel, *C. C.* 1887, 1529; Adrian a. Gallois, *J. Ph.* [5] 15, 193; Schlikum, *Ar. Ph.* [3] 25, 13; Dott, *Ph.* [3] 18, 82; Plugge, *Ar. Ph.* [3] 25, 343).

Methods for separating morphine from other alkaloids have been given by Dragendorff (*Ph.* [3] 7, 24), Hager (*C. C.* 1872, 727), Neubauer (*Fr.* 9, 134), and others.

Salts.—B′HCl 3aq: S. 5 in the cold; 100 at 100° (Regnault, *A. Ch.* [2] 68, 131; *A.* 26, 24); 4 at 15° (Hesse, *A.* 179, 190). $[\alpha]_j = -94°$ in a 2 p.c. solution containing excess (10 mols.) of HCl. Silky fibres (from water).—B′HCl: S. (MeOH) 2 at 15°. Minute prisms (from MeOH). The salt B′HCl 3aq is partially rendered anhydrous by solution in alcohol (Hesse, *A.* 202, 151).—$B'_2H_2PtCl_6$: yellow curdy pp., m. sol. water (Liebig, *A.* 26, 46). Decomposed by boiling water (O. de Coninck, *Bl.* [2] 45, 131).—$B'_2H_2PtCl_6$ 6aq (Hesse).—$B'HCl(HgCl_2)_2$. Crystalline pp. (Hinterberger, *A.* 77, 201).—$B'ZnCl_2$ 2aq.—$B'ZnCl_2$ 7aq (Gräffinghoff, *Z.* 1865, 600).—B′HBr 2aq: needles (Schmidt, *B.* 10, 194).—B′HI 2aq: long silky needles grouped in rosettes; sl. sol. cold water (Schmidt, *B.* 10, 194).—B′HI 3aq (Bauer, *Ar. Ph.* [3] 5, 289).—B′HI aq: hair-like needles (Kunz, *Ar. Ph.* [3]

26, 307).—B'_2I_3: crystalline mass (B.).—$B'HI_4$: obtained by ppg. a salt of morphine with iodine dissolved in HIAq. Brown pp., sol. KIAq, from which it crystallises in nearly black prisms, sol. alcohol and boiling ether (Bauer; Jörgensen, *J. pr.* [2] 2, 437; *Z.* [2] 5, 673).—$B'HHgI_3$: crystalline pp., m. sol. alcohol (Groves, *C. J.* 11, 97). —$B'_2H_2SO_4$ 5aq: $[\alpha]_D = -100{\cdot}47 - {\cdot}96p$ in a p p.c. solution at 22·5° (Hesse). S. 4 in the cold (Dott).—$B'HClO_4$ 2aq: needles (Bödeker, *A.* 71, 63).—$B'HVO_3$ (Ditte, *A. Ch.* [6] 13, 237).—$B'HCyS\,\frac{1}{2}$aq. [100°]. Needles (Dollfus, *A.* 65, 214).—$B'_2H_2PtCy_4$: groups of minute needles (Schwarzenbach, *C. C.* 1860, 304).—$^{\times}B'HOAc$. S. 50 in the cold (Dott). Tufts of needles, v. sol. water, m. sol. alcohol (Merck, *A.* 24, 48).—$B'CH_2Cl.CO_2H$ (Florio, *J.* 1883, 1343).—$B'CHCl_2.CO_2H\,\frac{1}{2}$aq. — $B'CCl_3.CO_2H\,1\frac{1}{2}$aq. — Butyrate $B'C_4H_8O_2$. S. 14 at 12° (Decharme, *J.* 1863, 444).—Valerate $B'C_5H_{10}O_2$. Large trimetric crystals (Pasteur, *A. Ch.* [3] 38, 455). S. 2·3 in the cold (Dott).—Lactate $B'C_3H_6O_3$: monoclinic crystals. S. 10 at 13° (Decharme).—Trichloro-lactate $B'C_3Cl_3H_3O_3$ 5aq (F.).—Oxalate $B'_2H_2C_2O_4$ aq: prisms. S. 4·8 at 12° (D.).—Tartrates:—$B'_2C_4H_6O_6$ 3aq. Nodular groups of needles, efflorescent at 20° (Arppe, *J. pr.* 3, 332). S. 11 in the cold (Dott).—$B'C_4H_6O_6\,\frac{1}{2}$aq. Tufts of long rectangular flattened prisms (A.).—Mellitate $B'_3C_{12}H_6O_{12}$: minute needles (Karmrodt, *A.* 81, 171). — Phenyl acetate $B'CH_2Ph.CO_2H$. [92°].—Nitroprusside (Davy, *Ph.* [3] 11, 756).

Metallic derivatives $C_{17}H_{18}KNO_3$ $2\frac{1}{2}$aq. Obtained in a crystalline state by evaporating a solution of morphine in KOHAq in a desiccator over H_2SO_4 (Chastaing, *J. Ph.* [5] 4, 19).—$(C_{17}H_{18}KNO_3)_2K_2CO_3$ 2aq.—$Ba(C_{17}H_{18}NO_3)_2$ 3aq: white crystalline solid.—$Ca(C_{17}H_{18}NO_3)_2$ 5aq.—$Ca(C_{17}H_{17}NO_3)_2$ 2aq.

(α)-*Acetyl derivative* $C_{17}H_{18}AcNO_3$. Obtained, together with the (β) modification, by boiling morphine (1 pt.) with HOAc (2 pts.) for several hours (Wright, *C. J.* 27, 1033; Beckett a. Wright, *C. J.* 28, 315). Crystallises from ether, either with aq or in the anhydrous state. Gives no colour with $FeCl_3$.—$B'HCl$ 3aq: crystals, sl. sol. cold water.—$B'_2H_2PtCl_6$: amorphous.—$B'EtI\,\frac{1}{2}$aq: crystals (from 85 p.c. alcohol).

(β)-*Acetyl derivative* $C_{17}H_{18}AcNO_3$. The chief product obtained by heating morphine (1 mol.) with acetic anhydride (1 mol.) at 100°. When less acetic anhydride is used a compound $(C_{17}H_{18}AcNO_3)(C_{17}H_{19}NO_3)$ is obtained (Wright). Amorphous.—$B'HCl$: amorphous, v. sol. water. Readily converted into morphine by boiling water, and hence usually gives a blue colour with $FeCl_3$.—$B'EtI$: amorphous.

(γ)-*Acetyl derivative* $C_{17}H_{18}AcNO_3$. Accompanies the (β)-isomeride to the extent of 25 p.c. Anhydrous crystals (from ether).—$^{\times}B'HCl$: crystallises with difficulty, v. sol. water.—$B'EtI\,1\frac{1}{2}$aq: crystals (from 85 p.c. alcohol).

Di-acetyl derivative $C_{17}H_{17}Ac_2NO_3$. [169°]. Formed by heating morphine with excess of Ac_2O at 85° (Wright; Hesse, *A.* 222, 205). The product is treated with water and dilute NH_3Aq, and extracted with ether. Colourless prisms (from ether); v. sol. cold alcohol, m. sol. ether. Gives no colour with $FeCl_3$. Converted by boiling water first into the (α)-acetyl derivative, and then into morphine.—$B'HCl$: crystals, extremely sol. water. — $B'_2H_2PtCl_6$. — $B'MeCl$. Formed by heating morphine methylo-chloride with Ac_2O at 85° (Hesse). Needles, v. e. sol. water.—$B'MeI$. Heated with AgOAc it yields the crystalline di-acetyl derivative of a compound $C_{14}H_{10}O_2$ [143°] (Fischer, *B.* 19, 792).—$B'EtI\,\frac{1}{2}$aq. Crystals (B. a. W.).

Di-propionyl derivative $C_{17}H_{17}(C_3H_5O)_2NO_3$. Formed by heating morphine with propionic anhydride at 85° (Hesse, *A.* 222, 207). White amorphous powder, v. e. sol. ether, alcohol, and chloroform, sl. sol. water. $FeCl_3$ gives no colouration. — $^{\times}B'HCl$. — $B'_2H_2PtCl_6$.

(α)-*Butyryl derivative* $C_{17}H_{18}(C_4H_7O)NO_3$. Formed by boiling morphine (1 pt.) with butyric acid (2 pts.) for 6 hours (Beckett a. Wright, *C. J.* 28, 16). Crystals (from ether). Gives no colour with $FeCl_3$.—$B'HCl$: more soluble and less readily crystallisable than the hydrochloride of the (α)-acetyl derivative.—$B'_2H_2PtCl_6$.—$B'EtI$: amorphous.

(β)-*Butyryl derivative* $C_{17}H_{18}(C_4H_7O)NO_3$. An amorphous base, accompanying the preceding isomeride. Gives a blue colour with $FeCl_3$.

Di-butyryl derivative $C_{25}H_{31}NO_5$ *i.e.* $C_{17}H_{17}(C_4H_7O)_2NO_3$. Formed by heating morphine (1 pt.) with butyric anhydride (2 pts.) for 3 hours at 140° (B. a. W.). Amorphous. Resolved by boiling water or boiling dilute alcohol into butyric acid and butyryl morphine.—$B'HCl$: amorphous. Gives no blue colour with $FeCl_3$.—$B'EtI$: amorphous. By boiling morphine with a mixture of acetic and butyric acids, Beckett and Wright obtained a product which formed a crystalline double salt with the formula $(C_{17}H_{18}AcNO_3)(C_{17}H_{18}(C_4H_7O)NO_3)H_2Cl_2$ 8aq, resolved into its components by boiling water.

Benzoyl derivative $C_{17}H_{18}BzNO_3$. Formed by heating morphine with benzoic acid at 160° (B. a. W.), and by boiling the di-benzoyl derivative with dilute alcohol. Amorphous.—$B'HCl$: crystalline; v. sl. sol. water. Not coloured by $FeCl_3$.

Di-benzoyl derivative $C_{17}H_{17}Bz_2NO_3$. [188°–191° cor.]. Formed from morphine and Bz_2O at 130° (B. a. W.) or BzCl at 105° (Wright a. Rennie, *C. J.* 37, 609; Dott a. Stockman, *Ph.* [3] 18, 231; *cf.* Broockmann a. Polstorff, *B.* 13, 96). Prisms, insol. water, sol. hot alcohol. Gives no colour with $FeCl_3$.—$B'HCl$: amorphous.—$B'_2H_2PtCl_6$.—$B'EtI\,\frac{1}{2}$aq: crystals.

Acetyl-benzoyl derivative $C_{17}H_{17}AcBzNO_3$. Formed from the (α)-acetyl derivative and Bz_2O at 130° (B. a. W.). Crystalline.—$B'HCl$: amorphous; v. sol. water.—$B'_2H_2PtCl_6$.—$B'EtI\,\frac{1}{2}$aq: crystals (from alcohol).

Succinoxyl derivative $(C_{17}H_{18}NO_3)CO.C_2H_4.CO_2H$. Formed by heating morphine (1 pt.) with succinic acid (2 pts.) at 180° (Beckett a. Wright, *C. J.* 28, 689). Separates from alcohol in crystals (containing 4aq); insol. water and ether.—$B'_2H_2PtCl_6$.

Methylo-iodide $C_{17}H_{19}NO_3MeI$ aq. Formed by warming morphine with MeI and alcohol (How, *C. J.* 6, 125; *A.* 88, 338). If NaOEt is also present the product is codeïne (Grimaux, *A. Ch.* [5] 27, 273; *C. R.* 92, 1140).

Methylo-chloride $C_{17}H_{19}NO_3MeCl$ 2aq.

Formed from the methylo-iodide and AgCl (Hesse, *A.* 222, 207). Long needles. Its aqueous solution is coloured blue by $FeCl_3$. Ac_2O forms $C_{17}H_{17}Ac_2NO_3MeCl$.—$(C_{17}H_{19}NO_3MeCl)_2PtCl_4$ aq.

Methylo-hydroxide $C_{17}H_{19}NO_3MeOH$ 5aq. Formed from the sulphate and baryta (Broockmann a. Polstorff, *B.* 13, 96). Colourless needles. Reduces Ag_2O.

Ethylo-iodide $C_{17}H_{19}NO_3EtI\frac{1}{2}$aq. Formed by heating morphine with EtI and alcohol at 100° (How). Needles (from water).

Methyl-morphine *v.* CODEÏNE.

Di-methyl-morphine $C_{17}H_{17}Me_2NO_3$. *Methylmorphimethine.* [118°]. $[\alpha]_D = -208{\cdot}6°$ in a 4 p.c. solution in 97 p.c. alcohol at 15°. Formed by heating codeïne methylo-iodide (1 mol.) with aqueous KOH (1 mol.), adding benzene, and shaking with acetic acid. The acid liquid is saturated with NaCl, and the hydrochloride of di-methyl-morphine then crystallises out. The free base is obtained by adding NaOH and extracting with ether (Hess, *A.* 222, 220). Prisms; m. sol. ether, v. sol. water and alcohol. Conc. H_2SO_4 gives a bluish-violet colour. Conc. HNO_3 forms a yellow solution.

Salts. — B'HCl 2aq. S. 9·2 at 18°. — $B'_2H_2PtCl_6$ aq.

Methylo-hydroxide ×$C_{17}H_{17}Me_2NO_3MeOH$. Formed from the iodide and moist Ag_2O (Knorr, *B.* 22, 181). Thick syrup. Split up at 160° into NMe_3 and the phenanthrene derivative $C_{14}H_7EtO_2$. Ac_2O at 160°–200° forms acetyl-methyl-dioxyphenanthrene $C_{14}H_8(OMe)(OAc)$, dimethylamine, and di-methyl-oxyethyl-amine $NMe_2.CH_2.CH_2OH$ (Fischer a. Von Gerichten, *B.* 19, 794).

(α)-*Methylo-iodide* $C_{17}H_{17}Me_2NO_3MeI\frac{1}{2}$aq. Formed from di-methyl-morphine and MeI dissolved in alcohol (Hesse, *A.* 222, 225). Prisms: v. sol. hot water.

(β)-*Methylo-iodide* $C_{17}H_{17}Me_2NO_3MeI$. Obtained by adding KOH to a solution of the (α)-isomeride, allowing the oily pp. to crystallise, and adding KI to the mother-liquor (Hesse, *A.* 222, 227). Crystals.

(α)-*Methylo-chloride* $C_{17}H_{17}Me_2NO_3MeCl\frac{1}{2}$aq. Obtained from the (α)-methylo-iodide by treatment with AgCl. With Ac_2O it forms $C_{17}H_{16}AcMe_2NO_3$ $2\frac{1}{2}$aq crystallising in needles; v. sol. hot water and alcohol.—$(B'MeCl)_2PtCl_4$ 8aq.

(β)-*Methylo-chloride* $C_{17}H_{17}Me_2NO_3MeCl$. Formed from the (β)-methylo-iodide and AgCl. Forms a neutral sulphate and a platinochloride.

Acetyl derivative $C_{17}H_{16}AcMe_2NO_3$. [66°]. Formed from di-methyl-morphine and Ac_2O at 85° (Hesse, *A.* 222, 223). V. sol. alcohol and ether, m. sol. water, insol. KOHAq. Gives a blue colour with conc. H_2SO_4.—B'HCl $\frac{1}{2}$aq.—$B'_2H_2PtCl_6$ 4aq.—$B'HNO_3$ 3aq.—$B'_2H_2SO_4$ 8aq.

Ethyl-morphine $C_{17}H_{18}EtNO_3$. *Codethyline.* [83°]. S. $2\frac{1}{2}$ at 100°. Formed by heating morphine (1 mol.) with NaOEt (1 mol.), alcohol, and EtI (Grimaux, *C. R.* 92, 1140, 1228; *A. Ch.* [5] 27, 278). Hard brilliant laminæ (containing aq); v. sol. alcohol and ether, m. sol. water. Ppd. from solutions of its salts by KOH and Na_2CO_3, but not by NH_3Aq. Gives a blue colour with H_2SO_4 containing $FeCl_3$.—×B'HCl: groups of slender needles.—$(C_{17}H_{18}EtNO_3)MeI$. Hard bulky crystals, converted by moist Ag_2O into a tertiary base [132°].

Di-ethyl-morphine ×$C_{17}H_{17}Et_2NO_3$. The iodide of this base appears to be formed by heating morphine with NaOH (1 mol.) and EtI (2 mols.). It is crystalline, and is converted by successive treatment with Ag_2O and MeI into $C_{17}H_{17}Et_2NO_3MeI$, which crystallises from alcohol, and is converted by Ag_2O into an hydroxide which is split up on distillation into NMeEtPr and a derivative of phenanthraquinone $C_{14}H_7EtO_2$ (Gerichten a. Schrötter, *B.* 15, 2182).

Ethylene-di-morphine $C_2H_4(C_{17}H_{18}NO_3)_2$. *Dicodethine. Dicodethylene.* Prepared by boiling morphine with alcoholic soda and ethylene bromide (Grimaux, *C. R.* 93, 67; *A. Ch.* [5] 27, 281). White needles (from alcohol), insol. ether, v. sol. alcohol. Blackens when heated, and decomposes above 200°. With H_2SO_4 and $FeCl_3$ it gives a blue colouration.—×$B''H_2Cl_2$. Hard prisms.

Morphinyl-sulphuric acid $C_{17}H_{18}(OSO_3H)NO_2$ 2aq. *Morphine sulphonic acid.* Formed by shaking morphine (20 g.) with KOH (8 g.), water (25 c.c.), and $K_2S_2O_7$ (15 g.) (Stolnikoff, *H.* 8, 242). Silvery needles (from water), not decomposed at 160°: v. sl. sol. cold water, alcohol, and ether. Hot dilute HClAq hydrolyses it to morphine and H_2SO_4. Does not give a blue colour with $FeCl_3$. Hot conc. H_2SO_4 gives a rose colour, changing to violet. Less poisonous than morphine, producing tetanus.

Nitroso-morphine $C_{17}H_{18}(NO)NO_3$ aq. Formed by passing nitrous acid gas into morphine suspended in water (E. L. Mayer, *B.* 4, 121). Reddish-yellow powder, turned black by $FeCl_3$.

Trimorphine $(C_{17}H_{19}NO_3)_3$. Formed by heating morphine (30 g.) with H_2SO_4 (30 c.c.) and water (30 c.c.) at 100° (Wright, *C. J.* 26, 220). Formed also by heating morphine (1 pt.) with dry oxalic acid (3 pts.) at 145° (Beckett a. Wright, *C. J.* 28, 698). Amorphous, sol. ether. Gives a purple colour with $FeCl_3$.—$B'''H_3Cl_3$. Amorphous. Converted by conc. hydrochloric acid at 100° into $C_{102}H_{112}Cl_2N_6O_{16}6HCl$, a brittle gum.

Tetramorphine $(C_{17}H_{19}NO_3)_4$. Formed, together with trimorphine, by heating morphine with dilute H_2SO_4 at 100°–140° (Wright, *C. J.* 26, 220). Amorphous. On heating with HClAq it forms the salt $(C_{17}H_{19}NO_3)_8(HCl)_8$ (?). On adding HCl to an aqueous solution of tetramorphine a flocculent pp. of $(C_{17}H_{19}NO_3HCl)_4$ is got.—$(C_{17}H_{19}NO_3)_4 2H_2SO_4$. *Sulphomorphide.* Obtained by heating morphine with dilute H_2SO_4 at 160° (Arppe, *A.* 55, 96; Matthiessen a. Wright, *Pr.* 17, 455; Wright, *C. J.* 26, 220).

Apomorphine $C_{17}H_{17}NO_2$. Formed by heating morphine or codeïne with HClAq at 145° for 2 or 3 hours (Matthiessen a. Wright, *Pr.* 17, 455). Formed also by heating morphine with aqueous phosphoric acid till the temperature reaches 185° (Wright, *C. J.* 25, 652). It is also one of the products when morphine is heated with aqueous $ZnCl_2$ for 20 minutes at 125° (Mayer a. Wright, *C. J.* 26, 211). Amorphous mass, which turns green in moist air. Sl. sol. water, especially if it contains CO_2; sol. alcohol, ether, and chloroform. Emetic; ·02 g. of the hydrochloride being sufficient to produce vomiting. A solution of apomorphine hydrochloride gives with caustic alkalis a white pp., quickly becoming black; with Na_2CO_3 a white pp., turning green; with

HNO_3 a blood-red colour; with $FeCl_3$ an amethyst colour; with $K_2Cr_2O_7$ an orange pp.; with KI an amorphous pp., quickly becoming green; and with platinic chloride a yellow pp., decomposing on warming. It reduces $AgNO_3$. AcCl yields a mono-acetyl derivative (Danckwortt, *Ar. Ph.* 228, 572).—B′HCl: crystals, sl. sol. cold water.

Polymeride of apomorphine $C_{136}H_{136}N_8O_{16}$ (?). Formed, together with apomorphine and several bases, which form the hydrochlorides $C_{136}H_{145}ClN_8O_{20}H_8Cl_8$ (?), $C_{68}H_{68}N_4O_8H_4Cl_4$ (?), and $C_{34}H_{37}ClN_2O_5H_2Cl_2$ (?) by heating morphine with aqueous $ZnCl_2$. It forms a hydrochloride $B^{viii}H_8Cl_8$ insol. alcohol (Mayer a. Wright).

Diapotetramorphine $C_{136}H_{148}N_8O_{22}$. Formed, together with apomorphine, by heating morphine with aqueous phosphoric acid (Wright). Amorphous, rapidly darkening in air. Evaporation with conc. hydrochloric acid converts it into $C_{136}H_{146}Cl_2N_8O_{20}8HCl$. Evaporation with HIAq and phosphorus yields the corresponding $C_{136}H_{146}I_2N_8O_{20}8HI$ (Wright).

Pseudomorphine $C_{17}H_{17}NO_3$ $1\frac{1}{2}$aq or $C_{34}H_{36}N_2O_6$ 3aq (Hesse, *A.* 235, 229). *Dehydromorphine. Oxydimorphine. Oxymorphine. Dimorphine.* Discovered by Pelletier (1832) in Levant opium. Occurs in morphine hydrochloride made by Gregory's method (Hesse, *A.* 141, 87).

Formation.—1. By heating a solution of morphine hydrochloride with $AgNO_2$ at 60° (Schützenberger, *Bl.* [2] 4, 176).—2. By oxidising morphine with $KMnO_4$, potassium nitrite, or K_3FeCy_6, or by exposing its ammoniacal solution to the air (Polstorff, *B.* 13, 86; *cf.* Pelletier, *A.* 16, 49).

Properties.—White, microcrystalline powder (from NH_3Aq), insol. water, alcohol, ether, and chloroform, sol. KOHAq and NH_3Aq, v. e. sol. alcoholic NH_3. Lævorotatory (Hesse, *A.* 176, 195). Decomposed by heat without melting. It is not affected by reducing agents. It is tasteless and not poisonous.

Colour-tests.—1. When evaporated with dilute H_2SO_4 until fumes of H_2SO_4 appear it becomes bluish-green, and, on adding water, rose-red; if HNO_3 or dilute $NaNO_2$ be now added the colour changes to deep violet. Under similar circumstances morphia gives a rose-red colour, turned brownish-red by water, and raspberry-red by HNO_3 (Donath, *J. pr.* [2] 33, 560).—2. Resembles morphia in its reaction with $FeCl_3$, with molybdic acid in H_2SO_4 (Fröhde's reagent), with HNO_3, and with HIO_3. For the reaction with iodic acid HCl must be absent. NH_4Cl interferes with these tests.—3. Conc. H_2SO_4 forms an olive-green colour.—4. Conc. HNO_3 gives an intense orange-red colour, changing to yellow.—5. A mixture of equal parts of cane-sugar and pseudomorphine is coloured by H_2SO_4 blue, changing to dark green (Hesse, *A.* 234, 255).

S a l t s.—B′HCl aq. Minute needles. S. 1·4 at 20°. $[\alpha]_D = -103°\ 13'$. — B′HCl 2aq. — B′HCl 3aq. — B′HCl 4aq. — B′HCl 6aq. — B′HCl 8aq. — $B'_2H_2PtCl_6$ 8aq. — B′HI aq. — $B'H_2SO_4$ 4aq: small colourless needles; sl. sol. cold water (Polstorff).—$B'H_2SO_4$ 6aq: laminæ. S. 2·37 at 20°.—$B'_2H_2Cr_2O_7$ 6aq: crystalline pp. S. ·1 at 18°.—$B'_2H_2C_2O_4$ 6aq. S. ·05 at 20°.— $B'_2H_2C_2O_4$ 8aq. — T a r t r a t e $B'C_4H_6O_6$ 3aq: needles.—$B'C_4H_6O_6$ 6aq. S. 2·4 at 18°.

Acetyl derivative $C_{17}H_{15}Ac_2NO_3$. [276°]. Formed by heating pseudomorphine (1 pt.) with Ac_2O (2 pts.) at 120° (Hesse, *A.* 222, 235; 234, 253). Crystallises from ether in prisms (containing 4 aq). V. e. sol. alcohol, m. sol. ether and chloroform. When mixed with cane-sugar and dissolved in conc. H_2SO_4 it gives a dark-green colour. If the H_2SO_4 contain $Fe_2(SO_4)_3$ the colour is at first blue.—$B'_2H_2PtCl_6$ 6aq.

Methylo-iodide $C_{17}H_{17}NO_3MeI$ 2aq. Formed by the action of HI on the crystalline body $(C_{17}H_{17}NO_3)_2Me(OH)MeI$, which is prepared by oxidising morphine methylo-iodide with alkaline K_3FeCy_6 (Polstorff, *B.* 13, 93). Small prisms.

Methylo-hydroxide $C_{17}H_{17}NO_3Me(OH)$ $3\frac{1}{2}$aq. Prepared by the action of moist Ag_2O on the iodide or of baryta on the sulphate. Crystalline; v. sol. water, insol. alcohol.

Methylo-sulphate $(C_{17}H_{17}NO_3)_2Me_2SO_4$ 4aq. Obtained by ppg. a solution of the oxyiodide with Ag_2SO_4. Leaflets; v. sol. hot water.

MORPHOTHEBAÏNE *v.* THEBAÏNE.

MORPHOTROPY. This term is applied to the relations between the crystalline form and the composition of those bodies which are chemically similar, and which are derived from the same parent body; *v.* this vol. p. 89.

MORRHUIC ACID $C_9H_{13}NO_3$ *i.e.* $CH{<}^{CH.C(OH)}_{CH_2.NH}{>}C.C_3H_6.CO_2H$ (?) *Oxy-propyl-pyridine dihydride carboxylic acid.* Occurs in cod-liver oil in a combination with glycerin and phosphoric acid, from which it is readily set free by acids and alkalis. Obtained by extracting the oil with dilute (35 p.c.) alcohol containing 5 p.c. of HCl (Gautier a. Mourgues, *C. R.* 107, 740). Square flattened prisms or large lanceolate plates; insol. cold, sol. hot, water; v. sol. alcohol, ether, and alkalis. The solutions have a disagreeable aromatic odour. (Gautier, *Bl.* [3] 2, 233). Morrhuic acid decomposes carbonates. A solution of the potassium salt gives pps. with lead acetate and $AgNO_3$, but not with cupric acetate. The silver salt is readily reduced, even in the cold. Morrhuic acid forms a crystalline platinochloride, an amorphous aurochloride, and a hydrochloride which is decomposed by boiling water. On distilling with lime it yields a basic oil which forms a crystalline methylo-iodide. Potassium morrhuate is oxidised by $KMnO_4$ to an acid which ppts. cupric acetate, and appears to be a pyridine derivative.

MORRHUINE $C_{19}H_{27}N_3$. An alkaloid occurring, together with aselline $C_{25}H_{32}N_4$, in cod-liver oil (Gautier a. Mourgues, *Bl.* [3] 2, 228; *C. R.* 107, 626). Thick oil, smelling like *syringa*; v. sl. sol. water, v. sol. alcohol and ether. Lighter than water. Ppts. copper salts. Strongly alkaline. It forms a very deliquescent h y d r o c h l o r i d e crystallising in groups of needles, a crystalline p l a t i n o c h l o r i d e and a yellow a u r o c h l o r i d e. Morrhuine constitutes one-third of the total bases in the oil, and is a diaphoretic and diuretic.

MORTARS *v.* CEMENTS, in DICTIONARY OF APPLIED CHEMISTRY.

MOSAIC GOLD. An alloy of Cu and Zn in equal parts; *v.* COPPER, ALLOYS OF, vol. ii. p. 254; *v.* also DICTIONARY OF APPLIED CHEMISTRY.

MUCEDIN *v.* PROTEÏDS.

MUCIC ACID $C_6H_{10}O_8$ *i.e.* $CO_2H.CH(OH).CH(OH).CH(OH).CH(OH).CO_2H$. Mol. w. 210. [206°–216°] (K. a. T.). S. ·33 at 14°; 17 at 100°. Formed by the oxidation of milk-sugar, galactose, melitose, dulcite, gum arabic, gum tragacanth, and plant mucus with dilute nitric acid (Scheele, *Opuscul.* 2, 111; Laugier, *A. Ch.* 41, 79; Berzelius, *A. Ch.* 92, 141; 94, 5; 95, 31; Malaguti, *A. Ch.* [2] 60, 195; 63, 86; Liebig a. Pelouze, *A.* 19, 258; Liebig, *A.* 9, 24; 26, 160; Hagen, *P.* 71, 531; *A.* 64, 347; Johnson, *A.* 94, 225; Schwanert, *A.* 116, 257; Tollens, *A.* 249, 220).

Preparation.—1. Milk-sugar (1 pt.) is heated with HNO_3 (2 pts. of S.G. 1·4) and water (2 pts.) until red fumes appear. The flame is then removed until the reaction has abated. The liquid is then evaporated, a further quantity ($\frac{1}{2}$ pt.) of HNO_3 being added during the evaporation. The product is washed with water and dried (Klinkhardt, *J. pr.* [2] 25, 43). The yield is 35 p.c.; *cf.* Guckelberger, *A.* 74, 348. — 2. Coarsely powdered milk-sugar (100 g.) is heated with HNO_3 (1200 c.c. of S.G. 1·15) in a basin on a water-bath until the volume is greatly reduced (to 150 or 200 c.c.). After cooling, water (200 c.c.) is added, and after some days the mucic acid is filtered off and washed with water (500 c.c.). The yield is good (40 g.). When galactose is treated in the same way the yield is 77 p.c. (Kent a. Tollens, *A.* 227, 221).

Properties.—Colourless tables; sl. sol. cold water, insol. alcohol. It does not reduce Fehling's solution.

Reactions.—1. When *boiled with water* it changes to the isomeric paramucic acid.—2. When heated with water at 180° it yields pyromucic acid.—3. On dry *distillation* it yields CO_2, pyromucic acid, and some diphenylene-oxide. When cautiously heated at 280° it forms a small quantity of de-hydro-mucic acid $C_4H_2O(CO_2H)_2$ which condenses on the neck of the retort as small crystals.—4. Boiling *nitric acid* oxidises it to oxalic and racemic acids.—5. On oxidation with H_2SO_4 and MnO_2 formic acid is given off.—6. *Potash-fusion* yields acetic and oxalic acids.—7. HIAq and phosphorus at 140° forms some adipic acid (Crum Brown, *A.* 125, 19), and diphenylene-oxide (Heinzelmann, *A.* 193, 186).—8. PCl_5 forms di-chloro-muconic chloride $C_6H_2Cl_4O_2$ (Liès-Bodart, *A.* 100, 325; Bode a. Wichelhaus, *A.* 132, 95).—9. When allowed to *ferment* for 9 months it yields alcohol and acetic, butyric, and traces of lactic acids (Béchamp, *Bl.* [3] 3, 770).—10. Ba_2S at 205° forms thiophene (β)-carboxylic acid.—11. Fuming HClAq (or HBrAq) at 100°–150° forms de-hydromucic acid.

Salts.—$(NH_4)_2A''$: flat four-sided prisms (from water), sl. sol. cold, v. sol. hot, water. Decomposed at 220°–240° into pyrrole, pyrrole carboxylic amide, NH_3, and CO_2.—NH_4HA'' aq: needles or thin prisms. More soluble in water than the normal salt.—Na_2A'' $4\frac{1}{2}$aq: transparent triclinic crystals.—Na_2A'' $\frac{1}{2}$aq: white powder.—$NaHA''$ $3\frac{1}{2}$aq: prisms. — K_2A'' $\frac{1}{2}$aq: granules. S. 12·5. Insol. alcohol.—K_2A'' 2aq (Schmidt a. Cobenzl, *B.* 17, 601).—KHA'' aq: decomposes at 150°–180° into CO_2 and pyromucate.—BaA'' $1\frac{1}{2}$aq (dried at 100°).—CaA'' $1\frac{1}{2}$aq.—MgA'' 2aq (at 100°).—PbA'' aq: white pp.—$Pb_3C_6H_4O_8$: obtained by ppg. ammonium mucate with basic lead acetate.—CuA'' aq (dried at 100°): bluish-white pp.—FeA'' 2aq (dried at 100°): yellow powder.—$K(SbO)A''$.—$Na(SbO)A''$ (dried at 100°). Obtained by dissolving Sb_2O_3 in $NaHA''$. Amorphous (Klein, *C. R.* 97, 1437).—Ag_2A'' (dried at 100°): white pp.—Methylamine salt. Decomposed by distillation into methyl-pyrrole and methyl-pyrrole carboxylic methylamide.—Ethylamine salt. Decomposed by distillation into ethyl-pyrrole, ethyl-pyrrole dicarboxylic diethylamide, and ethyl-pyrrole carboxylic ethylamide (Bell, *B.* 10, 1866).—Diethylamine salt. Decomposed by heat giving off $NHEt_2$.—Aniline salt $(C_6H_7N)_2H_2A''$. Insol. boiling alcohol, sol. boiling water (Köttnitz, *J. pr.* [2] 6, 138). Decomposed on distillation into phenyl-pyrrole, CO_2, aniline, and H_2O. On heating with water it forms mucic anilide.

Methyl ether Me_2A''. Laminæ or flattened six-sided prisms (from water), v. sol. hot water, v. sl. sol. hot alcohol. Decomposes at 165°.

Mono-ethyl ether $EtHA''$. Formed by boiling Et_2A'' with alcohol (Limpricht, *A.* 165, 255). Crystals (containing 3aq); sol. water and alcohol. Melts below 100°.—NH_4EtA''.

Di-ethyl ether Et_2A''. [158°]. S. 2·3 at 20°. S. (alcohol of S.G. ·814) ·64 at 15·5°. Formed by heating mucic acid (1 pt.) with H_2SO_4 (4 pts.) till it turns black, leaving it to cool, and adding alcohol (4 pts.) (Malaguti, *A. Ch.* [2] 63, 86). Crystals (from boiling alcohol). Limpricht was not able to obtain this ether by the action of alcohol and HCl on mucic acid. Mucic ether is reduced by sodium-amalgam to an acid which strongly reduces Fehling's solution, and which may be readily re-oxidised to mucic acid (E. Fischer, *B.* 23, 937).

Isoamyl ether $(C_5H_{11})HA''$. Needles.

Amide $C_6H_8O_6(NH_2)_2$. *Mucamide.* S.G. $\frac{13·5}{}$ 1·589. Formed from the normal ether and ammonia (Malaguti, *C. R.* 22, 854). Formed also by the action of ammonia on tetra-acetyl-mucic amide (Ruhemann, *B.* 20, 3366). Minute crystals (from water), v. sl. sol. boiling water, insol. alcohol and ether. Converted by water at 140° into ammonium mucate. On dry distillation it yields pyrrole carboxylic amide, paracyanogen, and a little pyromucic acid.

Anilide $C_6H_8O_6(NHPh)_2$. Formed by heating the aniline salt at 120°, or the ether with excess of aniline (Köttnitz). Plates, insol. water, alcohol, and dilute acids.

o-*Toluide* $C_6H_8O_6(NHC_7H_7)_2$. Formed like the preceding (K.). Plates.

Tetra-acetyl derivative $C_4H_4(OAc)_4(CO_2H)_2$. [266° cor.]. Formed by boiling mucic acid with Ac_2O and $ZnCl_2$ (Maquenne, *Bl.* [2] 48, 720). Efflorescent needles (containing 2aq), sl. sol. water, v. sol. alcohol.

Ethyl ether of the tetra-acetyl derivative $C_4H_4(OAc)_4(CO_2Et)_2$. [177°]. S. (95 p.c. alcohol) ·4 at 17°. Formed by heating mucic ether with AcCl at 100° (Werigo, *A.* 129, 195). Needles, sl. sol. ether, v. sol. boiling alcohol, v. sl. sol. boiling water.

Di-phenyl-hydrazide $C_4H_4(OH)_4(CO.N_2H_2Ph)_2$. [240°]. Formed by heating mucic acid with phenyl-hydrazine hydrochloride and NaOAc on the water-bath (Bülow, *A.* 236, 196; Maquenne, *Bl.* [2] 48,

722). Pale-yellow plates (from phenyl-hydrazine), v. sl. sol. water, alcohol, and ether. Crystallises unaltered from alcoholic potash.

Paramucic acid. S. 1·36 in the cold; 5·8 at 100°. Formed by evaporating an aqueous solution of mucic acid to dryness, dissolving the residue in alcohol, and allowing the alcoholic solution to evaporate in the air (Malaguti, *A.* 15, 179). Crystalline; more soluble in water than mucic acid. On recrystallisation from hot water it changes into mucic acid. Paramucates, with the exception of the normal ammonium salt, are more soluble than the corresponding mucates, but their boiling solutions deposit mucates.

Dehydromucic acid $C_6H_4O_5$.

Formation.—1. By heating mucic acid in sealed tubes with HBrAq (saturated at 0°) at 100° for two days. The product may be crystallised from water and separated from unaltered mucic acid by crystallisation of the Ba salt (Heinzelmann, *A.* 193, 184).—2. By heating mucic acid with fuming HClAq at 145° (Seelig, *B.* 12, 1083).—3. In small quantity by heating mucic acid at 180° (Klinkhardt).—4. By heating hydrogen potassium saccharate with conc. HClAq at 150° (Sohst a. Tollens, *A.* 245, 19).

Preparation.—Mucic acid (1 pt.), conc. HCl (1 pt.), and conc. HBr (1 pt.) are heated 8 hours at 150° in sealed tubes. The solid contents of the tubes are collected and distilled with steam. If this steam be condensed it is found to contain di-phenylene oxide. The residue is neutralised by ammonia, filtered, and mixed with HCl. The dehydro-mucic acid is then ppd. Yield 20 p.c. (Klinkhardt, *J. pr.* 133, 44).

Properties.—Plates (from alcohol) or needles (from hot water). Does not melt at 320°. V. sl. sol. cold water, alcohol, and ether. May be sublimed.

Reactions.—1. $FeCl_3$ produces, especially on warming, in a solution of dehydro-mucic acid, a transparent gelatinous pp. This result is prevented by the presence of other acids.—2. *Bromine water* converts it into fumaric acid, the reaction being $C_4H_2O(CO_2H)_2 + 3Br_2 + 3H_2O = C_2H_2(CO_2H)_2 + 2CO_2 + 6HBr$.—3. A mixture of HNO_3 and H_2SO_4 converts it into nitro-pyromucic acid (*q. v.*).—4. *Sodium-amalgam* reduces it to two acids of the formula $C_6H_6O_5$, melting at 146° and 173° (Graebe a. Bungener, *B.* 12, 1079). The (α)- acid [146°] crystallises in thin plates and forms the crystalline salts $CaA''3\frac{1}{2}aq$, $BaA''4\frac{1}{2}aq$, and $Ag_2A''\frac{1}{2}aq$. The (β)- acid [173°] forms large crystals (containing aq) and the salts $CaA''1\frac{1}{2}aq$ (amorphous), $BaA''1\frac{1}{2}aq$ (needles) and Ag_2A''.—5. On *dry distillation* it splits up into CO_2 and pyromucic acid (*q. v.*).

Salts.—$BaA''2\frac{1}{2}aq$.—$BaA''6aq$. Sol. water. —$CaA''3aq$.—Ag_2A'': white pp., decomposed by boiling water.

Ethyl ether Et_2A''. [47°].

Chloride $C_4H_2O(COCl)_2$. [80°]. (c. 245°). From PCl_5 on the acid (Klinkhardt, *J. pr.* 133, 46). Smells like $POCl_3$. Sol. ether, alcohol, and $CHCl_3$. At 100° it sublimes forming flat needles. Boiling water reconverts it into dehydro-mucic acid.

Amide $C_4H_2O(CONH_2)_2$. Formed by the action of NH_3 on an ethereal solution of the chloride. Slender needles (from water). Nearly insol. cold water, alcohol, and ether. Does not melt below 240°.

MUCILAGE. The gum of plants from which it is obtained by steeping these in hot water, which on cooling forms a jelly. When linseed mucilage is strained through linen, and the filtrate mixed with alcohol and HClAq, a pp. is obtained which after washing with alcohol and ether has the composition $C_6H_{10}O_5$ (Schmidt, *A.* 51, 50; Frank, *J. pr.* 95, 484; Nägeli a. Cramer, *Pharm. Cent.* 1855, 426; Kirchner a. Tollens, *A.* 175, 215). Brittle gum, resembling bassorin (*q. v.*), sol. cold water, insol. alcohol. Dextrogyrate. Insoluble in ammoniacal cupric oxide. Boiling dilute H_2SO_4 partially converts it into glucose.

Quince-mucilage is coloured blue by iodine, and gives no mucic acid on oxidation with nitric acid. Boiling dilute H_2SO_4 yields a mixture of cellulose, gum, and sugar. The mucilage from salep (*Orchis mascula*), from *Tamarindus indica*, and from some other plants, is also turned blue by iodine (*v.* Starch). Quince-mucilage yields furfuraldehyde on distillation with dilute H_2SO_4, indicating the presence of arabinose or xylose. It contains neither glucose nor galactose, since neither saccharic nor mucic acid is formed on oxidation.

Salep mucilage yields no furfuraldehyde on distillation with dilute H_2SO_4; but on oxidation it yields saccharic (but not mucic) acid. It contains glucose and mannose, but no galactose or arabinose (Gans a. Tollens, *A.* 249, 245).

MUCIN *v.* Proteïds, *Appendix* C.

MUCOBROMIC ACID $C_4H_2Br_2O_3$ *i.e.* $CHO.CBr:CBr.CO_2H$. *Semi-aldehyde* of *di-bromo-maleïc acid.* [121°]. Formed by adding bromine to pyromucic acid covered with a little water without cooling. The product is boiled and evaporated, the yield being 70 p.c. of the theoretical (Schmelz a. Beilstein, *A. Suppl.* 3, 276; Jackson a. Hill, *B.* 11, 1671; *Am.* 3, 41). Formed also from ($\beta\gamma$)-di-bromo-pyromucic acid and hot dilute HNO_3 (Hill a. Sanger, *A.* 232, 89) and by oxidation of di-bromo-maleïc aldehyde.

Properties.—White plates, v. sol. alcohol, ether, and hot water, v. sl. sol. cold water. Reddens litmus and decomposes carbonates, but its salts are very unstable.

Reactions.—1. When *heated* it partially sublimes, and the rest decomposes into HBr, di-bromo-maleïc acid, and CO_2 (Hill, *Am.* 3, 105).—2. Boiling *baryta-water* forms CO_2, bromo-acetylene, malonic acid, and formic acid (Jackson a. Hill, *B.* 11, 289). Cold baryta-water forms HBr and bromo-maleïc acid. A cold paste of baryta and water forms bromo-propiolic acid and β-di-bromo-acrylic acid. Baryta-water at 0° forms mucoxybromic acid (*q. v.*).—3. *Bromine-water* forms di-bromo-maleïc acid (Hill, *B.* 13, 734). By heating with water and bromine (3 mols.) in sealed tubes at 125° it is converted into penta- and hexa-bromo-ethane, di-bromo-maleïc acid, and tetra-bromo-butyric acid (Limpricht, *A.* 165, 293). Bromine (1 at.) at 145° forms di-bromo-maleïc acid, mucobromyl bromide, and a little dibromo-succinic acid.—4. PBr_5 forms the bromide (*v. infra*).—5. *Phenol* (25 g.) dissolved in water (30 g.) containing KOH (17·5 g.) converts mucobromic acid (20 g.) into 'phenoxy-mucobromic' acid $C_{10}H_7BrO_4$, which crystallises from water in prisms [105°]. Phenoxy-muco-

bromic acid forms the crystalline salts KA′ and BaA'_2 3aq, and is converted by Ag_2O in hot water into phenoxy-bromo-maleïc acid $C_{10}H_7BrO_5$, which crystallises in slender needles [104°], and forms a crystalline silver salt Ag_2A'' (Hill a. Stevens, *Am.* 6, 188).—6. Moist Ag_2O oxidises it to di-bromo-maleïc acid. *Nitric acid* acts in like manner.—7. Alcoholic *potassium nitrite* forms a pp. of $K_2C_3HN_3O_7$, v. sol. cold water, converted by hot water into CO_2, HCy, HNO_2, and $KC_3H_2NO_4$. Bromine in CS_2 converts the salt $K_2C_3HN_3O_7$ into $C_3HBr_3N_2O_5$ (Hill a. Sanger, *B.* 15, 1906).—8. KNO_2 at 50° forms the acid $C_3H_3NO_4$, which forms the crystalline salts NaA′ aq, KA′ aq, CaA'_2 4aq, BaA'_2 5aq, PbA'_2 4aq, CuA'_2, and AgA′.

Salts.—BaA'_2: white plates, sol. cold water and alcohol.—AgA′: felted needles, insol. water.

Ethyl ether EtA′. [51°]. (255°–260°). Formed from the acid, alcohol, and H_2SO_4. Large monoclinic crystals with aromatic odour. KNO_2 converts it into crystalline $C_6H_6KNO_7$.

Mucobromic acetic anhydride $C_4HBr_2O_2$.OAc. [54°]. Formed by heating mucobromic acid with AcCl at 120°. Long needles, v. e. sol. alcohol, ether, and chloroform.

Bromide $C_4HBr_3O_2$. [56°]. Obtained by heating mucobromic acid (1 pt.) with PBr_5 (4 pts.) at 115°. Small slender prisms (from alcohol), sol. alcohol, ether, benzene, chloroform, and CS_2. Boiling water slowly reconverts it into mucobromic acid.

MUCOCHLORIC ACID $C_4H_2Cl_2O_3$ *i.e.* CHO.CCl:CCl.CO_2H or CHO.CCl_2.C.CO_2H. *Semi-aldehyde* of *di-chloro-maleïc acid.* [125°]. Formed by passing chlorine into a solution of pyromucic acid (1 pt.) in water (10 pts.) at 0° in presence of iodine, the yield being 40 p.c. of the theoretical (Beilstein a. Schmelz, *A. Suppl.* 3, 276; Bennett a. Hill, *B.* 12, 655). Plates, v. sol. hot water, alcohol, and ether, insol. ligroïn and CS_2. Split up by alkalis, even in the cold, into di-chloro-acrylic acid and formic acid.

MUCONIC ACID (of Limpricht) $C_6H_6O_4$ *i.e.* $CO_2H.CH_2.C\!\!<\!\!{CH.CH_2 \atop O\;.CO}\!\!>$. [100°–125°]. Formed by adding silver oxide to a hot solution of dibromo-adipic acid [175°–190°] (formed by adding bromine to a warm solution of hydromuconic acid in HOAc), and decomposing the resulting silver salt with HCl or H_2S (Limpricht, *A.* 165, 274). Large crystals, v. sol. water, alcohol, and ether. Boiling baryta-water decomposes it into CO_2, acetic acid, succinic acid, and another acid.

Salts.—BaA'_2 4aq: nodules, v. sol. water.

Muconic acid $CO_2H.CH:CH.CH:CH.CO_2H$. [above 260°]. S. ·02 at 15°. Formed by the action of alcoholic potash on $\beta\gamma$-di-bromo-adipic acid (Rupe, *A.* 256, 22; Ruhemann a. Blackman, *C. J.* 57, 373). Branching white needles, sl. sol. hot water, m. sol. hot alcohol and HOAc. Completely decomposed by $KMnO_4$ in presence of Na_2CO_3. Combines with bromine forming the acid $CO_2H.CHBr.CHBr.CHBr.CHBr.CO_2H$. [c. 250°]. Sodium-amalgam reduces it to hydromuconic acid [195°].

Salts.—K_2A'': transparent plates, v. sol. water, insol. alcohol.—BaA″.—PbA″.—Ag_2A'': curdy white pp. The cupric salt is a bluish-green heavy amorphous pp.

Methyl ether Me_2A''. [154°]. Fan-shaped groups of needles.

Ethyl ether Et_2A''. [64°]. Plates (from dilute alcohol).

Di-chloro-muconic acid $C_6H_4Cl_2O_4$ *i.e.* $CO_2H.CH:CCl.CCl:CH.CO_2H$. S. 10 at 100°. Obtained by heating mucic acid or saccharic acid with PCl_5 and decomposing the resulting chloride with water (Liès-Bodart, *A.* 100, 325; Bode, *A.* 132, 95; Bell, *B.* 12, 1272; Limpricht, *A.* 165, 253; Rupe, *A.* 256, 6). Long needles (containing 2aq), v. sl. sol. cold water, v. sol. alcohol, m. sol. ether. Not decomposed by boiling aqueous alkalis.

Reactions.—1. Reduced by *sodium-amalgam* to two acids of the formula $C_6H_8O_4$, one of which melts at 195°, and yields malonic acid on oxidation; the other melts at 169°, and yields succinic acid on oxidation. Boiling with sodium-amalgam reduces it to adipic acid [148°].—2. Alcoholic *potash* at 190°–200° forms oxalic and acetic acids.

Salts.—The Ba and Ca salts are m. sol. water.—Ag_2A'': insoluble pp.

Methyl ether Me_2A''. [156°]. Pearly plates, v. sol. ether, hot alcohol, and HOAc.

Ethyl ether Et_2A''. [96°]. From the chloride and alcohol (Wichelhaus, *A.* 135, 251; Bell, *B.* 12, 1273). Prisms.

Chloride $C_6H_2Cl_4O_2$. Formed by the action of PCl_5 (6 mols.) on mucic acid (1 mol.). Large crystals (from CS_2), decomposed by moist air.

$\Delta^{\beta\gamma}$-Hydromuconic acid $C_6H_8O_4$ *i.e.* $CO_2H.CH_2.CH:CH.CH_2.CO_2H$. [195°]. S. ·58 at 15°. Formed by reducing di-chloro-muconic acid with sodium amalgam or with zinc-dust and acetic acid. White needles or prisms. Converted by boiling NaOHAq into the isomeric acid [169°]. Oxidised by $KMnO_4$ to oxalic and acetic acids. Its Ba and Ca salts are less soluble in hot than in cold water. Bromine added to its aqueous solution forms bromohydromuconic acid $CO_2H.CH_2.CBr:CH.CH_2.CO_2H$ [183°], which yields an ether melting at 80°. Bromine without water forms unstable dibromoadipic acid of the formula $CO_2H.CH_2.CHBr.CHBr.CH_2.CO_2H$.

Ethyl ether Et_2A''. (163° at 35 mm.). Oil.

Amide $C_6H_6O_2(NH_2)_2$. [210°] (Ruhemann a. Blackman, *C. J.* 57, 371).

$\Delta^{\alpha\beta}$-Hydromuconic acid $C_6H_8O_4$ *i.e.* $CO_2H.CH:CH.CH_2.CH_2.CO_2H$. [169°]. S. $\frac{51}{}$ ·9. Formed by boiling the isomeric acid with aqueous NaOH (Rupe, *A.* 256, 13). Nodular aggregates of plates, v. sol. hot, insol. cold water, v. sl. sol. ether. Yields oxalic and succinic acids on oxidation with $KMnO_4$. Bromine forms a monobromo- derivative [160°] crystallising in branching needles, but no di-bromo-adipic acid.

Methyl ether. Oil. Forms with bromine $CO_2Me.CH_2.CH_2.CHBr.CHBr.CO_2Me$ [85°].

MUCOXYBROMIC ACID $C_4H_3BrO_4$ *i.e.* $CO_2H.C(OH):CBr.CHO$. [112°]. Formed by the action of baryta-water at 0° upon mucobromic acid (Hill a. Palmer, *Am.* 9, 148). Thick prisms, with bevelled ends, v. sol. water, alcohol, and ether, v. sl. sol. chloroform, benzene, ligroïn, and CS_2. $FeCl_3$ gives an intense garnet-red colour. $AgNO_3$ forms a white crystalline pp. On heating with baryta-water it yields oxalate and formate. Bromine-water converts it into bromalhydrate

$CBr_3.CH(OH)_2$ and oxalic acid. Aniline yields $C_4H_3BrO_3(NPh)$.

Salts.—K_2A'' aq: plates, v. sol. cold water, decomposed on warming.—BaA'' 2aq: needles, sl. sol. cold water, decomposed on boiling.—PbA'': yellow pp.—Ag_2A'': crystalline pp.; explodes on heating or on moistening with HNO_3.

Methyl ether Me_2A''. Sticky liquid.

Mono-ethyl ether $EtHA''$. [89°]. Prisms, sol. alcohol and ether.

Di-ethyl ether Et_2A''. Viscous liquid.

'Anilmucoxybromic' acid $CO_2H.C(OH):CBr.CH:NPh$. [132°]. Formed by the action of aniline hydrochloride on a dilute solution of mucoxybromic acid (Hill a. Palmer, *Am.* 9, 156). Pale-yellow needles (containing aq), sl. sol. cold water, v. sol. alcohol, and ether. $FeCl_3$ gives a brown pp. Hot acids and alkalis set free aniline. Phenyl-hydrazine ppts. the phenyl hydrazine salt $(C_6H_8N_2)C_{10}H_8BrNO_3$ aq.

Salts.—K_2A''.—BaA'_2 $\frac{1}{2}$aq: bright yellow crystalline pp.—Ag_2A'': bright orange-yellow pp.

MUCOXYCHLORIC ACID $C_4H_3ClO_4$ *i.e.* $CO_2H.C(OH):CCl.CHO$. [115°]. Formed from mucochloric acid by treatment with a very slight excess of baryta, added slowly at a low temperature (Hill a. Palmer, *Am.* 9, 159). The yield is 73 p.c. of the theoretical. Stout prisms, v. sol. water, alcohol, and ether, v. sl. sol. chloroform and benzene. With $FeCl_3$ it gives a deep garnet-red colour. On heating with excess of baryta it yields oxalate and formate. Bromine-water forms oxalic acid and $CClBr_2.CHO$. Phenyl-hydrazine yields an unstable condensation-product. Aniline produces anilmucoxychloric acid.

Salts.—K_2A'': small tables.—BaA'' 2aq: crystalline pp., sl. sol. cold water, v. sl. sol. dilute alcohol.—BaA''aq.—Ag_2A''.

Mono-ethyl ether $EtHA''$. [95°]. Prisms, which may be sublimed, sol. water, alcohol, and ether, v. sol. boiling benzene.

Di-ethyl ether Et_2A''. Viscous liquid.

Anilmucoxychloric acid $C_{10}H_8ClNO_3$ *i.e.* $CO_2H.C(OH):CCl.CH:NPh$. [147°]. Formed from mucoxychloric acid and aniline. Pale yellow needles (containing aq), becoming brilliant yellow when anhydrous; sl. sol. cold water, v. sol. alcohol and ether. When it is heated with acids or alkalis aniline is split off. $FeCl_3$ gives a deep-brown pp.

Salts.—K_2A''.—$BaH_2A''_2$ $\frac{1}{2}$aq: bright yellow needles.—Ag_2A'': bright orange pp.—Phenyl-hydrazine salt $PhN_2H_3H_2A''$ aq: white crystalline mass, sl. sol. cold water, v. sol. alcohol.

MUCUS OF PLANTS *v.* Mucilage.

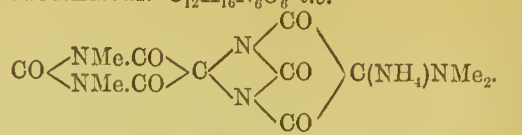
MUNJEET. The root of *Rubia munjista*, used in India as a dye-stuff. If ground munjeet is boiled with a solution of aluminic sulphate, and the red liquid filtered and acidified with HCl, a yellow pp. is formed. If the pp. be boiled with alcohol, pectic acid remains undissolved, and the alcohol contains purpurin and munjistin. They are separated by boiling dilute acetic acid, which dissolves munjistin.

Munjistin is identical with purpuroxanthic acid, $C_{14}H_7(CO_2H)O_4$ [231°] *v.* Di-oxy-anthraquinone carboxylic acid (E. Schunck a. H. Roemer, *C. J.* 33, 422; *cf.* Stenhouse, *Pr.* 12, 633; 13, 86, 145).

MUNTZ'S METAL. An alloy of Cu and Zn; *v.* Dictionary of Applied Chemistry.

MUREXIDE. The ammonium hydrogen salt of Purpuric acid (*q.v.*)

MUREXOÏN $C_{12}H_{16}N_6O_6$ *i.e.*



Formed by converting caffeïne into di-methyl-alloxan (Fischer, *B.* 14, 1912), and reducing this by H_2S to tetra-methyl-alloxantin, which is then subjected to the action of air and ammonia (Brunn, *B.* 21, 514; *cf.* Rochleder, *J. pr.* 51, 405). Red prisms, sl. sol. water and alcohol. Its aqueous solution is purple, resembling that of $KMnO_4$. Sublimes at about 230°. Decolourised by potash (difference from murexide). Dilute HCl decomposes it, forming di-methyl-parabanic acid.

MURIATIC ACID. Synonymous with Chlorhydric acid; *q.v.* vol. ii. p. 5.

MURRAYIN $C_{18}H_{22}O_{10}$. [170°]. A glucoside obtained from the flowers of *Murraya exotica* by extracting with water (Blas, *Z.* 1869, 316; De Vrij, *Z.* 1876, 850; Hoffmann, *Ar. Ph.* [3] 14, 139). White powder, composed of small needles, sl. sol. cold water, v. sol. boiling water and alcohol, insol. ether. Tastes bitter, but is not poisonous. Its solutions in alkalis and in Na_2CO_3 exhibit a greenish-blue fluorescence and turn brown on heating. The aqueous solution is not ppd. by salts of Cu or Hg. $FeCl_3$ colours its solution blue. Lead subacetate gives a pp. It reduces ammoniacal $AgNO_3$ and Fehling's solution on warming. Dilute acids split it up into glucose and murrayetin.

Murrayetin $C_{12}H_{12}O_5$. [c. 110°]. Formed by boiling murrayin with dilute H_2SO_4. Prisms (containing $\frac{1}{2}$aq); sl. sol. cold, m. sol. boiling water, v. sol. alcohol, m. sol. ether. Tasteless. Its solutions exhibit strong greenish-blue fluorescence, which is increased by KOH and by Na_2CO_3. $FeCl_3$ gives a bluish-green colour. Lead acetate gives, after a time, a yellow pp.

MUSCARINE $C_5H_{15}NO_2$ *i.e.* $CH(OH)_2.CH_2.NMe_3.OH$. An alkaloid occurring, together with neurine, in the fly agaric (*Agaricus muscarius*) (Schmiedeberg a. Koppe, *J.* 1870, 875; Ruckert, *N. Rep. Pharm.* 21, 193), in the fungus *Amanita Pantherina* (Giacosa, *J.* 1883, 1488), and in putrefying flesh (Gautier, *Bl.* [2] 48, 13; *cf.* Brieger, *B.* 17, 2741). Formed by oxidising neurine $CH_2OH.CH_2.NMe_3.OH$ with conc. HNO_3 (Schmiedeberg a. Harnack, *C. C.* 1876, 554). Deliquescent tasteless crystals, v. e. sol. water and alcohol, insol. ether. Its solution is strongly alkaline, ppts. ferric and cupric hydrates from solutions of their salts, and acts as a narcotic poison antagonistic to atropine. Not affected by boiling dilute acids or alkalis. Gives amorphous pps. with mercury-potassium iodide and bismuth-potassium iodide.

Salts.—$(CH(OH)_2.CH_2.NMe_3Cl)_2PtCl_4$ 2aq.—$CH(OH)_2.CH_2.NMe_3AuCl_4$.

Di-ethyl ether $(HO)Me_3N.CH_2.CH(OEt)_2$. Formed by heating chloro-acetal $CH_2Cl.CH(OEt)_2$ (from di-chloro-ether) with tri-methyl-amine (Berlinerblau, *B.* 17, 1139). By heating the compound $C_5H_5NBr.CH_2.CH(OEt)_2$, formed by the action of bromo-acetal upon pyridine, with moist Ag_2O at 80° there is formed syrupy $C_5H_5N(OH).CH_2.CH(OEt)_2$, which is inappro-

priately termed by Lochert (*Bl.* [3] 3, 859) di-ethyl-muscarine-pyridine.

MUSCLE. Muscular tissue consists of fibres bound together into fasciculi by connective tissue. The fibres may be transversely striated (voluntary and cardiac muscle) or not (other involuntary muscle). The plain or unstriated fibres are elongated cells with oval nuclei, and inclosed by a delicate envelope; they are singly refracting. The cardiac fibres have no sheath. The voluntary muscular fibres have a well-marked sheath or sarcolemma, under which are situated numerous nuclei; the contents of the sarcolemma (muscle plasma) have a semi-liquid consistency during life. Kühne, and later Eberth, observed a nematode worm (*Myoryctes Weismanni*) crawling up the interior of a muscular fibre (*Zeit. f. wiss. Zool.* 12, 530); the contents of the sarcolemma are not, however, homogeneous; this is denoted by the transverse striping, which is probably an optical effect produced by the presence of certain more solid structures which are described as rods, membranes, tubules, and networks of fibres by different observers; these solid bodies are isotropous and are suspended in an anistropous (doubly refracting) viscous fluid. (For the various theories of the histological structure of striated muscle during rest and on contraction, *v.* Quain, *Anat.* 9th edit., London, 1882, p. 118 *et seq.*; also O. Nasse, *Zur Anat. u. Physiol. d. quergestreiften Muskelsubstanz*, Leipzig, 1882; Schäfer, *Pr.* 1891).

The sarcolemma is homogeneous and elastic; it is composed of an elastin-like substance (Ewald, *Zeit. Biol.* 26, 1).

The muscle plasma, fluid during life, coagulates after death, producing the stiffening called *rigor mortis*. As blood plasma separates into a solid substance, fibrin, and a liquid residue, serum, after it is shed, so the muscle plasma separates into a clot composed of myosin and a liquid residue muscle serum. Like the coagulation of the blood this can be hindered by cold; and by squeezing the frozen muscles of the frog Kühne obtained a liquid muscle plasma, which set into a clot which expressed serum subsequently when it contracted. This occurred most readily at about 30°–40°C. This can also be demonstrated in the muscles of warm-blooded animals, but as *rigor* occurs there more rapidly, great expedition in manipulation is required. *Rigor mortis* is also accompanied by the formation of sarcolactic acid.

Admixture of muscle plasma with solutions of neutral salts prevents the coagulation of the latter. Dilution of such salted muscle plasma brings about coagulation; this occurs most readily at 37°–40° C. Saline extracts of rigid muscle differ from salted muscle plasma in being acid, but resemble it very closely in the way in which myosin can be made to separate from it; myosin in fact undergoes a recoagulation. This is not a simple precipitation; it is first a jellying through the liquid; the clot subsequently contracts, squeezing out a colourless fluid or salted muscle serum. This does not take place at 0°C.; it occurs most readily at the temperature of the body, and is hastened by the addition of a ferment prepared from muscle in the same way as Schmidt's ferment is prepared from blood. The ferment is not identical with fibrin ferment, as it does not hasten the coagulation of salted blood plasma; nor does the fibrin ferment hasten the coagulation of muscle plasma. The recoagulation of myosin is also accompanied by the formation of lactic acid.

The proteïds of muscle plasma are—

1. Paramyosinogen, which is coagulated by heat at 47°C.

2. Myosinogen, which is coagulated at 56°C. It is on the presence of this proteïd that the power of fresh muscle juice to hasten the coagulation of blood plasma depends.

3. Myoglobulin, which differs chiefly from serum globulin in its coagulation temperature (63°C.).

4. Albumin, which is apparently identical with serum albumin α, coagulating at 73°C.

5. Myo-albumose; this has the properties of deutero-albumose, and is identical with, or closely connected to, the myosin ferment.

The first two proteïds in the above list go to form the clot of myosin; paramyosinogen (called musculin by Hammarsten) is, however, not essential for coagulation; the three last remain in the muscle serum.

Paramyosinogen, myosinogen, and myoglobulin are proteïds of the globulin class. They are all completely precipitated by saturation with magnesium sulphate, or sodium chloride, or by dialysing out the salts from their solutions. They can be separated by fractional heat coagulation, or by fractional saturation with neutral salts.

When muscle turns acid, as it does during *rigor mortis*, the pepsin which it contains is enabled to act, and at a suitable temperature (35°–40°C.) albumoses and peptones are formed by a process of self-digestion. It is possible that the passing off of *rigor mortis*, which is apparently due to the reconversion of myosin into myosinogen, may be the first stage in the self-digestion of muscle. The usual theory with regard to the cause of the disappearance of *rigor* is that it is due to putrefaction setting in. Cossar Ewart (*Proc. R. Soc.* 1887) has shown that the disappearance of *rigor* and the appearance of bacteria in the muscle are simultaneous. C. Schipiloff's theory is that the lactic acid which is formed from the glycogen in muscle (Otto) produces *rigor* by precipitating the myosin; and the disappearance of *rigor* is due to more acid being formed, which redissolves the precipitate. R. Böhm has, however, shown that lactic acid is not derived from glycogen, but from a proteïd source; and Latham has been able to deduce a formula which represents the formation of the acid from a combination of cyan-hydrins such as he supposes a proteïd to be.

For the properties of myosin *v.* PROTEÏDS.

For fuller details respecting muscle plasma and the proteïds of muscle consult Kühne, *Protoplasma*, Leipzig, 1864; E. Grubert, Maly's *Jahrsber.* 13, p. 307; J. Klemptner, *ibid.* p. 310; E. Kügler, *ibid.* p. 311; Demant, *Zeit. physiol. Chem.* 3, 241; 4, 386; Halliburton, *J. Physiol.* 8, 133. Concerning the formation of acid during coagulation, *v.* Kühne, *l.c.*; Nasse, *l.c.*; Weyl a. Seitler, *Zeit. physiol. Chem.* 557 (W. a. S. suppose that the acidity is partially due to the formation of acid potassium phosphate, the phos-

phoric anhydride being derived from the lecithin and nuclein of the muscle); Berzelius (*Lehrbuch*, 9, 569); Du Bois Reymond (*Gesammelte Abhandl. zur allgem. Muskel und Nervenphysik*, Leipzig, 1877, 2, p. 3); Heidenhain (*Mechanische Leistung*, p. 143); R. Böhm (*Pf.* 23, 44); Hoppe-Seyler (*H.* 666); Latham (*Brit. Med. Journal*, vol. i. 1886, p. 630); C. Schipiloff (*Centralb. f. d. med. Wissens.* 1882, 291); Chittenden (*Studies from Lab. Physiol. Chem.* Yale, 3, 116). Concerning the digestion of myosin, see Kühne and Chittenden (*Zeit. Biol.* 25, 358).

Pigments of muscle.—Hæmoglobin is present in small quantities in nearly all muscles; it is contained in the muscle plasma, and it is especially abundant in the slowly-contracting red muscles which occur in rodents, and occasionally also in other animals. In the gastropods, Limnæus and Paludina, the muscles contain hæmoglobin, but there is none in the blood (Lankester; *v.* also Hæmoglobin).

Myohæmatin is one of a group of colouring matters called histohæmatins, *i.e.* pigments occurring in the tissues. These substances are probably respiratory in function; they have not been definitely separated from the tissues, but are probably proteïd in nature and contain iron; myohæmatin can be recognised most easily, after soaking the muscle in glycerine, by the spectroscope; myohæmatin is contained in the muscle plasma. Myohæmatin exhibits four absorption bands: one just below D, two between D and E, and one just below F. By soaking the muscle in ether, as a result of osmotic phenomena, the liquid separates out two layers, the lower of which is watery, yellowish-red in colour, and contains myohæmatin which presents a slightly different spectrum from that just described, viz. one band between D and E and one between E and *b*. In both cases the bands are very feeble when the pigment is oxygenated, but become well marked on the addition of reducing agents (MacMunn, *Phil. Trans.* 1, 1886, p. 267; *J. Physiol.* 8, 51). Hoppe-Seyler believes myohæmatin is altered hæmoglobin (*Zeit. physiol. Chem.* 13). This, however, has been shown by MacMunn to be untenable (*ibid.*).

Constituents of Muscle.—Muscle contains on the average 75 p.c. of water; this percentage is higher in young animals and in cold-blooded animals; of the 25 p.c. of solids, 21 p.c. consists of the proteïds already described, and the remaining 4 p.c. of extractives and salts (*cf.* Hofmann, *Lehrbuch der Zoochemie*, 104). The extractives are divided into (1) *nitrogenous*, viz.: creatine the most abundant (0·2 to 0·3 p.c. Voit, *Z. B.* 4, 77; increased by starvation, Demant, *Zeit. physiol. Chem.* 3, 387); creatinine, xanthine, hypoxanthine, and carnine; (2) *non-nitrogenous*: viz. fats, glycogen (C. Bernard, *C. R.* 48, 673, Nasse, *Pf.* 2, 97, Brücke, *Sitz. W.* 63, 214, Abeles, *Med. Jahrbücher*, 1877, 551, Külz, *Z. B.* 22, 161); inosite (Scherer, *Annal. d. Chem. u. Pharm.* 73, 322, Gauret a. Villiers, *C. R.* 86, 486); sarcolactic acid and lactic acid. In addition to the ferments already described (pepsin and myosin-ferment), muscle also contains an amylolytic ferment (Nasse, *l.c.*). Fresh muscle yields on ignition 1 to 1·5 p.c. of mineral matters, of which the most important constituents are potassium and phosphoric acid (*cf.* Hofmann, *l.c.*, and Bunge, *Zeit. physiol. Chem.* 9, 60).

Contraction of muscle.—The processes that occur in resting muscle are twofold: one a change of matter; this chemical tonus, as it may be called, is lessened by curare poisoning, by which the influence of the nervous system over the muscular is shut off: and the other set of changes is a change of the potential energy of chemical affinity into actual energy evidenced by the production of heat. On the contraction of a muscle, there is a sudden acceleration of both these changes; viz. an increase in chemical decomposition, and in the conversion of potential into actual energy which is evidenced as heat, electrical inequality, and mechanical motion. It is with the former of these, the chemical changes, that we have here specially to deal. They may be briefly summarised as follows:—

1. *Change in reaction.*—The muscle ordinarily alkaline becomes acid, as it does during *rigor mortis*; and the acid produced is lactic acid. The acidity can be easily demonstrated by litmus paper (Kühne). It is the accumulation of this and other waste products, including alkaloidal substances (Mosso), in the muscle which produces fatigue.—2. There is a relative increase of water (Ranke, *Tetanus*, cap. 2, p. 63). 3. The extractives soluble in water decrease; those soluble in alcohol increase (Helmholtz, *Arch. f. Anat. u. Phys.* 1845. 72; Ranke, *l.c.* 141; Heidenhain, *Pf.* 3, 574).—4. Glycogen diminishes and sugar increases in amount (Ranke, Nasse, *Pf.* 2, 97).—5. Creatine diminishes and creatinine increases in amount (Sarokin, *Virchow's Archiv*, 28; Voit, *Z. B.* 4, 77).—6. Tetanised muscle is not able to oxidise pyrogallic acid as resting muscle is (Grützner, *Pf.* 7, 255).—7. Nitrates are converted into nitrites (Gschleidlen, *ibid.* 8, 506).—8. *Gaseous changes*: The amount of oxygen used and of carbonic acid given out increases; the amount of carbonic acid exhaled is never equal in amount to that of the oxygen absorbed; and during tetanus, *i.e.* continuous contractions, the quotient $\frac{CO_2 \text{ exhaled}}{O \text{ absorbed}}$ increases. The following numbers from Ludwig and Schmidt illustrate the differences in the gases of the blood leaving muscle during rest and activity:

Venous blood.	Oxygen less than arterial blood.	CO_2 more than arterial blood.
Muscle at rest	9 p.c.	6·71 p.c.
„ during activity	12·26 „	10·79 „

(For analyses of the gases of muscle *v.* Hermann, *Stoffwechsel der Muskeln*; Ludwig, Sezelkow u. A. Schmidt, *Sitz. W.* 45; *Sitzungsb. der math.-phys. Classe der k. s. Gesellsch. der Wissensch.* 20, 12; *Arbeiten aus d. physiol. Anstalt zu Leipzig*, 1869. Full references of the literature on the effect of muscular exercise on respiration are given by Gamgee, *Physiol. Chem.* p. 382).

No trustworthy results exist which show that the proteids of muscle undergo any change during activity; and the effect of muscular exercise on the nitrogeneous excreta is very small; the increase of urea being quite out of proportion to the amount of work done. (For experiments on dogs *v.* Voit, *Untersuchungen über den Einfluss*

der Kochsalzes des Kaffee's und der Muskelbewegungen auf den Stoffwechsel, München, 1860. For experiments on man, *v.* Fick u. Wislicenus, *Vierteljahresschrift d. nat. Gesellsch. in Zurich*, 10; Parkes, *Pr.* 15, 339; 16, 44; E. Smith, *Phil. Trans.* 1862, 747; A. Flint, *Journ. of Anat. and Physiol.* 12, 91; F. W. Pavy, *Lancet*, 1876; North, *Journ. of Physiol.* 1, 171; *Pr.* 39, 443).

Hermann's theory of muscular contraction.—No oxygen is obtainable from muscle *in vacuo*. Hermann considers that the formation of carbonic acid is not simply the result of oxidation, but due to the splitting of a complex substance *inogen* into carbonic acid, lactic acid, and a gelatinous proteid myosin; the same occurs, but to a greater extent, in *rigor mortis*; the process of clotting especially going further. Each contraction is thus the partial death of the muscle. This is supported by the fact that the electrical conditions, like the chemical, are similar in dead and contracted muscle. There is, however, no evidence to prove that a clot of myosin is formed at each contraction. Bernstein has more recently formulated a theory in which he seeks to show that changes in form, in composition, and in electrical potential are all parts of the same mechanism (*Untersuch. a. d. physiol. Inst. Halle*, 1888). See also Burdon Sanderson (*Reports Brit. Ass.* 1889). W. D. H.

MUSTARD OILS. The seeds of black mustard (*Sinapis nigra*) contain potassium myronate, which, in presence of water, is decomposed by the ferment myrosin (also present in the seeds) into $KHSO_4$, glucose, and allyl thiocarbimide or oil of mustard. Small quantities of crotonitrile and free sulphur are formed in the hydrolysis (Förster, *L. V.* 1888, 209). Black mustard seed also contains a fixed oil which yields stearic and erucic acids on saponification (Darby, *A.* 69, 1). The allyl thiocarbimide amounts to about ·5 p.c. of the weight of the seeds. White mustard seed (*Sinapis alba*) yields on pressure 36 p.c. of a fixed oil containing glyceryl erucate. The seeds also contain a glucoside, sinalbin $C_{30}H_{44}N_2S_2O_{16}$ which is decomposed by myrosin into sinapin sulphate $C_{16}H_{23}NO_5H_2SO_4$, glucose, and an oil C_8H_7NSO (Will, *Z.* [2] 7, 89; *A.* 199, 150). The term 'mustard oil' has been applied not only to the fixed and volatile oils from mustard seed, but also to all compounds of the form RN:CS where R denotes a hydrocarbon radicle. In this dictionary these compounds are described as thiocarbimides. Thus the essential oil of black mustard is described as allyl thiocarbimide.

MYCOMELIC ACID $C_4H_4N_4O_2\frac{1}{2}aq.$ When alloxan is gently warmed with aqueous NH_3 it forms a yellow solution which deposits on cooling a transparent jelly of ammonium mycomelate, from the hot aqueous solution of which salt H_2SO_4 ppts. mycomelic acid (Liebig a. Wöhler, *A.* 26, 304). Mycomelic acid is also produced by boiling azulinic acid with water (Emmerling a. Jacobsen, *B.* 4, 951) and by heating uric acid with water at 180° (Wöhler, *A.* 103, 118; Hlasiwetz, *A.* 103, 211). Gelatinous pp., drying up to a loose yellow powder. Reddens litmus. Almost insol. cold water, m. sol. hot water and alkalis, insol. alcohol and ether.—$AgC_4H_3N_4O_2$.

MYCOSE *v.* TREHALOSE and SUGARS.

MYOCTONINE $C_{27}H_{30}N_2O_8$ 5aq. [144°]. Occurs, together with lycaconitine, in *Aconitus lycoctonum* (Dragendorff a. Salomonovitch, *C. C.* 1886, 861). V. sol. chloroform and benzene, nearly insol. ether (difference from lycaconitine). Poisonous; ·01 g. killing a frog. Produces paralysis of the extremities of the motor nerves.

MYO-HÆMATIIN *v.* MUSCLE.

MYOSIN *v.* PROTEÏDS and MUSCLE.

MYRICIN $C_{46}H_{92}O_2$. [72°]. The portion of bees'-wax insoluble in alcohol. It is myricyl palmitate (Brodie, *A.* 71, 144). Light feathery crystals (from ether); readily saponified by alcoholic potash. According to Nafzger (*A.* 224, 251) myricin also contains an ether of oleïc acid.

MYRICYL ALCOHOL $C_{30}H_{62}O$ *i.e.* $C_{29}H_{59}.CH_2OH$. [85·5°]. Obtained by saponifying carnaüba wax, in which it occurs both free and combined (Maskelyne, *C. J.* 22, 87; Von Pieverling, *A.* 183, 344; Stürcke, *A.* 223, 294). According to Brodie (*A.* 71, 147) myricyl alcohol is obtained by saponifying the myricin of bees'-wax, but Schwalb (*A.* 235, 106) considers that the myricyl alcohol so obtained has the homologous formula $C_{31}H_{64}O$.

Properties. — Small white needles (from ether); almost insol. cold alcohol, ether, and benzene, but readily soluble in these liquids when hot. On heating with soda-lime at 200° it forms melissic acid $C_{29}H_{59}.CO_2H$ [90°].

DI-MYRICYL-AMINE $C_{60}H_{123}N$ *i.e.* $NH(C_{30}H_{61})_2$. [78°]. Formed by passing NH_3 for 24 hours over myricyl iodide at 120° (Von Pieverling, *A.* 183, 351). Crystalline; nearly insol. boiling alcohol and ether, v. sol. boiling benzene.

MYRICYL CHLORIDE $C_{30}H_{61}Cl$. [64·5°]. Formed from myricyl alcohol and PCl_5 (Von Pieverling, *A.* 183, 348). Waxy mass (from ether); sol. alcohol, benzene, and ligroïn.

MYRICYL CYANIDE $C_{30}H_{61}CN$. [75°]. Amorphous (Von Pieverling, *A.* 183, 357).

MYRICYL IODIDE $C_{30}H_{61}I$. [70°]. Formed by adding phosphorus and iodine in successive small portions to myricyl alcohol heated to 120° (Von Pieverling, *A.* 183, 347). Plates (from ligroïn); v. sol. hot alcohol and ether. When heated with finely-divided potassium it yields $C_{60}H_{122}$ [102°] (Hell a. Hägele, *B.* 22, 502).

MYRICYL MERCAPTAN $C_{30}H_{61}SH$. [94·5°]. An amorphous yellow powder, formed by the action of alcoholic KSH on myricyl chloride (Von Pieverling, *A.* 183, 349). Sl. sol. boiling ether, ligroïn, and alcohol.

MYRISTIC ACID $C_{14}H_{28}O_2$ *i.e.* $C_{13}H_{27}.CO_2H$. Mol. w. 228. [54°]. (250·5° i.V. at 100 mm.) Krafft, *B.* 12, 1668; 15, 1724; 16, 1719). S.G. $\frac{54}{4}$ ·8622. H.F. 107,000 (Von Rechenberg). H.C. 2,061,712 (Louguinine, *A. Ch.* [6] 11, 222). Occurs as glyceryl ether (myristin) in nutmeg-butter (from *Myristica moschata*) (Playfair, *P. M.* [3] 18, 202; *A.* 37, 153; Flückiger, *N. Rep. Pharm.* 24, 213), in Otoba-wax or otobite (from *Myristica otoba*) (Uricoechea, *A.* 91, 369), in dika-bread (prepared from the fruit of *Mangifera Gabonensis*) (Oudemans, *J. pr.* 81, 356) amounting to more than one-half of the fatty acids contained therein, in the oil of *Cyperus esculentus* (Hell a. Twerdomedoff, *B.* 22, 1742), in small quantity in cocoa nut-oil (Görgey, *A.* 66, 314), in common butter (Heintz, *P.* 87, 267; 90, 137; 92, 429, 588; *J. pr.* 66, 1), in croton-oil

(Schlippe, *A.* 105, 1), and in Bicuhyba-wax (from *Myristica Bicuhyba*). It occurs in combination with æthal in spermaceti (Heintz, *A.* 92, 291). It also occurs in the seeds of *Nigella sativa* (Greenish, *Ph.* [3] 11, 909, 1013) and in lycopodium spores (from *Lycopodium clavatum*) (Langer, *Ar. Ph.* [3] 27, 241, 289). Myristic acid is formed by fusing stearolic acid with potash (Marasse, *B.* 2, 361).

Preparation.—By saponifying nutmeg-butter or myristin and distilling the acid obtained under reduced pressure.

Properties.—Shining laminæ (from alcohol); insol. water, v. sol. hot alcohol and ether. A mixture of 30 pts. myristic acid and 70 pts. lauric acid melts at 35°. Nitric acid (S.G. 1·5) readily oxidises it, forming various products (Uverdlinger, *B.* 19, 1893). The dry distillation of the calcium salt yields myristone. Distillation with MeOH *in vacuo* yields tridecane (Mai, *B.* 22, 2133).

S a l t s.—KA′: crystalline soap; v. sol. water and alcohol, insol. ether (Playfair).—NaA′.—BaA'_2: minute laminæ; v. sl. sol. water and alcohol.—$MgA'_2$3aq: minute needles (Heintz).—CuA'_2: minute bluish-green needles.—PbA'_2: amorphous mass.—$(PbA'_2)_4Pb(OAc)_2$: insoluble powder.—AgA′: amorphous powder.

Ethyl ether EtA′. [11°] (Lutz, *B.* 19, 1433). (295°). S.G. (liquid) ·864 (Playfair). Formed from the acid, alcohol, and HCl. Crystals; sl. sol. alcohol and ether, m. sol. ligroïn.

Glyceryl ether $C_{45}H_{86}O_6$ or $C_3H_5A'_3$. *Myristin. Trimyristin.* [55°] and [49°]. H.C. 6,601,895 (Louguinine). Occurs in the cases mentioned above, and also in large quantity in the fat of the oil-nut (*Myristica surinamensis*) (Reimer a. Will, *B.* 18, 2011), and to the extent of 1·5 or 2 p. c. in cochineal (Liebermann, *B.* 18, 1975). It is best obtained by extracting powdered nutmeg with ether (Masino, *G.* 10, 72). Brilliant leaflets; v. sol. warm alcohol, ether, benzene, and $CHCl_3$, nearly insol. cold alcohol. It forms two varieties, melting at 55° and at 49°, which are interchangeable by heating 1° above the melting-point for half-a-minute (R. a. W.; L.).

Phenyl ether $A'C_6H_5$: [36°]; (230° at 15 mm.).

p-Tolyl ether $A'C_7H_7$: [39°]; (240° at 15 mm.) (Krafft a. Bürger, *B.* 17, 1379).

Chloride $C_{13}H_{27}.COCl$. [−1°]. (168° at 15 mm.). Colourless liquid (Krafft a. Bürger).

Amide $C_{13}H_{27}.CONH_2$. [102°]. Formed by heating the glyceryl ether with alcoholic NH_3 at 100° (Masino, *A.* 202, 173) or the ethyl ether with aqueous NH_3 at 250°. Formed also by heating the ammonium salt at 230° in a sealed tube (Reimer a. Will, *B.* 18, 2016), and by the action of NH_3 on the chloride (Krafft a. Stauffer, *B.* 15, 1730). Plates (from alcohol); v. sol. benzene, alcohol, and chloroform, sl. sol. ether, insol. water. Bromine and NaOHAq forms $C_{13}H_{27}.NH.CO.NH.CO.C_{13}H_{27}$ [103°].

Anilide $C_{13}H_{27}.CONHPh$. [84°]. Prepared by boiling the acid with aniline for some days (Masino, *G.* 10, 75). Silky needles; sol. ether, benzene, and chloroform.

Nitrile $C_{13}H_{27}.CN$. [19°]. (226·5° at 100 mm.). S.G. $\frac{19}{4}$ ·8281; $\frac{99}{4}$ ·7724. Formed from the amide by distilling with P_2O_5 (Krafft a. Stauffer, *B.* 15, 1730).

Myristic-benzoic-anhydride $C_{13}H_{27}.CO.O.CO.C_6H_5$. [38°]. Formed from BzCl and potassium myristate (Chiozza a. Malerba, *A.* 91, 102). Silky laminæ; m. sol. ether.

Bromo-myristic acid $C_{14}H_{27}BrO_2$. [31°]. Formed from myristic acid, amorphous P and Br (Hell a. Twerdomedoff, *B.* 22, 1745). Needles, insol. water, sol. alcohol and ether.

Tetra-bromo-myristic acid $C_{14}H_{24}Br_4O_2$. Formed from myristolic acid and Br (Masino).

Amido-myristic acid $C_{14}H_{27}(NH_2)O_2$. [253°]. Formed from bromo-myristic acid and alcoholic NH_3 (H. a. T.). Needles, insol. alcohol.

Phenyl-amido-myristic acid $C_{14}H_{27}(NHPh)O_2$. [143°]. Formed from bromo-myristic acid and aniline (H. a. T.). White mass, insol. water, sl. sol. benzene, v. sol. alcohol. Gives a dark-green pp., with cupric acetate in hot alcoholic solution.

Oxy-myristic acid $C_{14}H_{27}(OH)O_2$. [51·5°]. Formed by boiling bromo-myristic acid with excess of aqueous NaOH (H. a. T.). Crystalline; insol. hot water, v. sol. alcohol and benzene.—BaA'_2: flocculent pp., sl. sol. cold water, v. sl. sol. hot water.—AgA′: white pp.

MYRISTIC ALDEHYDE $C_{13}H_{27}CHO$. [53°]. (169° at 22 mm.). Crystalline solid. Prepared by dry distillation of a mixture of calcium myristate and formate (Krafft, *B.* 13, 1415).

Isomeride:—TETRADECOIC ALDEHYDE.

MYRISTICIN $C_{12}H_{14}O_3$. [30°]. (c. 145° at 10 mm.). S.G. $\frac{25}{}$ 1·1501. Occurs in oil of mace (Semmler, *B.* 23, 1803). Yields benzene when distilled with zinc-dust. Bromine forms $C_{12}H_{14}Br_2O_3$ [105°].

MYRISTICOL $C_{10}H_{16}O$. (212°–218°). The chief constituent of the volatile oil of nutmeg (Gladstone, *C. J.* 25, 11; Wright, *C. J.* 26, 549, 686). Resinified by heat. P_2S_5 converts it into cymene. PCl_5 yields a chloride, $C_{10}H_{15}Cl$ [100°], slowly split up on boiling into HCl and cymene.

MYRISTIN *v. Glyceryl ether* of MYRISTIC ACID.

MYRISTOLIC ACID $C_{14}H_{24}O_2$. [12°]. Formed by passing chlorine into myristic acid heated to 100°, and decomposing the product with alcoholic potash (Masino, *A.* 202, 175). Oil. Not solidified by nitrous fumes. Gives Pettenkofer's reaction with sugar and H_2SO_4.

MYRISTONE $C_{26}H_{54}CO$. [76°]. S.G. $\frac{80}{4}$ =·801; $\frac{100}{4}$ =·792. Silvery plates. Formed by distilling calcium or barium myristate with lime (Overbeck, *P.* 86, 591; *A.* 84, 290; Krafft, *B.* 15, 1713). Does not combine with $NaHSO_3$.

Oxim $C_{26}H_{54}.C:NOH$. [51°]. Amorphous; sl. sol. alkalis (Spiegler, *B.* 17, 1575; *M.* 5, 242).

MYRISTONITRILE *v. Nitrile* of MYRISTIC ACID.

MYRONIC ACID $C_{10}H_{19}NS_2O_{10}$ (from μύρον, a fragrant ointment). Occurs as potassium salt in the seeds of black mustard (Bussy, *J. Ph.* 16, 39; Ludwig a. Lange, *Z.* 1860, 430, 577; Will a. Körner, *A.* 125, 257), in horse-radish (Winckler, *J.* 1849, 436), in rape seed (*Brassica rapa*), and in turnip seed (*Brassica napus*) (Ritthausen, *J. pr.* [2] 24, 273). This salt may be obtained by boiling mustard seeds (1 pt.) with alcohol (6 pts.), macerating the residue with cold water, and evaporating the aqueous extract after addition of a little $BaCO_3$. The free acid may be

obtained by adding tartaric acid to a solution of the potassium salt, evaporating, and extracting with alcohol. Syrup, readily decomposed by heat. Its aqueous solution gives off H_2S on boiling. An aqueous solution of myrosin splits it up into glucose, allyl thiocarbimide, and H_2SO_4. Boiling baryta-water forms a pp. of $BaSO_4$, with evolution of allyl thiocarbimide. Caustic potash solution acts vigorously, yielding allyl cyanide, NH_3, glucose, and allyl thiocarbimide. Conc. HCl sets free H_2SO_4; boiling dilute H_2SO_4 yields H_2S, glucose, H_2SO_4, and NH_3. Zinc and HClAq give off H_2S.

Salts.—KA′. Groups of silky needles (from alcohol) or glassy prisms (from water); v. e. sol. water, nearly insol. alcohol, insol. ether. Tastes bitter. Its solution is hydrolysed by myrosin:

$KC_{10}H_{18}NS_2O_{10} = C_6H_{12}O_6 + C_3H_5NCS + KHSO_4$.

The hydrolysis is not brought about by emulsion, yeast, or saliva. Water at 115° yields allyl cyanide, H_2S, and sulphur. Silver nitrate solution gives a pp. $C_4H_5NSAg_2SO_4$.—BaA′$_2$ (at 100°): plates, v. sol. water.

MYROSIN. A proteïd ferment contained in the seeds of black and white mustard, and of many other cruciferous plants. It may be obtained by exhausting white mustard with cold water, evaporating below 40° to a syrup, and ppg. by alcohol (Bussy, *J. Ph.* 26, 44; Winckler, *Jahrb. pr. Pharm.* 3, 93). Its aqueous solution is coagulated by heat and by alcohol, when it loses its hydrolytic power, but it recovers this after a day's immersion in water. It does not hydrolyse amygdalin.

MYROXOCARPIN $C_{48}H_{70}O_6$. [115°]. Deposited in crystals from an alcoholic solution of white balsam of Peru (Stenhouse, *A.* 77, 306). Trimetric crystals; $a:b:c = 1:\cdot936:\cdot755$. Insol. water, v. sol. hot alcohol and ether. Does not dissolve in acids or alkalis.

MYRRH. A gum-resin which exudes from *Balsamodendron myrrha*, a shrub growing in Arabia and Abyssinia. The resin yields protocatechuic acid and pyrocatechin on potash-fusion (Hlasiwetz a. Barth, *J.* 1866, 630). Besides resin and gum (Bückner, *N. Rep. Pharm.* 16, 76), myrrh contains a small quantity of an essential oil, boiling about 266°, S.G. $\frac{15\cdot5}{}$ 1·0189, μ_A 1·5196 at 7·5°; μ_D 1·5278; μ_H 1·5472 (Gladstone, *C. J.* 17, 11). The oil quickly resinifies when exposed to atmospheric oxidation. It contains $C_{22}H_{32}O$ (263°) (Flückiger, *B.* 9, 471). According to Köhler (*Ar. Ph.* 228, 291) myrrh contains a gum $C_6H_{10}O_5$, a resin $C_{26}H_{31}O_2(OH)_3$, two dibasic acids $C_{13}H_{16}O_8$ and $C_{26}H_{32}O_9$, and 7 p.c. of an essential oil $C_{10}H_{14}O$.

MYRTLE OIL. A volatile oil obtained from the berries and leaves of the myrtle (*Myrtus communis*) (Riegal, *Pharm. Centr.* 1850, 319). It contains a terpene $C_{10}H_{16}$ (160°–170°), S.G. $\frac{15\cdot5}{}$ ·891, μ_A 1·462 at 18°, μ_D 1·468, μ_H 1·488 (Gladstone, *J.* 1863, 548). Jahns (*Ar. Ph.* [3] 27, 174) found in Spanish oil of myrtle pinene $C_{10}H_{16}$ (159°) $[\alpha]_D = 36\cdot8$, and cineol (170°).

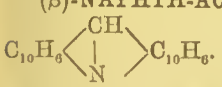
MYTILOTOXINE $C_6H_{15}NO_2$. Occurs in mussels (*Mytilus edulis*) and in putrid flesh (Brieger, *Die Ptomaïne*; Gautier, *Bl.* [2] 48, 13). Its hydrochloride crystallises in tetrahedra, and is very poisonous, but gradually decomposes, losing its poisonous properties.—B′HAuCl$_4$. [182°]. Minute cubes.

N

NANDININE $C_{19}H_{19}NO_4$. Occurs in the root-bark of *Nandina domestica* of Japan (Eijkman, *R. T. C.* 3, 197). White amorphous powder, insol. water, v. sol. alcohol, ether, benzene, and chloroform. Poisonous. Gives the alkaloidal reactions. H_2SO_4 forms a reddish-violet colour, changed by a drop of HNO_3 to an intense blue. Nitric acid gives a green colour changing to brown.—B′$_2$H$_2$PtCl$_6$: turned blue by H_2SO_4.

NAPHTHA *v.* PETROLEUM.

(β)-NAPHTH-ACRIDINE $C_{21}H_{13}N$ *i.e.*



[216°]. Formed by the action of methylal, and HCl upon (β)-naphthyl-amine (Reed, *J. pr.* [2] 34, 160; 35, 317). Long, straw-yellow, needles, v. sol. alcohol, v. sl. sol. ether. The alcoholic solution fluoresces dark-blue.

Nitrate B′HNO$_3$: small needles.

Picrate B′C$_6$H$_2$(NO$_2$)$_3$OH: amorphous.

Derivative v. PHENYL-NAPHTHACRIDINE.

NAPHTHALDEHYDE *v.* NAPHTHOIC ALDEHYDE.

NAPHTHALENE $C_{10}H_8$. *Naphthalin.* Mol. w. 128. [80·2°] (Reissert, *B.* 23, 2243); [80°] (Landolt, *Z. P. C.* 4, 349); [79·5°] (Vohl); [79°] (Lossen a. Zander, *A.* 225, 111); [80·06°] (Mills, *P. M.* [5] 14, 27). (218°) at 760 mm. (Vohl, *J. pr.* 102, 29; Crafts, *Bl.* [2] 39, 282); (217°) at 740 mm. S.G. $\frac{15}{}$ 1·152 (V.); $\frac{4}{}$ 1·145 (Schröder, *B.* 12, 1613). S.G. (liquid) $\frac{79}{}$ ·978 (Kopp, *A.* 95, 329); $\frac{79}{0}$ ·982 (L. a. Z.). H.C.v. 1,232,400. H.C.p. 1,233,600 (Stohmann); 1,245,000 (Berthelot a. Vieille, *Bl.* [2] 47, 863); 1242000 (Berthelot, *A. Ch.* [6] 13, 302, 326). H.F. −17,600 (Stohmann, Kleber, a. Langbein, *J. pr.* [2] 40, 90); −29,000 (Berthelot a. Vieille, *A. Ch.* [6] 10, 442); −42,000 (von Rechenberg). S.V. 149·2 (L. a. Z.); 148 (Lossen, *A.* 254, 53); 145·46 (Ramsay); S.V.S. 130·61 (Schiff). R_∞ 74·12 in a 6·66 p.c. alcoholic solution (Kanonnikoff); 71·78 (Nasini a. Bernheimer, *G.* 14, 153; 15, 93). S. (toluene) 32 at 16·5°; S. (alcohol) 5·29 at 15° (Biechi, *B.* 12, 1978). Its absorption in the ultra-violet spectrum has been studied by Hartley (*C. J.* 39, 161).

Occurrence.—In petroleum from Rangoon (Warren a. Storer, *Mem. Amer. Acad.* 9, 208). In coal-tar, from which it may be obtained by shaking the fraction 180°–220° with aqueous NaOH and then with dilute H_2SO_4, and distilling the residue alone or with steam (Garden, *Thomson's Annals*, 15, 74; Faraday, *Tr.* 1826; Kidd, *B. J.* 3, 186; Reichenbach, *S.* 61, 175; 68, 233).

Formation.—1. A product of the passage through a red-hot tube of the vapour of the fol-

lowing substances:—petroleum, alcohol (Reichenbach, *B. J.* 12, 307), ether, acetic acid, essential oils, toluene (Ferko, *B.* 20, 660), xylene, ψ-cumene, a mixture of ethylene with benzene, with styrene, with anthracene or with chrysene (Berthelot, *Bl.* [2] 6, 272, 279), ethylene alone, acetylene, a mixture of benzene and acetylene (Berthelot, *Bl.* [2] 7, 218, 278, 306), oil of turpentine (Schulz, *B.* 9, 548), wood-tar (Letney a. Atherberg, *B.* 11, 1210, 1222).—2. By passing over red-hot quicklime the vapour of the bromide of phenyl-butylene derived from benzyl bromide, allyl iodide and sodium (Aronheim, *B.* 6, 67; *A.* 171, 233).—3. By passing the vapour of isobutyl-benzene over heated lead oxide (Wreden a. Znatovitch, *B.* 9, 1606).—4. By distilling colophony and gum-benzoin with zinc-dust (Ciamician, *B.* 11, 269).—5. By heating dimethyl-aniline (1 pt.) with bromine (1 pt.) at 115° (Brunner a. Brandenburg, *B.* 11, 697).—6. By oxidising pyrenic acid and distilling the resulting naphthalene tetra-carboxylic acid with slaked lime (Bamberger a. Philip, *B.* 19, 1999).—7. By hydrolysis of its sulphonic acids: this takes place when superheated steam is passed through a solution of naphthalene (β)-sulphonic acid in dilute H_2SO_4 at 135° (Armstrong a. Miller, *C. J.* 45, 148).

Synthesis.—By dry distillation of the silver salt of tetra-hydro-naphthalene di-carboxylic acid $C_6H_4\left<\begin{matrix}CH_2.CH(CO_2H)\\ |\\ CH_2.CH(CO_2H)\end{matrix}\right.$ which acid is formed by the action of o-xylylene bromide $C_6H_4\left<\begin{matrix}CH_2.Br\\ CH_2.Br\end{matrix}\right.$ on di-sodio-ethane tetra-carboxylic-ether $C_2Na_2(CO_2Et)_4$, and boiling the product with alcoholic KOH. Naphthalene is also formed by passing the tetra-hydro-naphthalene di-carboxylic acid through a red-hot tube (Baeyer a. Perkin, *B.* 17, 448) (*v.* NAPHTHOL and NAPHTHALENE DERIVATIVES, *Constitution of*).

Purification.—Commercial naphthalene may be purified by sublimation. It may also be purified by repeatedly heating with a little H_2SO_4 (best with MnO_2) at 180° and distilling with steam (Stenhouse a. Groves, *B.* 9, 683).

Properties.—Monoclinic tables, insol. cold, almost insol. hot, water, v. sol. alcohol, ether, fatty and essential oils, and HOAc. Volatile with steam; 1 pt. distilling over with about 570 pts. of water (Naumann, *B.* 4, 646; 10, 2014, 2100; 11, 33). Burns with smoky flame. Boiling naphthalene dissolves S, P, and the sulphides of As, Sb, and Sn; it also dissolves indigo, iodine, $HgCl_2$, HgI_2, and As_2O_3.

Reactions.—1. *Chlorine* forms derivatives by substitution and by addition (Laurent, *A. Ch.* 49, 218; 52, 275; 69, 214).—2. *Bromine* forms derivatives by substitution.—3. *Nitric acid* forms nitro- and di-nitro-naphthalene.—4. The vapour of *aqua regia* in the cold forms $C_{10}H_8Cl_4$ and $C_{10}H_7Cl_5$ (Bunge, *B.* 4, 289).—5. *Phosgene* has no action (Berthelot, *Bl.* [2] 13, 301).—6. The vapour passed through a *red-hot tube* yields carbon, methane (Kletzinsky, *J.* 1865, 561), and dinaphthyl (Ferko, *B.* 20, 662). When passed through a red-hot tube together with hydrogen it is mainly unaltered, but yields some acetylene and benzene (Berthelot, *Bl.* [2] 6, 281). When passed together with acetylene through a red-hot tube it yields much anthracene. At a white heat it reacts with benzene forming anthracene (Berthelot). When passed through a red-hot tube containing charcoal it yields some dinaphthyl. When passed with ethylene through a red-hot tube it yields acenaphthene, phenanthrene, and dinaphthyl (Ferko, *B.* 20, 662).—7. Saturated HIAq at 280° yields the dihydride $C_{10}H_{10}$, and finally ethyl and di-ethyl-benzene and decane (Berthelot, *J.* 1867, 709). When heated with conc. HIAq and red phosphorus the products are naphthalene hexahydride, and oily $C_{10}H_{18}$ (173°–180°) and $C_{10}H_{20}$ (153°–158°) (Wreden, *A.* 187, 164).—8. Boiling aqueous $KMnO_4$ oxidises it to phthalic acid. Aqueous $K_2Cr_2O_7$ and H_2SO_4 yield phthalic acid and dinaphthyl (Lossen, *A.* 144, 71). Dilute HNO_3 at 130° also yields phthalic acid (Beilstein a. Kurbatow, *A.* 202, 215). A mixture of CrO_3 and HOAc oxidises it to naphthoquinone. Oxidation with MnO_2 and H_2SO_4 yields dinaphthyl and a resinous acid $C_{20}H_{14}O_4$, which forms the amorphous salts $Pb_3A'''_2$, $PbHA'''$, and Ag_2HA''' (Lossen).—9. $KClO_3$ and H_2SO_4 form phthalic acid, di-chloro-naphthalenes, and syrupy chloro-oxy-naphthalic acid $C_{10}H_7ClO_5$ (Hermann, *A.* 151, 79).—10. CrO_2Cl_2 yields di-chloro-naphthoquinone.—11. Aqueous *hypochlorous acid* forms $C_{10}H_8(HOCl)_2$ crystallising in prisms, sl. sol. water, converted by alcoholic potash into $C_{10}H_8(OH)_4$ which crystallises in prisms, almost insol. water, v. sol. alcohol, and forms an insoluble lead compound $Pb_2C_{10}H_8O_4$ (dried at 100°) and a sulphonic acid which yields a crystalline calcium salt $CaC_{10}H_{10}S_2O_{10}$ (Neuhoff, *A.* 136, 342).—12. When heated with excess of $AlCl_3$ it forms benzene and hydrides of naphthalene. At 160° iso-dinaphthyl is formed (Friedel a. Crafts, *Bl.* [2] 39, 195; *C. R.* 100, 692).—13. *Methyl chloride* in presence of $AlCl_3$ forms $C_{16}H_{12}$ [181°] crystallising in plates, v. sol. hot ether, sl. sol. cold alcohol (Bischoff, *B.* 23, 1905; *cf.* Liebermann, *A.* 163, 122; Fürth, *B.* 16, 2171).—14. *Iodine* at 250° appears to form a compound $C_{40}H_{23}I$ (Bleunard a. Vrau, *C. R.* 94, 534).—15. On passing a mixture of *cyanogen* and naphthalene vapour through a red-hot tube there is formed the nitrile of (α)-naphthoic acid.—16. Heating with *chloride of sulphur* yields di-chloro-naphthalene (Laurent, *A.* 76, 298).—17. *Nitric peroxide* forms nitro- and di-nitro-naphthalene and, at 100°, the compounds $C_{10}H_8O_4$ [225°] and $C_{10}H_4O_4$ [131°] (Leeds, *Am. Ch.* 2, 283).—18. When heated with *potassium* it forms a black powder $C_{10}H_8K_2$, which is decomposed by water, yielding KOH and $C_{10}H_{10}$ (Berthelot, *Bl.* [2] 7, 110).—19. Naphthalene (2 pts.) fused with *antimonious chloride* (3 pts.) yields on cooling deliquescent crystals of $(C_{10}H_8)_23SbCl_3$ (W. Smith, *C. J.* 41, 411).—20. Naphthalene taken internally appears in the urine as (β)-naphthol and (β)-naphthoquinone (Edlefsen, *C. C.* 1888, 1007).

Combinations with nitro-compounds.—$C_{10}H_8C_6H_4(NO_2)_2$ [1:3]. [53°]. Prisms (Hepp, *A.* 215, 379).—$C_{10}H_8C_6H_4(NO_2)_2$ [1:4]. [119°]. White needles, v. sl. sol. alcohol, separated into its components by distillation with steam.—$C_{10}H_8C_6H_3Cl(NO_2)_2$ [1:2:4]. [78°]. Long white needles (from alcohol), decomposed by heating with potash or aniline, naphthalene being set free (Willgerodt, *B.* 11, 603).—$C_{10}H_8C_6H_3(NO_2)_3$. [152°]. White needles, deposited from a mixture

of the alcoholic solutions of naphthalene and tri-nitro-benzene (Hepp, *A.* 215, 377). — $C_{10}H_8C_6H_2Cl(NO_2)_3$. [96°]. Flat canary-yellow needles (Liebermann a. Palm, *B.* 8, 378).— $C_{10}H_8C_6H_3Me(NO_2)_2$. [61°]. Formed by mixing naphthalene and di-nitro-toluene dissolved in benzene (Hepp). — $C_{10}H_8C_6H_2Me(NO_2)_3$. [98°]. Formed from (α)-tri-nitro-toluene and naphthalene in alcoholic solution (Hepp). Needles.— $C_{10}H_8C_6H_2Me(NO_2)_3$. [100°]. Formed from (β)-tri-nitro-toluene and naphthalene. Yellowish needles (from alcohol). — $C_{10}H_8C_6H_2Me(NO_2)_3$. [89°]. Formed from (γ)-tri-nitro-toluene (H.).— $C_{10}H_8C_6H_2(NO_2)_3NH_2$. [169°]. Orange prisms. $C_{10}H_8C_6H_3(NO_2)_2OH$. Yellow needles (Gruner, *Z.* 1868, 213). — $C_{10}H_8C_6H_2(NO_2)_3OH$. [73°]. Formed from (β)-tri-nitro-phenol and naphthalene (Henriques, *A.* 215, 332). V. e. sol. alcohol.—$C_{10}H_8C_6H_2(NO_2)_3OH$. [100°]. Formed from naphthalene and (γ)-tri-nitro-phenol (Henriques). Golden needles (from alcohol), sl. sol. alcohol.—$C_{10}H_8C_6HMe(NO_2)_3OH$. [106°]. From naphthalene and tri-nitro-*o*-cresol (Nölting a. Collin, *B.* 17, 271). Yellowish needles (from acetone).—$C_{10}H_8C_6HMe(NO_2)_3OH$. [127°]. From naphthalene and tri-nitro-*m*-cresol (Nölting a. Salis, *B.* 15, 1862).—$C_{10}H_8C_4H_2(NO_2)_2S$. [50°]. Yellow needles (from benzene). Formed from naphthalene and di-nitro-thiophene (Rosenberg, *B.* 17, 1778).

Picric acid compound $C_{10}H_8C_6H_2(NO_2)_3OH$. [149°]. Golden-yellow monoclinic needles, sol. alcohol, ether, and benzene. Slowly separated into its components by boiling water.

Naphthalene dichloride $C_{10}H_8Cl_2$. Formed by passing chlorine over naphthalene. $KClO_3$ and HCl may also be used (E. Fischer, *B.* 11, 735, 1411). Oil, miscible with ether, m. sol. alcohol. Begins slowly to decompose at 40°–50° into HCl and chloro-naphthalene. Alcoholic potash also converts it into chloro-naphthalene. Sodium or sodium-amalgam at 150° converts it into naphthalene.

Naphthalene tetrachloride $C_{10}H_8Cl_4$. Mol. w. 270. [182°]. R_∞ 105·35 in a 2·39 p.c. chloroform solution (Kanonnikoff). Formed by passing a rapid current of chlorine over naphthalene until the product, after having become liquid, thickens again, when it is washed with ether and crystallised from benzene. Formed also by treating naphthalene with a saturated solution of chlorine in $CHCl_3$ (Grimaux, *B.* 5, 222; Schwarzer, *B.* 10, 379), by chlorinating naphthalene in direct sunlight (Leeds a. Everhart, *A. C. J.* 2, 205), and by the action of $KClO_3$ and HCl on naphthalene (Fischer, *B.* 11, 735). Large monoclinic prisms, insol. water, sl. sol. alcohol, m. sol. ether, v. sol. benzene and petroleum. Sublimes at 225°–230°. Decomposed on distillation into HCl and (α)- and (β)-di-chloro-naphthalenes (Krafft a. Becker, *B.* 9, 1088). Alcoholic potash forms (α)- and some (ι)-di-chloro-naphthalene reconverted into naphthalene on digesting with iron (Zinin, *B.* 4, 288). Boiling dilute $AgNO_3$ slowly converts it into $C_{10}H_8(ClO)_2$ [196°]. When boiled with water it yields $C_{10}H_8Cl_2(OH)_2$, which crystallises in prisms (from ether) [156°], S. 3·3 at 100°, and is decomposed on distillation with HCl into water, HCl, and chloro-naphthol. Zn and H_2SO_4 reduce it to (α)-naphthol. It gives rise to $C_{10}H_8Cl_2(OAc)_2$ [131°] and $C_{10}H_8Cl_2(OBz)_2$ [150°].

The existence of an isomeric naphthalene tetra-chloride [118°] has been denied by Atterberg (*B.* 11, 1223; *cf.* Fischer, *B.* 11, 735).

Naphthalene tri-chloro-bromide $C_{10}H_8Cl_3Br$. Formed from the tetrachloride and bromine; after 48 hours the product is washed with warm alcohol and crystallised from ether. Prisms.

Naphthalene dihydride $C_{10}H_{10}$. [15·5°]. (212°). V.D. 4·7 (calc. 4·56). Occurs in heavy coal-tar oil (Berthelot, *Bl.* [2] 9, 288). Formed by heating naphthalene with conc. HIAq for a short time at 280° (Berthelot), and by reducing naphthalene dissolved in isoamyl alcohol with sodium (Bamberger a. Lodter, *B.* 20, 3073). Naphthalene dihydride is formed by distilling the bromide of naphthalene-tetra-hydride, or by heating it with alcoholic KOH (Graebe a. Guye, *B.* 16, 3032). It is likewise obtained by the action of sodium on an alcoholic solution of the nitrile of naphthoic acid (Bamberger a. Lodter, *B.* 20, 1704) and, as a by-product, when (β)-naphthylamine dissolved in isoamyl alcohol is reduced with sodium (Bamberger a. Müller, *B.* 21, 859).

Properties.—Tables. Does not combine with picric acid. By treatment with bromine dissolved in chloroform it is converted into the dibromide $C_{10}H_{10}Br_2$, which crystallises in thick colourless prisms, v. sol. alcohol and ether, and gives off HBr on heating (B. a. L.).

Naphthalene dihydride $C_{10}H_{10}$. (200°). Formed by distilling the dihydride of naphthoic acid with soda-lime (von Pechmann, *B.* 16, 517). Liquid.

Naphthalene tetrahydride $C_{10}H_{12}$ *i.e.* $C_6H_4{<}\begin{matrix}CH_2.CH_2\\ CH_2.CH_2\end{matrix}$. (205°) at 716 mm. S.G. $\frac{12}{}$ ·978. Formed by heating naphthalene with HIAq at 280° (Berthelot), with PH_4I at 180° (Baeyer, *A.* 155, 276), or by adding sodium to its solution in isoamyl alcohol (Bamberger a. Kitschelt, *B.* 23, 1561). Formed also by suspending the tetrahydride of (α)-naphthyl-hydrazine (1 pt.) in boiling water and allowing a solution of cupric sulphate (2 pts.) to drop in slowly; nitrogen is evolved, and the naphthalene tetrahydride may be separated from ppd. cuprous oxide by steam-distillation (Bamberger a. Bordt, *B.* 22, 631). Prepared by heating naphthalene (10 pts.) with HI (9 pts.) and amorphous phosphorus (3 pts.) for 8 hours at 220°–225°; the yield is good (8 pts.) (Graebe a. Guye, *B.* 16, 3028; *cf.* Graebe, *B.* 5, 678).

Properties.—Oil, slowly turning brown in air. Smells like naphthalene. Its solution in chloroform absorbs bromine, giving off HBr. It immediately decolourises an acid solution of $KMnO_4$, and is oxidised to $C_6H_4(CO_2H).CH_2.CH_2.CO_2H$ (Bamberger). The compound obtained by Baeyer and by Graebe yielded phthalic acid on oxidation by $KMnO_4$, and may perhaps not be identical with Bamberger's tetrahydride. When passed through a red-hot tube it is resolved into naphthalene and hydrogen.

Naphthalene hexahydride $C_{10}H_{14}$. *Hexahydronaphthalene.* (200°) (G. a. G.); (205° at 764 mm.) (A.). S.G. $\frac{0}{0}$ ·9419. C.E. (0°–26·3°) 000817 (Lossen a. Zander, *A.* 225, 112). R_∞ 71·15 (Nasini a. Bernheimer, *G.* 15, 93). S.V.

171·2 (Lossen, *A.* 254, 53). Formed by heating naphthalene with conc. HIAq and phosphorus (Wreden a. Znatovitch, *B.* 9, 278, 1606; *A.* 187, 164). Prepared by heating naphthalene (67 pts.) with HI (100 pts.) and amorphous phosphorus (30 pts.) for 10 hours at 240°–250° (Graebe a. Guye, *B.* 16, 3031); or by heating naphthalene (10 g.), amorphous phosphorus (3 g.), and HIAq (9 g., boiling at 127°) at 235° for 7½ hours (Agrestini, *G.* 12, 495). Liquid, which absorbs oxygen from the air. Does not combine with picric acid. Reacts with bromine, giving off HBr, and forming a product which is converted by alcoholic potash into $C_{10}H_9Br$ (270°).

Naphthalene octohydride $C_{10}H_{16}$. (185°–190°). S.G. $\frac{0}{0}$ ·910; $\frac{22}{0}$ ·892. Formed by heating naphthalene (5 g.) with HIAq (9 g. of S.G. 1·7) and red phosphorus for 15 hours at 260° (Guye, *Bn.* 2, 138). Liquid, smelling like oil of turpentine. Absorbs oxygen from the air.

References.—Tri-amido-, Amyl-, Bromo-, Bromo-iodo-, Bromo-nitro-, Chloro-, Chloro-nitro-, Iodo-, Iodo-nitro-, Nitro-, Di-oxy-, Methyl-, Ethyl-, Propyl-, Phenyl-, and Benzyl-naphthalenes. Also Naphthol, Naphthylamine, and Naphthylene-diamine.

NAPHTHALENE, CONSTITUTION OF, *v.* Dictionary of Applied Chemistry.

NAPHTHALENE ALDEHYDE *v.* Naphthoic aldehyde.

NAPHTHALENE-DIAMINE *v.* Naphthylene-diamine.

NAPHTHALENE-ARSONIC ACID *v. Organic compounds* of Arsenic.

NAPHTHALENE-AZO- compounds *v.* Azo-compounds and *Dis*-azo- compounds.

NAPHTHALENE CARBOXYLIC ACID *v.* Naphthoic acid.

Naphthalene *Peri*-dicarboxylic acid $C_{12}H_8O_4$ *i.e.* $C_{10}H_6(CO_2H)_2$ [1:1′]. *Naphthalic acid.* Mol. w. 216. [266°].

Formation.—1. By oxidising acenaphthene with $K_2Cr_2O_7$ and H_2SO_4 or HOAc (Behr a. Dorp, *B.* 6, 852; *A.* 172, 266; Anselm, *B.* 22, 869). — 2. By oxidising pyrene-ketone with $KMnO_4$ (Bamberger a. Philip, *B.* 19, 3040).—3. By saponification of its semi-nitrile $C_{10}H_6Cy.CO_2H$ which is formed by the action of cuprous cyanide upon diazotised *peri*-amido-naphthoic acid (Bamberger a. Philip, *B.* 20, 248).—4. By oxidising di-*exo*-oxy-acenaphthene with alkaline $KMnO_4$ (Ewan a. Cohen, *C. J.* 55, 580).

Properties.—Long silky hair-like needles (from alcohol); almost insol. water, sl. sol. ether. Split up into water and its anhydride by heating alone at 145°, by boiling with HOAc, or even by exposure over H_2SO_4 (Blumenthal, *B.* 7, 1092). Distillation with limo yields naphthalene. Yields a fluoresceïn on heating with resorcin.

Salts.—$(NH_4)_2A''EtOH$. Plates (from alcohol).—Na_2A''.—$K_2A''EtOH$. Plates.—$BaA''aq$: sparingly soluble white silvery plates—$CaA''aq$. —$Al_2A''_3aq$.

Di-methyl ether Me_2A''. [103°].

Anhydride $C_{10}H_6<\begin{smallmatrix}CO\\CO\end{smallmatrix}>O$. [266°]. Needles (from alcohol); sl. sol. alcohol and benzene. Not attacked by boiling HNO_3.

Imide $C_{10}H_6<\begin{smallmatrix}CO\\CO\end{smallmatrix}>NH$. [above 280°]. Formed by boiling the acid or its anhydride with aqueous ammonia. White needles. Sol. warm KOHAq. When $AgNO_3$ is added to its solution in alcoholic NH_3 there is formed a crystalline pp. $Ag_2C_{24}H_{15}N_3O_4$.

Naphthalene dicarboxylic acid $C_{10}H_6(CO_2H)_2$. [255°]. Formed by reducing di-oxy-naphthalene dicarboxylic acid [162°] with HIAq and amorphous phosphorus (Claus a. Meixner, *J. pr.* [2] 37, 8). Flocculent pp., insol. water and ether, sol. alcohol. Yields naphthalene on distillation with lime.—PbA'': greyish-white pp.

Naphthalene 'α'-dicarboxylic acid $C_{10}H_6(CO_2H)_2$ [2:2′]. Obtained by digesting its nitrile with HClAq at 200° (Ebert a. Merz, *B.* 9, 606). Long needles (from alcohol). Melts far above 300°. V. sl. sol. boiling benzene, toluene, and HOAc, m. sol. boiling alcohol. Yields naphthalene on distillation with lime.—$CaA''4aq$: minute needles, sl. sol. water.—Ag_2A''.

Nitrile $C_{10}H_6(CN)_2$. [268°]. Formed by distilling naphthalene (α)-disulphonic acid with potassium cyanide. White needles (by sublimation), m. sol. boiling alcohol.

Naphthalene 'β'-dicarboxylic acid $C_{10}H_6(CO_2H)_2$ [2:3′]. Obtained in the same way as the 'α'-isomeride, from naphthalene 'β'-disulphonic acid (E. a. M.). Short needles (from alcohol). Melts far above 300°. Almost insol. boiling benzene, toluene, and HOAc, m. sol. boiling alcohol.—$K_2A''\frac{1}{2}aq$: tufts of needles, v. e. sol. water.—$CaA''3\frac{1}{2}aq$: minute needles, almost insol. water.—Ag_2A''.

Nitrile $C_{10}H_6(CN)_2$. [297°]. Long needles (from HOAc). Almost insol. boiling ether, alcohol, and benzene.

Naphthalene (γ)-dicarboxylic acid $C_{10}H_6(CO_2H)_2$. Obtained from its nitrile, which is formed by distilling with KCy potassium bromo-naphthalene sulphonate (obtained by sulphonating (α)-bromo-naphthalene) (Darmstädter a. Wichelhaus, *A.* 152, 309; *Z.* [2] 5, 571). Small needles, v. sol. alcohol, insol. boiling water.—$BaA''2aq$: crystalline grains.

Nitrile $C_{10}H_6(CN)_2$. [204°]. Thin needles, sl. sol. alcohol and ether.

Naphthalene (δ)-dicarboxylic acid. *Nitrile* $C_{10}H_6(CN)_2$. [236°]. Obtained by distilling potassium bromo-naphthalene (α)-sulphonic acid with KCy (D. a. W.). Needles, v. sol. alcohol.

Naphthalene (ε)-dicarboxylic acid. *Nitrile* $C_{10}H_6(CN)_2$. [170°]. Obtained by distilling potassium bromo-naphthalene (β)-sulphonate with KCy (D. a. W.). Small needles, v. sol. alcohol

Naphthalene tri-carboxylic acid $C_{10}H_5(CO_2H)_3$. Obtained by quickly heating the tetra-carboxylic acid to 200°–250° (Bamberger a. Philip, *B.* 19, 3037).

Naphthalene tetra-carboxylic acid $C_{14}H_8O_8$ *i.e.* $C_{10}H_4(CO_2H)_4$ [1:1′:4:4′]. Formed by oxidising pyrenic acid with dilute $KMnO_4$ (Bamberger a. Philip, *B.* 19, 1998; 20, 368; *A.* 240, 182). Colourless glistening plates or needles; m. sol. hot HOAc and water, v. sl. sol. alcohol and benzene. Not attacked by HNO_3 even at 160°. Yields naphthalene on distillation with lime. —Ba_2A^{iv} (dried at 130°).—Ag_4A^{iv}.

Anhydride $C_{10}H_4\left(<\begin{smallmatrix}CO\\CO\end{smallmatrix}>O\right)_2$. Formed by heating the acid at 150°–170° (Bamberger a. Philip, *B.* 19, 3037). Needles (from HOAc).

Sublimes above 300°. Gives a fluoresceïn when heated with resorcin.

Imide $C_{10}H_4\left(<\begin{smallmatrix}CO\\CO\end{smallmatrix}>NH\right)$. Formed by treating the anhydride with NH_3Aq. Needles and prisms. Sublimes in needles above 270°. V. sl. sol. alcohol, ether, and benzene. Aqueous NaOH colours it yellow (forming the Na salt), without dissolving it; on adding acids it turns white again.

Naphthalene dihydride dicarboxylic acid $C_{10}H_8(CO_2H)_2$. *Dihydronaphthalic acid.* Formed by reducing naphthalic acid with sodium-amalgam (Anselm, *B.* 22, 859). Colourless crystalline solid, v. sol. warm alcohol, sl. sol. ether and water. Reduces alkaline $KMnO_4$. It turns yellow at 150°–160°, froths at 199°, and changes to the anhydride, but is not melted at 275°.

Naphthalene tetrahydride dicarboxylic acid $C_6H_4<\begin{smallmatrix}CH_2.CH(CO_2H)\\CH_2.CH(CO_2H)\end{smallmatrix}>$. [199°]. When an alcoholic solution of ethane tetra-carboxylic ether $C_2H_2(CO_2Et)_4$ (1 mol.) and NaOEt (2 mols.) is heated at 130° with di-ω-bromo-o-xylene $C_6H_4(CH_2Br)_2$ (1 mol.) there is formed naphthalene tetrahydride tetracarboxylic ether $C_6H_4<\begin{smallmatrix}CH_2.C(CO_2Et)_2\\CH_2.C(CO_2Et)_2\end{smallmatrix}>$; and when this is saponified with alcoholic potash it loses CO_2 (2 mols.) yielding the dicarboxylic acid. The yield is 70 p.c. of the theoretical (Baeyer a. Perkin, *B.* 17, 448; *C. J.* 53, 11). Minute tables, sl. sol. cold, m. sol. hot, water; v. sol. chloroform, alcohol, ether, and acetone. Splits up at its melting-point into H_2O and its anhydride. On passing through a red-hot tube it yields naphthalene. —Ag_2A'': white crystalline pp. which yields the anhydride and naphthalene on dry distillation.

Anhydride $C_6H_4<\begin{smallmatrix}CH_2.CH.CO\\|\\CH_2.CH.CO\end{smallmatrix}>O$. [184°]. Four-sided prisms (from ether) or needles (by sublimation); sl. sol. ether, m. sol. alcohol and chloroform, insol. cold water. Slowly re-converted into the acid by hot water.

Naphthalene tetra-hydride tetra-carboxylic acid $C_6H_4<\begin{smallmatrix}CH_2.C(CO_2H)_2\\CH_2.C(CO_2H)_2\end{smallmatrix}>$. *Tetrahydronaphthalene tetracarboxylic acid.* The ether is formed by heating an alcoholic solution of sodio-chloro-malonic ether $CNaCl(CO_2Et)_2$ (2 mols.) with o-xylylene bromide (1 mol.), reducing the resulting $C_6H_4(CH_2.CCl(CO_2Et)_2)_2$ by means of zinc-dust and HOAc to o-xylylene-di-malonic ether $C_6H_4(CH_2.CH(CO_2Et)_2)_2$, and treating the sodium derivative $C_6H_4(CH_2.CNa(CO_2Et)_2)_2$ with an ethereal solution of iodine (Baeyer a. Perkin, jun., *B.* 17, 448). The ether may also be obtained from $C_6H_4(CH_2Br)_2$, sodium ethylate and $C_2H_2(CO_2Et)_4$ (*v. supra*). The free acid, which may be obtained by careful saponification of the ether with alcoholic potash, is a syrup which splits up at 185° into CO_2 and the dicarboxylic acid described above.

Reference.—Bromo-naphthalene dicarboxylic acid.

DI-NAPHTHALENE OXIDE *v.* Dinaphthylene oxide.

NAPHTHALENE DI-OXIM *v. Di-oxim* of Naphthoquinone.

NAPHTHALENE - DIPHENYL AZAMMONIUM HYDRATE *v.* Azammonium compounds.

NAPHTHALENE PHOSPHINIC ACID $C_{10}H_7.P(OH)_2$. *Naphthyl-phosphorous acid.* [126°]. S.G. 1·377 (Schröder, *B.* 12, 564). Formed by the action of water on its chloride. Aggregates of small needles, sl. sol. cold water, almost insol. HClAq. Melts under water. Reduces silver solution. It is accompanied by an acid $(C_{10}H_7)_2PO.OH$ [204°] which is insol. water.

Chloride $C_{10}H_7PCl_2$. (above 360°). Formed by heating mercuric dinaphthyl $Hg(C_{10}H_7)_2$ with PCl_3 at 190° for several hours (Kelbe, *B.* 9, 1051; 11, 1499). Liquid. Combines with chlorine forming $C_{10}H_7PCl_4$.

NAPHTHALENE PHOSPHONIC ACID $C_{10}H_7.PO(OH)_2$. [190°]. S.G. 1·440. Formed by the action of water on its tetrachloride (Kelbe). Long needles, v. sol. hot, sl. sol. cold, water. When strongly heated it decomposes, with separation of carbon, into naphthalene and metaphosphoric acid.—Ag_2A'': white pp.

Chloride $C_{10}H_7PCl_4$. Formed from the compound $C_{10}H_7PCl_2$ and chlorine.

NAPHTHALENE-STYRENE *v.* Naphthyl-ethylene.

NAPHTHALENE (α)-SULPHINIC ACID $C_{10}H_7SO_2H$. Formed by digesting a solution of the chloride of naphthalene (α)-sulphonic acid in ether with sodium amalgam (Gessner, *B.* 9, 1500; *cf.* Otto a. Mories, *B.* 6, 860). White scales, v. sol. water, sl. sol. HClAq, m. sol. alcohol, sl. sol. ether. Decomposed by HClAq at 180° into naphthalene and SO_2.

Salts.—$KA'\frac{1}{2}aq$: glistening scales. —$BaA'_2 1\frac{1}{2}aq$. Slender needles. S. ·5 at 14°; 2 at 100°.—PbA'_2 aq: long branched needles. —AgA'. Soluble plates, not decomposed at 200°.

Naphthalene (β)-sulphinic acid $C_{10}H_7.SO_2H$. [105°]. Formed in the same way as the preceding isomeride from naphthalene (β)-sulphonic acid, and ppd. by adding HCl to a solution of the Na salt as a white crystalline powder, m. sol. alcohol, ether, and water, almost insol. HClAq. Readily decomposed by HClAq at 150° into naphthalene and SO_2.

Salts.—$KA'\frac{1}{2}aq$: scales.—BaA'_2: glistening needles. S. 4·7 at 15°; 6·25 at 100°.—$CaA'_2 3aq$: white crystalline solid, v. sol. water and alcohol.—$MgA'_2 6aq$: scales, more sol. alcohol than water.

References.—Bromo- and Chloro-naphthalene sulphonic acid.

NAPHTHALENE (α)-SULPHONIC ACID $C_{10}H_7.SO_3H$. Formed, together with the (β)-isomeride, by dissolving naphthalene in H_2SO_4. At 160°–170° the chief product is the (β)-acid, but at 80°–100° the product consists mainly of the (α)-acid (Merz a. Weith, *B.* 3, 195; *cf.* Faraday, *P.* 7, 104; Berzelius, *P.* 44, 377; Liebig a. Wöhler, *P.* 24, 169; *A.* 37, 197). Naphthalene is converted by $Cl.SO_3H$ (1 mol.) into a mixture of the (α)- and (β)- sulphonic acids (Armstrong, *C. J.* 24, 173). It may be separated from the (β)-isomeride by means of the calcium or lead salts. Crystalline and deliquescent, v. e. sol. water, sol. alcohol, sl. sol. ether. Partially converted into the (β)-isomeride by heating with H_2SO_4 at 100°, more completely at higher temperatures. Decomposed into naphthalene and H_2SO_4 by heating with HClAq at 200°. Oxidised by $KMnO_4$ in acid solution to phthalic acid (Beil-

stein a. Kurbatoff, *C. C.* 1881, 359; *A.* 202, 216). Alkaline $KMnO_4$ yields $C_6H_4(CO_2H).CO.CO_2H$ (Henriques, *B.* 21, 1607) and phthalic acid. Bromine forms dibromo-naphthalene and bromo-naphthalene sulphonic acid.

S a l t s.—$KA'\frac{1}{2}aq$. Plates (from alcohol). S. 7·7 at 11°.—$CaA'_2 2aq$. Plates (slowly decomposed at 80°). S. 6 at 11°.—$BaA'_2 aq$. Plates. S. 1·15 at 10° (M.); 1·13 at 15°; 4·76 at 100° (Regnault, *J. pr.* 12, 99).—$PbA'_2 3aq$. Plates. S. 3·7 at 10°.—$Pb_2OA'_2$.—AgA'. S. 10·3 at 10°.

Ethyl ether EtA'. Formed by boiling the chloride (1 mol.) with alcohol (2 mols.) (Kimberly, *A.* 114, 133). Viscid liquid, which slowly solidifies. Insol. water, miscible with alcohol and ether. Decomposed on distillation, giving off SO_2 and naphthalene. Aqueous or alcoholic potash merely saponifies it. Water at 150° resolves it into alcohol, naphthalene, and H_2SO_4. Converted by PCl_5 at 160° into (α)-chloro-naphthalene and $SOCl_2$ (Carius, *A.* 114, 145).

Chloride $C_{10}H_7.SO_2Cl$. [66°]. Glistening plates (from ether), v. sol. ether, CS_2, and benzene (Maikopar, *Z.* 1869, 710; Kimberly, *A.* 114, 129). On passing chlorine into a solution in CS_2 there is formed the tetrachloride $C_{10}H_7Cl_4.SO_2Cl$, a thick liquid, sol. CS_2, chloroform, benzene, and ether, and converted by alcoholic potash into di-chloro-naphthalene sulphonic chloride (Widmann, *B.* 12, 2228).

Amide $C_{10}H_7.SO_2NH_2$. [150°]. Prepared by warming the chloride with conc. NH_3Aq. Sol. water, v. sol. alcohol and ether. Its alcoholic solution gives with $AgNO_3$ a crystalline pp. $C_{10}H_7.SO_2NHAg$, v. sol. alcohol and ether, quickly blackening in light.

Benzoyl derivative of the amide $C_{10}H_7.SO_2NHBz$. [195°]. Formed by heating the amide with BzCl (Kimberly). Minute four-sided prisms (from alcohol) (Wolkoff, *Z.* 1871, 422; *B.* 5, 142). Insol. water, m. sol. alcohol and ether. Decomposed by boiling KOHAq into benzoic acid, NH_3, and naphthalene sulphonic acid. PCl_5 converts it into $C_{10}H_7.SO_2.N:CCl.C_6H_5$, which crystallises from ether in large four-sided plates [94°] and is re-converted by boiling water or alcohol into $C_{10}H_7.SO_2.NH.COC_6H_5$, and by ammonium carbonate into crystalline $C_{10}H_7.SO_2.N:C(NH_2)C_6H_5$. Behaves like an acid, decomposing carbonates, and forming the salts. —$C_{10}H_7.SO_2.NKBz$: prisms, v. sol. water and alcohol. — $CaA'_2 aq$: needles. — BaA'_2: slender needles, sl. sol. water.—AgA': minute needles.

Anilide $C_{10}H_7.SO_2.NHPh$. [112°]. Needles (Carleson, *Bl.* [2] 27, 360).

(α) - *Naphthalide* $C_{10}H_7.SO_2.NHC_{10}H_7$. [82°]. Small needles (C.).

Naphthalene (β)-sulphonic acid $C_{10}H_7.SO_3H$. Produced by the action of H_2SO_4 upon phenyl (α)-naphthyl ketone, the isomeric change resulting from the heat evolved in the reaction (Elbs a. Steinike, *B.* 19, 1966). Prepared by heating naphthalene (500 g.) with H_2SO_4 (400 g.) for 8 hours at 160° and purifying the acid by means of the Ca salt (Merz a. Weith, *B.* 3, 196). Non-deliquescent crystals. Not decomposed by dilute HClAq at 200°. Split up into naphthalene and H_2SO_4 by distilling with dilute H_2SO_4 at 135° in a current of superheated steam (Armstrong a. Miller, *C. J.* 45, 148). Oxidised by alkaline $KMnO_4$ to $C_6H_4(CO_2H).CO.CO_2H$ (Henriques, *B.* 21, 1607). $KMnO_4$ in neutral or acid solution yields phthalic acid (Beilstein a. Kurbatoff, *C. C.* 1881, 359; *A.* 202, 215). CrO_3 and dilute H_2SO_4 yield naphthoquinone sulphonic acid (B. a. K.). The Ca salt yields phthalic acid on oxidation by CrO_3. Bromine-water forms bromo-naphthalene sulphonic acid.

S a l t s.—$KA'\frac{1}{2}aq$. Plates (from water) or needles (from dilute alcohol). S. 6·6 at 10°. S. (85 p.c. alcohol) ·9.—CaA'_2. Plates. S. 1·3 at 10°. — BaA'_2aq. Plates. S. ·345 at 10°.— $PbA'_2 1\frac{1}{2}aq$. Scales. S. ·9 at 10°.

Chloride $C_{10}H_7.SO_2Cl$. [76°]. Plates; less soluble in ether than the (α)-isomeride (Maikopar). Reduced by HI to (β)-di-naphthyl disulphide [139°] (Cleve, *B.* 21, 1100). Combines with chlorine (dissolved in CS_2) forming a tetrachloride $C_{10}H_7Cl_4.SO_2Cl$, which separates from chloroform in colourless cubes [131°]; v. sol. chloroform, CS_2, and hot HOAc, insol. water (Widmann, *B.* 12, 959). The tetrachloride is converted by boiling alcoholic KOH into di-chloro-naphthalene (β)-sulphonic acid

Amide $C_{10}H_7.SO_2NH_2$. [212°] (Cleve, *Bl.* [2] 25, 258). Small thin plates (from alcohol); sl. sol. water and ether.

Ethylamide $C_{10}H_7.SO_2NHEt$. [82·5°] (Carleson, *Bl.* [2] 27, 360).

Anilide $C_{10}H_7.SO_2NHPh$. [132°]. Needles.

(α) - *Naphthalide* $C_{10}H_7.SO_2.NHC_{10}H_7$. [177·5°]. Needles.

Naphthalene tetrahydride sulphonic acid $C_{10}H_{11}.SO_3H$. Formed by heating naphthalene tetrahydride with H_2SO_4 for 3 hours at 40° (Graebe a. Guye, *B.* 16, 3030; Bamberger a. Kitschelt, *B.* 23, 1565). Crystals; v. sol. water and alcohol. Decomposed by distillation with dilute H_2SO_4 and a current of superheated steam at 175°, or by dilute H_3PO_4 at 130° (Friedel a. Crafts, *Bl.* [2] 42, 66; *C. R.* 109, 95).—NaA'2aq. Tables; v. sol. water.—$BaA'_2 2aq$. Tables; sol. hot alcohol, sl. sol. cold water.

Naphthalene 'α'-disulphonic acid $C_{10}H_6(SO_3H)_2$ [2:2]. Formed, together with about an equal quantity of the (β)-isomeride and some of the (δ)-isomeride, by heating naphthalene (1 pt.) with H_2SO_4 (5 pts.) for 4 hours at 160° (Ebert a. Merz, *B.* 9, 592; Armstrong, *B.* 15, 204; cf. Berzelius, *A. Ch.* [2] 65, 290; Laurent, *Compt. Chim.* 1849, 390). The acids may be partially separated by their Ca salts, that of the (β)- acid crystallising out first, while that of the (α)- acid is the most soluble. The potassium salt of the (α)- acid is more soluble than that of the (β)- acid, and less soluble than that of the (δ)-acid. Long, very deliquescent needles; sl. sol. cold conc. HClAq. Gives di-oxy-naphthalene [186°] on fusion with KOH (*cf.* Griess, *B.* 13, 1959; Dusart, *C. R.* 64, 859; Darmstädter a. Wichelhaus, *A.* 152, 306). Water at 200° splits it up into naphthalene and H_2SO_4. Fusion with NaOH forms (β)-naphthol (δ)-sulphonic acid $C_{10}H_6(OH)SO_3H$ (Weinberg, *B.* 20, 2906). PBr_5 forms (δ)-di-bromo-naphthalene. Yields di-chloro-naphthalene [114°].

S a l t s. — $K_2A''2aq$. Transparent needles (from hot saturated solutions). S. (of K_2A'') 71 at 18°.—$Na_2A''6aq$. Glistening needles. S. (of Na_2A'') 45·5 at 18°.—$CaA''6aq$. S. 16 at 18°.— $CaA''3aq$ (from a rapidly-cooled hot saturated

solution).—BaA″2aq. Long, broad needles. S. 1·2 at 19°.—PbA″2aq. Long needles; sol. water.

Chloride $C_{10}H_6(SO_2Cl)_2$. [158°] (E. a. M.); [162°] (A.). Obtained by heating the K salt with PCl_5 at 140°. Plates (from benzene), or needles (from ether). S. (benzene) 13·3 at 14°.

Amide $C_{10}H_6(SO_2NH_2)_2$. [243°]. Needles; m. sol. hot NH_3Aq and alcohol.

Naphthalene 'β'-disulphonic acid $C_{10}H_6(SO_3H)_2$. [2:3′]? Almost the sole product obtained by heating a mixture of naphthalene (1 pt.) and H_2SO_4 (5 pts.) for 24 hours at 180° (Ebert a. Merz). Formed also from its 'α'-isomeride by prolonged heating with H_2SO_4 at 180°. Somewhat deliquescent plates. Gives (β)-naphthol 'β' sulphonic acid and (β)-di-oxy-naphthalene on fusion with potash. Yields $C_{10}H_6Cl_2$ [135°].

Salts.—$Na_2A''aq$: aggregates of minute prisms. S. (of Na_2A'') 1·2 at 19°.—K_2A''. Bushy groups of needles. S. 5·2 at 18°.—CaA″aq. S. 6·2 at 18°. When once dry this salt dissolves in water with great difficulty.—BaA″aq.—PbA″aq.

Chloride $C_{10}H_6(SO_2Cl)_2$. [226°]. S. (benzene) ·45 at 14°. Tufts of small needles or thin plates; v. sl. sol. HOAc (difference from the (α)-isomeride), v. sol. benzene.

Amide $C_{10}H_6(SO_2NH_2)_2$. Small needles, v. sl. sol. NH_3Aq, almost insol. alcohol, ether, benzene, and toluene. Not melted at 305°.

Naphthalene (γ)-disulphonic acid $C_{10}H_6(SO_3H)_2$ [1:4′]. Formed by treating naphthalene (1 mol.) with $ClSO_3H$ (2 mols.) below 100° and also by sulphonating naphthalene with SO_3 (Armstrong, *B.* 15, 204; Armstrong a. Wynne, *C. J. Proc.* 2, 230; 3, 42). Its Pb, Ca, and Ba salts resemble those of the (β)-acid, dissolving very sluggishly in water. On fusion with potash it yields di-oxy-naphthalene [260°].—Na_2A'' 2aq.—K_2A'' 2aq: plates, less soluble than the corresponding salt of the 'α'-acid.

Chloride $C_{10}H_6(SO_2Cl)_2$. [184°]. Prisms (from benzene). Yields (γ)-di-chloro-naphthalene [107°] on treatment with PCl_5.

Naphthalene (δ)-disulphonic acid $C_{10}H_6(SO_3H)_2$ [1:3′]. *Also called* (γ). Occurs in small quantity in the product of sulphonation of naphthalene by H_2SO_4 at 160° (Armstrong, *B.* 15, 204). Formed by treating potassium naphthalene (β)-sulphonate with $ClSO_3H$ (Armstrong a. Wynne, *C. J. Proc.* 2, 230).—BaA_2' 4aq.—NaA′ 7aq. Formed also by heating naphthalene (β)-sulphonic acid with fuming H_2SO_4 at 100° (Ewer a. Pick, *G. P.* 45,229 [1887]; Armstrong, *C. J. Proc.* 4, 10). Long needles. Gives dioxy-naphthalene [135·5°] on fusion with potash. Yields $C_{10}H_6Cl_2$ [49°]. The potassium salt is more soluble than that of the (α)- or (β)-acid. — $K_2A''aq$. — Na_2A'' 4aq. — BaA″ 4aq.—CaA″ 4aq.—PbA″3½aq.

Chloride $C_{10}H_6(SO_2Cl)_2$. [125°]. Small prisms (from benzene). On treatment with PCl_5 it yields di-chloro-naphthalene [59°].

Naphthalene (1, 2′)-disulphonic acid. Formed from (α)-naphthylamine disulphonic acid (Armstrong a. Wynne, *C. J. Proc.* 5, 136). Yields $C_{10}H_6Cl_2$ [62·5°].—$K_2A''aq$.

Chloride [122·5°].

Naphthalene (1, 3)-disulphonic acid. Obtained from (1′, 1, 3) or (2, 2′, 4′) naphthylamine disulphonic acid by eliminating NH_2 (Armstrong a. Wynne, *C. J. Proc.* 5, 13, 129). Yields $C_{10}H_6Cl_2$ [61°].—K_2A'' 2aq.—BaA″ 4aq.

Chloride [137°].

Naphthalene hexahydride (α)-di-sulphonic acid $C_{10}H_{12}(SO_3H)_2$. Formed by heating naphthalene hexahydride with H_2SO_4 and SO_3, and separated from the (β)-isomeride by means of the K salt (Agrestini, *G.* 12, 495).—K_2A'' (dried at 105°). Nodules, sol. alcohol.

Naphthalene hexahydride (β)-sulphonic acid $C_{10}H_{12}(SO_3H)_2$. Formed as above.—K_2A'' 1½aq. Insol. alcohol.

Naphthalene trisulphonic acid $C_{10}H_5(SO_3H)_3$ [2:4:2′]. Formed from naphthalene and $ClSO_3H$ (Wynne, *C. J. Proc.* 3, 146). Yields $C_{10}H_5Cl_3$ [194°].—Na_3A'''5aq.

Naphthalene tetra-sulphonic acid $C_{10}H_4(SO_3H)_4$. Formed by heating naphthalene with H_2SO_4 and P_2O_5 for three or four hours at 260° (Stenhofer, *B.* 8, 1486; *M.* 3, 111). Two isomeric acids are formed in the process, and when a solution of their Ba salts is slowly evaporated at 30° to 35° the salt of the acid here described crystallises out in striated prisms. Prisms (containing 4aq), v. e. sol. water, sl. sol. alcohol, insol. ether. Decomposes above 170°.

Salts.—K_4A^{iv}2aq: non-deliquescent needles.—Na_4A^{iv} 2aq (at 100°).—Na_4A^{iv} 10aq: very deliquescent prisms. — Ba_2A^{iv} *x*aq: prisms. — Pb_2A^{iv} 6aq: crystalline pp. —Cu_2A^{iv} 12aq: blue prisms.—Ag_4A^{iv} 2½aq: very soluble needles.

References.—Bromo-, Chloro-, Iodo- and Nitro- naphthalene sulphonic acids.

NAPHTHAL-FLUORESCEÏN $C_{24}H_{14}O_5$ *i.e.* $O<\begin{matrix}C_6H_3(OH)\\C_6H_3(OH)\end{matrix}>C<\begin{matrix}O—\\C_{10}H_6\end{matrix}>CO$. [308°]. Formed by heating naphthalic anhydride and resorcin at 250° (Terrisse, *A.* 227, 136). Yellow rhombic prisms. Its alkaline solution is red, with splendid green fluorescence.

Acetyl derivative $C_{24}H_{13}AcO_5$ [191°] $C_{24}H_{13}AcO_5aq$. [120°]. Needles (from acetone). Insol. alkalis, but saponified slowly. By treatment with PCl_5 it is converted into the chloride $C_{24}H_{12}O_3Cl_2$, which crystallises in scales, sol. chloroform, acetone, or glacial acetic acid; hardly sol. benzene, ether, or alcohol.

Naphthal-eosin $C_{24}H_{10}Br_4O_5$. [above 310°]. Formed by adding bromine to an alcoholic solution of naphthal-fluoresceïn. Its alkaline solutions are orange, with yellow fluorescence, and dye silk scarlet.

NAPHTHALIC ACID *v.* Naphthalene dicarboxylic acid.

NAPHTHALIDES. Alkoyl derivatives of Naphthylamine (*q. v.*).

NAPHTHALIDINE SULPHONIC ACID *v.* (1,4′)-Naphthylamine sulphonic acid.

NAPHTHALIN *v.* Naphthalene.

(β)-NAPHTHAMIDINE $C_{10}H_7.C(NH).NH_2$. White crystalline mass, obtained from its hydrochloride, which is prepared by the action of alcoholic NH_3 at 50° to 60° upon (β)-naphthimido-ether $C_{10}H_7.C(NH).OEt$ (Pinner a. Klein, *B.* 11, 1486).—B′HCl. [226°]. Needles.

(α)-NAPHTHAMIDOXIM $C_{11}H_{10}N_2O$ *i.e.* $C_{10}H_7.C(NOH).NH_2$. [149°]. Obtained by mixing the nitrile of (α)-naphthoic acid with hydroxylamine hydrochloride, Na_2CO_3, and alcohol (Ekstrand, *B.* 20, 223). Plates (from dilute alcohol), v. sol. alcohol, insol. ligroïn. On boil-

ing with Ac_2O it yields $C_{10}H_7.C{<}\genfrac{}{}{0pt}{}{NO}{N}{>}CMe$. [36°]. $ClCO_2Et$ yields $C_{10}H_7.C(NO.CO_2Et).NH_2$. [111°]. $COCl_2$ forms $C_{10}H_7.C{<}\genfrac{}{}{0pt}{}{N.O}{NH}{>}CO$. [189°] (Richter, *B.* 22, 2458).—B'HCl. [160°]. Needles.—$B'_2H_2PtCl_6$: yellow prismatic needles.

Acetyl derivative $C_{10}H_7C(NOH).NHAc$. [129°] (Richter, *B.* 20, 227). White needles, insol. water, v. sol. alcohol and ether.

(α)-*Naphthoyl derivative* $C_{22}H_{16}N_2O_2$ *i.e.* $C_{10}H_7.C(NOH).NH.CO.C_{10}H_7$. [228°]. Needles; almost insol. HClAq.

(β)-Naphthamidoxim $C_{10}H_7.C(NOH).NH_2$. [150°]. Formed from (β)-naphthonitrile and alcoholic hydroxylamine (Ekstrand). Scales, decomposed by boiling water. On heating with Ac_2O it yields $C_{10}H_7.C{<}\genfrac{}{}{0pt}{}{N.O}{N}{>}CMe$ [86°], which is also formed by boiling the acetyl derivative with water. (β)-Naphthoyl chloride forms the corresponding azoxim $C_{10}H_7{<}\genfrac{}{}{0pt}{}{N.O}{N}{>}C.C_{10}H_7$. [175°]. Acetic aldehyde yields the compound $C_{10}H_7.C{<}\genfrac{}{}{0pt}{}{N.O}{NH}{>}CH.CH_3$ [122°] crystallising in needles. Cyanogen passed into an alcoholic solution of (β)-naphthamidoxim forms the compound $C_{10}H_7.C(NOH).NH.C(NH).CN$ [119°] (Brühl, *B.* 23, 1463). $ClCO_2Et$ in chloroform forms $C_{10}H_7.C(NO.CO_2Et).NH_2$ crystallising in needles [121°]. $COCl_2$ yields white felted needles of $C_{10}H_7.C{<}\genfrac{}{}{0pt}{}{N.O}{NH}{>}CO$ [216°]. Boiling acetoacetic ether forms $C_{10}H_7.C{<}\genfrac{}{}{0pt}{}{N.O}{N}{>}C.CH_2.CO.CH_3$ crystallising in plates [109°].

Salt.—B'HCl. [178°]. Needles, v. sol. water.

Acetyl derivative $C_{10}H_7.C(NOH).NHAc$. [154°]. Faintly yellow needles, insol. water, sl. sol. cold alcohol and ether.

Benzoyl derivative $C_{10}H_7.C(NOH).NHBz$. [179°]. Silky felted needles (from alcohol), insol. water, sl. sol. cold alcohol. On boiling with water it yields $C_{10}H_7.C{<}\genfrac{}{}{0pt}{}{N.O}{N}{>}C.C_6H_5$. [116°].

Ethyl ether $C_{10}H_7.C(NOEt).NH_2$. [75°]. Formed from (β)-naphthamidoxim, NaOEt, and EtI at 100° (Richter, *B.* 20, 227; 22, 2455). Shining felted needles, v. sl. sol. water, v. sol. alcohol, ether, chloroform, and ligroïn, sol. HClAq, insol. NaOHAq.

NAPHTHANISOL *v.* *Methyl ether* of NAPHTHOL.

NAPHTHANTHRACENE $C_{18}H_{12}$ *i.e.* $C_6H_4{<}\genfrac{}{}{0pt}{}{CH.C}{CH.C.CH:CH}{>}C_6H_4$. [141°]. Formed by boiling naphthanthraquinone with zinc-dust and aqueous NH_3Aq till the red colour has disappeared, extracting the residue with alcohol and adding HOAc to the extract (Elbs, *B.* 19, 2211). Large colourless serrated plates with powerful green-yellow fluorescence. May be sublimed. — Picrate $C_{18}H_{12}2C_6H_2(NO_2)_3OH$. [133°]. Rod needles (from benzene), decomposed by alcohol.

NAPHTHANTHRAQUINONE $C_{18}H_{10}O_2$ *i.e.* $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_{10}H_6$. [168°]. Formed by heating naphthoyl-*o*-benzoic acid with conc. H_2SO_4 (Elbs, *B.* 19, 2209). Glittering deep-yellow grains or prisms, sl. sol. alcohol and ether, m. sol. acetone, HOAc, and EtOAc, v. sol. chloroform and benzene, insol. petroleum-ether. May be sublimed as needles arranged in leaflets. Conc. H_2SO_4 forms a brown solution. Sodium-amalgam added to its alcoholic solution forms a dark-violet zone (like anthraquinone), but on warming the liquid becomes red (anthraquinone gives a green liquid). It does not combine with picric acid.

NAPHTHAQUINOLINE *v.* NAPHTHOQUINOLINE.

NAPHTHAQUINONE *v.* NAPHTHOQUINONE.

NAPHTHAZARIN *v.* DI-OXY-NAPHTHOQUINONE.

(αβ)-NAPHTHAZINE $C_{20}H_{12}N_2$ *i.e.* $C_6H_4{<}\genfrac{}{}{0pt}{}{CH:CH.C.N.C}{C.N.C.CH:CH}{>}C_6H_4$. *Naphthase.* [275°].

Formation.—1. By heating (α)-nitro-naphthalene to redness with lime (Laurent), or zinc-dust (Doerr, *B.* 3, 291; 10, 772; Klobukowski, *B.* 10, 570).—2. By the action of (β)-naphthoquinone in HOAc solution upon naphthylene o-diamine (Witt, *B.* 19, 2795).—3. By fusing (β)-naphthoquinone with ammonium acetate, the yield being small (Japp, *C. J.* 51, 100).—4. By heating (α)-chloro-(β)-naphthylamine with lime (Cleve, *B.* 20, 1991).

Properties.—Yellow needles; sl. sol. alcohol and benzene, with pale violet fluorescence, m. sol. phenol and aniline. Conc. H_2SO_4 forms a violet solution becoming orange-yellow on dilution, and finally colourless, depositing the naphthazine. Bromine in presence of iodine yields $C_{20}H_5Br_5N_2$ melting above 320°.

(ββ)-Naphthazine $C_6H_4{<}\genfrac{}{}{0pt}{}{CH:CH.C.N.C.CH:CH}{C.N.C}{>}C_6H_4$. [243°]. Formed by adding a strongly acid solution of diazobenzene chloride to a warm solution of (ββ)-di-naphthylamine (Matthes, *B.* 23, 1333). Woolly bunches of long yellow needles (from hot alcohol or hot HOAc). Its solutions in alcohol and benzene exhibit a blue fluorescence; its solution in HOAc shows green fluorescence.

NAPHTHENES C_nH_{2n}. A class of hydrocarbon, forming the principal constituents of Caucasian petroleum; they are isomeric with the olefines, from which they differ in behaving as saturated compounds. They resemble the paraffins in yielding by substitution chloro-derivatives, readily dissociated into hydrochloric acid and a hydrocarbon of formula C_nH_{2n-2}. On oxidation they are converted into hydrocarbons poorer in hydrogen and oxygenated products, thus resembling naphthalene.

As regards their constitution the carbon atoms are arranged in a closed chain, and the determination of the specific refractive energy of the members of the series appears to show that they contain no olefinoid combination of carbon atoms. They are probably hexahydrides of the aromatic hydrocarbons.

They also probably occur in petroleum from Hanover, Galicia, Borislau, and Burmah, but have been mistaken by former observers for the olefines. They are also formed in the dry distillation of resin (*cf.* Renard, *C. R.* 95, 141, 243).

The following are the physical properties of some of the members examined:

	S.G. $\frac{16-18}{4}$	μ_α	μ_β	μ_γ	μ_D	R_α
Decanaphthene . . .	·7808	1·43066	1·43863	1·4427	1·433	77·2
Endecanaphthene . . .	·8019	1·43883	1·4466	1·45156	1·441	84·2
Dodecanaphthene . . .	·812	1·4438	1·45173	1·45646	1·44606	91·8
Tetradecanaphthene . .	·8215	1·44913	1·45706	1·4619	1·4514	107·1
Pentadecanaphthene . .	·8290	1·4544	1·46136	1·4661	1·4544	114·7

The naphthenes are obtained from the following fractions of Caucasian petroleum:

	Fraction
Octonaphthene C_8H_{16} . .	116°–120°
Nonaphthene C_9H_{18} . . .	135°–140°
Decanaphthene $C_{10}H_{20}$ . .	155°–165°
Endecanaphthene $C_{11}H_{22}$ . .	180°–185°
Dodecanaphthene $C_{12}H_{24}$ . .	196°–197°
Tetradecanaphthene $C_{14}H_{28}$.	240°–241°
Pentadecanaphthene $C_{15}H_{30}$.	246°–248°

(Markownikoff a. Oglobine, *A. Ch.* [6] 2, 446).

Some of these hydrocarbons (*e.g.* octonaphthene and nonaphthene) occur in two isomeric forms. Octonaphthene on treatment with H_2SO_4 and HNO_3 yields tri-nitro-*m*-xylene, and it is therefore probably *m*-xylene hexahydride (Markownikoff a. Spady, *B.* 20, 1851). Nonaphthene (136°), S.G. $\frac{20}{0}$ ·7667 is identical with pseudocumene hexahydride, for it yields some tri-nitro-ψ-cumene on nitration and ψ-cumene sulphonic acid with excess of H_2SO_4 (Konovaloff, *C. C.* 1887, 1133; *J. R.* 22, 4, 118). Heptanaphthene C_7H_{14} also occurs in Caucasian petroleum and boils at 101° (Milkowsky, *Bl.* [2] 45, 182).

Hexanaphthene carboxylic acid $C_6H_{11}.CO_2H$. *Hexahydro-benzoic acid?* (216°). S.G. $\frac{18·4}{18·4}$ ·9503. Obtained from the oils of Baku by extracting with caustic soda, and purified by fractional distillation of its methyl ether (Aschau, *B.* 23, 867). Thick colourless oil, smelling like valeric acid. Not solid at −10°. Not attacked by bromine in the cold. HNO_3 and $KMnO_4$ act slowly upon it. It slowly expels HCl from $CaCl_2$. Conc. H_2SO_4 dissolves it, and, on warming, decomposes it. Phosphoric acid decomposes it gradually in the cold.

Salts.—KA′. Very hygroscopic soap-like mass, gradually becoming crystalline; v. sol. water and alcohol.—NaA′. Flat hygroscopic prisms.—$CaA'_2$4aq: long pointed needles. A saturated solution becomes milky on heating and clear again on cooling.—BaA'_2. Large thin plates, v. sol. alcohol, m. sol. water.—BaA'_2*x*aq. Amorphous.—CdA'_2. Pearly plates, sl. sol. cold water.—AgA′. Curdy pp.

Methyl ether MeA′. (167°). S.G. $\frac{18·4}{18·4}$ ·9055. Colourless liquid with sickly odour.

Chloride $C_6H_{11}.COCl$. (168°). Slowly decomposed by water.

Amide $C_6H_{11}.CONH_2$. [123·5°]. Melts under water. Extremely thin pearly plates, m. sol. water, v. sol. other solvents.

Anilide $C_6H_{11}.CO.NHPh$. [94°]. Long elastic needles.

NAPHTHENYL-AMIDINE *v.* NAPHTHAMIDINE.

NAPHTHIDINE *v.* DI-AMIDO-DINAPHTHYL.

NAPHTHIL-BENZOIN *v.* BENZOIN.

(β)-**NAPHTH-IMIDO-ACETATE** $C_{13}H_{11}NO_2$ *i.e.* $C_{10}H_7.C(NH)(OAc)$. [152°]. Prepared by boiling naphth-imido-isobutyl ether with Ac_2O (Pinner a. Klein, *B.* 11, 1487). White needles.

(β)-**NAPHTH-IMIDO-ISOBUTYL ETHER** $C_{15}H_{17}NO$ *i.e.* $C_{10}H_7.C(NH).OC_4H_9$. [38°]. Prepared by the action of gaseous HCl on a solution of (β)-naphthonitrile $C_{10}H_7.CN$ in isobutyl alcohol (Pinner a. Klein, *B.* 11, 1487). Long white needles.—B′HCl. Decomposed by heat into isobutyl chloride and the amide of (β)-naphthoic acid.

(β)-**NAPHTHIMIDO- ETHYL ETHER** $C_{10}H_7.C(NH).OEt$. *Hydrochloride* B′HCl. Prepared by leading HCl into an alcoholic solution of the nitrile of (β)-naphthoic acid (Pinner a. Klein, *B.* 11, 1485). Decomposed by heat into EtCl and the amide of (β)-naphthoic acid.

(α)-**NAPHTHINDOLE** $C_{12}H_9N$ *i.e.* $C_{10}H_6{<}^{CH}_{NH}{>}CH$. [175°]. Obtained by distilling its carboxylic acid (Schlieper, *A.* 239, 229). Plates (from ligroïn), v. sol. alcohol, ether, and benzene, sl. sol. hot water. Colours pine-wood, in presence of HCl, bluish-violet. Its solution in acetic acid gives a red colour with conc. HNO_3, and a bluish-green pp. on boiling with hydrogen peroxide. Its picrate crystallises in needles.—B'_2HCl. Colourless pp., got by adding HCl to the solution in HOAc.

On boiling an alcoholic solution of (α)-naphthindole with zinc-dust and HCl there is formed a *hydride* which yields an oxalate melting at 166°.

(β)-**Naphthindole** $C_{10}H_6{<}^{CH}_{NH}{>}CH$. (above 360°) at 760 mm.; (222° i.V. at 18 mm.).

Formation.—1. By heating ethylidene-(β)-naphthyl-hydrazine with $ZnCl_2$; the yield being small.—2. By heating the (β)-naphthyl-hydrazido of pyruvic ether with $ZnCl_2$ at 195°; the intermediate body being (β)-naphthindole carboxylic acid (Schlieper, *A.* 236, 178).

Properties.—Yellow oil, v. sol. alcohol, ether, benzene, and HOAc, sl. sol. ligroïn. Yields a picrate, crystallising in dark-red needles, and a nitrosamine. Conc. HClAq solidifies the oil. It colours pine-wood, in presence of HCl, violet. Oxidising agents yield a solid product.

(α)-**NAPHTHINDOLE CARBOXYLIC ACID** $C_{13}H_9NO_2$ *i.e.* $C_{10}H_6{<}^{CH}_{NH}{>}C.CO_2H$. [202°]. Formed by the action of boiling alcoholic potash upon its ether, which is obtained by heating the (α)-naphthyl-hydrazide of pyruvic ether with $ZnCl_2$ (Schlieper, *A.* 239, 232). Silvery laminæ (from water), v. sl. sol. hot water, v. sol. alcohol and ether. Decomposes above 210° into CO_2 and (α)-naphthindole.

Ethyl ether EtA'. [170°].

(β)-Naphthindole-carboxylic acid $C_{13}H_9NO_2$ *i.e.* $C_{10}H_6<\substack{CH\\NH}>C.CO_2H$. [226°]. Obtained by saponifying its ether, which is formed when the (β)-naphthyl-hydrazide of pyruvic ether is heated with $ZnCl_2$ (Schlieper, *A.* 236, 181). Colourless plates, insol. water, sl. sol. ether, v. sol. hot HOAc and alcohol. Does not colour pine-wood. Bromine gives a yellow pp.

(α)-**NAPHTHINDOLE SULPHONIC ACID** $C_{10}H_6<\substack{NH\\CH}>C.SO_3H$ (?). The sodium salt of this acid, formed by the action of (α)-naphthylamine on the compound of glyoxal with $NaHSO_3$, is converted by mineral acids into (α)-naphthoxindole (Hinsberg, *B.* 21, 116).

β-Naphthindole sulphonic acid $C_{10}H_6<\substack{NH\\CH}>C.SO_3H$ or $C_{10}H_6<\substack{N\\CH_2}>C.SO_3H$. The sodium salt of this acid is obtained by the action of (β)-naphthylamine on the compound of glyoxal and $NaHSO_3$ (Hinsberg, *B.* 21, 113). It is stable towards alkalis, but converted by mineral acids into (β)-naphthoxindole.

NAPHTHIONIC ACID *v.* (1, 4)-NAPHTHYL-AMINE SULPHONIC ACID.

NAPHTHISATIN *v.* ISATIN.

NAPHTHOACRIDINE *v.* NAPHTHACRIDINE.

NAPHTHOBENZALDOXIM so-called, *v. Oxim* of NAPHTHOIC ALDEHYDE.

NAPHTHOBENZYL ALCOHOL *v.* NAPHTHYL-CARBINOL.

NAPHTHOBENZYLAMINE *v.* NAPHTHYL-CARBINYL-AMINE.

NAPHTHO-CINNAMIC ACID so-called, *v.* NAPHTHYL-ACRYLIC ACID.

NAPHTHOCOUMARIC ACID *v.* OXY-NAPHTHYL-ACRYLIC ACID.

NAPHTHOCOUMARIN *v. Anhydride* of OXY-NAPHTHYL-ACRYLIC ACID.

NAPHTHOCYAMIC ACID $C_{29}H_{18}N_8O_9$. The potassium salt of this acid is prepared by boiling di-nitro-naphthalene with alcoholic KCy (Mühlhäuser, *A.* 141, 214). The free acid is a brownish-black mass, insol. ether, nearly insol. water, m. sol. alcohol.—KA' aq. Dark mass, with coppery lustre, forming a fine blue solution in hot water and hot alcohol. The barium salt is a dark-blue pp., and explodes when heated. The silver salt is insol. water, has a bronze lustre, and explodes violently when heated.

NAPHTHO-HYDROQUINONE *v.* HYDRO-NAPHTHOQUINONE.

(α)-**NAPHTHOIC ACID** $C_{11}H_8O_2$ *i.e.* $C_{10}H_7CO_2H$. *Naphthalene* (α)-*carboxylic acid.* Mol. w. 172. [162°]. H.C.v. 1,232,000. H.C.p. 1,232,600. H.F. 77,400 (Stohmann, Kleber, a. Langbein, *J. pr.* [2] 40, 137).

Formation.—1. By saponifying its nitrile by boiling alcoholic potash (Merz, *Z.* [2] 4, 34; 5, 396) or conc. HClAq (Hofmann, *B.* 1, 39).—2. By heating a mixture of bromo-naphthalene and $Cl.CO_2Et$ with sodium-amalgam at 110° for several hours, and saponifying the resulting ether with alcoholic potash (Eghis, *C. R.* 69, 360).—3. By fusing potassium naphthalene (α)-sulphonate with sodium formate (V. Meyer, *A.* 156, 274).—4. By boiling with potash its amide which is formed by the action of $ClCO.NH_2$ on naphthalene in presence of $AlCl_3$ (Gattermann, *A.* 244, 56).

Preparation.—A mixture of 3 pts. of sodium naphthalene-(α)-sulphonate and 2 pts. of potassium ferrocyanide (both quite dry) is distilled from an iron tube, the nitrile is rectified and saponified by heating it with an equal volume of HCl to 200°; the yield is 25 p.c. of the sulphonate (Boessneck, *B.* 16, 639).

Properties.—Needles (from dilute alcohol), v. sl. sol. water, m. sol. hot alcohol. Yields naphthalene on distillation with lime, and phthalic acid on oxidation by CrO_3 in HOAc.

Salts.—BaA'_2 4aq. Needles, sl. sol. water.—$CaA'_2$2aq. S. 1·08 at 15°.—AgA'.

Ethyl ether EtA'. (309° cor.).

Chloride $C_{10}H_7.CO.Cl$. (297·5°). From the acid (4 pts.) and PCl_5 (5 pts.). Hydroxylamine converts it into $C_{10}H_7.CO.NH.OH$ [187°] and $(C_{10}H_7.CO)_2NOH$ [150°] (Ekstrand, *B.* 20, 1358). Reacts with potassium (β)-naphthoate, forming (αβ)-naphthoic anhydride $C_{10}H_7.CO.O.CO.C_{10}H_7$ (Hausmann, *B.* 9, 1515).

Amide $C_{10}H_7.CONH_2$. [202°]. Formed from the chloride and NH_3, or from the nitrile and alcoholic soda (Hofmann; Ekstrand, *J. pr.* [2] 38, 146). Prepared by passing dry gaseous cyanic acid and HCl into a solution of naphthalene in CS_2, containing $AlCl_3$ heated on the water-bath (Gattermann a. Rossolymo, *B.* 23, 1197). Colourless monoclinic tables (from alcohol) (Bamberger a. Philip, *B.* 20, 241).

Anilide $C_{10}H_7.CONHPh$. [160°]. White silky crystals.

(α)-*Naphthalide* $C_{10}H_7.CO.NHC_{10}H_7$. [244°].

Anhydride $(C_{10}H_7.CO)_2O$. [145°]. Obtained by distilling calcium naphthoate with naphthyl chloride (Hofmann). Prisms (from boiling benzene).

Nitrile $C_{10}H_7.CN$. (α)-*Cyano-naphthalene.* Mol. w. 153. [37°]. (298° cor.). *Formation.*—1. By distilling naphthylamine with oxalic acid, and heating the resulting formyl derivative of naphthylamine with HClAq (Hofmann, *A.* 142, 121; *B.* 1, 39).—2. By distilling potassium naphthalene (α)-sulphonate with KCy (Merz, *Bl.* [2] 9, 335; 10, 47) or K_4FeCy_6 (Boessneck, *B.* 16, 639; Hausmann, *B.* 9, 1514).—3. By passing a mixture of cyanogen and naphthalene through a red-hot tube (Merz a. Weith, *B.* 10, 746).—4. By heating di-naphthyl-thio-urea with copper powder (Weith, *B.* 6, 967).—5. By heating tri-(α)-naphthyl phosphate with KCy; the yield being 20 p.c. of the theoretical (Heim, *B.* 16, 1779).—6. By boiling the formyl derivative of (α)-naphthylamine with zinc-dust in a current of hydrogen; the yield being 11 p.c. (Gasiorowski a. Merz, *B.* 18, 1006).—7. By the action of cuprous cyanide on (α)-diazo-naphthalene salts (Bamberger a. Philip, *B.* 20, 257). *Properties.* — Needles. Reduced in alcoholic solution by sodium to the tetrahydride of naphthyl-carbinylamine $C_{10}H_{11}.CH_2NH_2$. On heating with hydroxylamine it yields $C_{10}H_{11}.CONH_2$ and naphthamidoxim [149°].

(β)-Naphthoic acid $C_{10}H_7.CO_2H$. *Isonaphthoic acid.* [185° cor.]. (above 300°). H.C.v. 1,227,800. H.C.p. 1,228,400. H.F. 81,600 (Stohmann, Kleber, a. Langbein, *J. pr.* [2] 40, 137).

Formation.—1. By saponification of its

nitrile, which is formed by heating potassium naphthalene (β)-sulphonate with KCy (Merz a. Mühlhäuser, *Z.* [2] 5, 70).—2. By boiling (β)-methyl-naphthalene with conc. HNO_3 (Ciamician, *B.* 11, 272).—3. By oxidising (β)-naphthoic aldehyde with $KMnO_4$ (Schulze, *B.* 17, 1530).

Properties.—Long white needles (from hot water); sl. sol. hot water, v. sol. alcohol and ether. Yields naphthalene on distillation with baryta. Oxidised to phthalic acid by CrO_3 in HOAc.

Salts.—NaA'$\frac{1}{2}$aq (Vieth, *A.* 180, 314). Small tables, v. e. sol. water.—KA' $\frac{1}{2}$aq.—BaA'$_2$ 4aq.—Needles (from hot water). S. ·07 at 15°.—CaA'$_2$ 3aq. S. ·055 at 15°.—MgA'$_2$ 5aq.—AgA'.

Methyl ether MeA'. [77°]. (290°). H.F. 70,600 (Stohmann, *J. pr.* [2] 40, 353).

Ethyl ether EtA'. (309°).

Chloride $C_{10}H_7$.COCl. [43°]. (305°). Formed from the acid and PCl_5 (Vieth; *cf.* Grucarevic a. Merz, *B.* 6, 1242). Hydroxylamine solution at 100° attacks it, forming the compounds $C_{10}H_7$.CO.NH.OH [168°], and $(C_{10}H_7.CO)_2NOH$ [171°] (Ekstrand, *B.* 20, 1359). The (β)-naphthoyl hydroxylamine reacts with (α)-naphthoyl chloride forming ($\alpha\beta$)-di-naphthoyl-hydroxylamine [160°]. With urea it forms di-naphthoyl-urea [215°].

Anhydride $(C_{10}H_7.CO)_2O$. [134°]. Plates composed of needles (Hausmann, *B.* 9, 1515).

Amide $C_{10}H_7.CONH_2$. [192°]. Formed by warming the chloride with powdered ammonium carbonate. Formed also by heating the nitrile with alcoholic potash (Leone, *G.* 14, 120). Plates.

Anilide $C_{10}H_7$.CO.NHPh. [170°]. Small plates (from benzene).

p-Toluide $C_{10}H_7.CO.NHC_7H_7$. [191°]. Silky needles.

(α)-*Naphthalide* $C_{10}H_7.CO.NH.C_{10}H_7$. [157°]. Very small needles, sl. sol. ether.

Nitrile $C_{10}H_7$.CN. [66·5°]. (305° cor.). Formed by reactions like those used for preparing its (α)-isomeride (*v. supra*). White mass, nearly insol. water, v. sol. alcohol and ether. When its alcoholic solution is saturated with HCl there is formed the hydrochloride of naphthimido-ethyl ether (*q.v.*) (Pinner a. Lohmann, *B.* 11, 1485). By exhaustive chlorination with $SbCl_5$ it yields per-chloro-benzene (Merz a. Weith, *B.* 16, 2887).

References.—Amido-, Bromo-, Bromo-nitro-, Chloro-, Chloro-nitro-, Nitro-, Oxy-, and Thio-, naphthoic acids, and Amido-, and Bromo-amido-naphthoic anhydride.

(α)-**NAPHTHOIC ACID TETRAHYDRIDE** $C_{10}H_{11}.CO_2H$ [128°]. Formed, together with the amide, by heating its nitrile with alcoholic potash for 5 or 6 hours at 165° (Bamberger a. Bordt, *B.* 22, 629). Slender dendritic prisms, v. sol. alcohol, sl. sol. cold water.—CuA'$_2$: bluish-green pp.—PbA'$_2$: needles grouped in stars.—AgA': flaky pp.

Amide $C_{10}H_{11}.CONH_2$. [182°]. Flat needles, v. sol. boiling water.

Nitrile $C_{10}H_{11}$.CN. (278°) at 721 mm. Formed from (α)-naphthylamine tetrahydride by Sandmeyer's reaction, and purified by steam-distillation.

(α)-**NAPHTHOIC ALDEHYDE** $C_{10}H_7$.CHO. '*Naphthobenzaldehyde.*' Mol. w. 156. (292° cor.). Formed from naphthyl-carbinol by oxidation with chromic acid mixture (Bamberger a. Lodter, *B.* 21, 258). Pale-yellow viscid liquid, with faint aromatic odour. Conc. HNO_3 at −5° yields a nitro-derivative [136°]. It forms with $NaHSO_3$ a compound crystallising in glistering leaflets. The phenyl hydrazide [185°] forms yellow leaflets, which turn red on exposure to light. Aniline forms $C_{10}H_7$CH:NPh [71°]; o-toluidine yields $C_{10}H_7CH{:}NC_7H_7$ [59°]; *p*-toluidine produces $C_{10}H_7CH{:}NC_7H_7$ [93°]; and (α)-naphthylamine $C_{10}H_7CH{:}NC_{10}H_7$ [117°].

Oxim $C_{10}H_7$.CH.NOH. '*Naphthobenzaldoxim.*' [98°]. Colourless needles (from alcohol), sl. sol. water (Brandes, *B.* 22, 2151).

(β)-Naphthoic aldehyde $C_{10}H_7$.CHO. [61°]. Formed by distilling a mixture of calcium (β)-naphthoate and calcium formate at a high temperature (Battershall, *Z.* [2] 7, 292, 673; *A.* 168, 116). Formed also by heating ω-chloro-(β)-methyl-naphthalene ($C_{10}H_7.CH_2Cl$) with lead nitrate (Schulze, *B.* 17, 1530), and by oxidising (β)-naphthyl-carbinol (Bamberger a. Brekmann, *B.* 20, 1118). Silvery plates; volatile with steam. Reduces ammoniacal $AgNO_3$. Alcoholic NH_3 converts it into the hydramide $(C_{10}H_7.CH)_3N_2$ [146°–150°].

(α)-**NAPHTHOL** $C_{10}H_7$.OH. Mol. w. 144, [94°]. (279°). S.G. $\frac{4}{4}$ 1·224 (Schröder, *B.* 12, 1613). R_∞ 76·97 in an 8·6 p.c. alcoholic solution (Kanonnikoff, *J. pr.* [2] 31, 348); 75·25 (Nasini a. Bernheimer, *G.* 14, 153). Occurs in anthracene-oil obtained from coal tar (K. E. Schulze, *A.* 227, 150).

Formation.—1. By the action of nitrous acid on (α)-naphthylamine (Griess, *J.* 1866, 460). 2. From naphthalene (α)-sulphonic acid by potash-fusion (Eller, *A.* 152, 275).—3. By heating γ-phenyl-isocrotonic acid $CHPh{:}CH.CH_2.CO_2H$ at its boiling-point for 5 or 10 minutes, water being eliminated (Fittig a. Erdmann, *B.* 16, 43; *A.* 227, 242).

Preparation.—By heating naphthalene (1 pt.) with H_2SO_4 (2 pts.) at 60° to 70°, and fusing the sodium salt of the (α)-sulphonic acid formed with three times its weight of NaOH.

Properties.—Short trimetric prisms (Léger, *C. R.* 111, 110); sl. sol. hot water, v. sol. alcohol, ether, and benzene. Volatile with steam. Pine-wood, moistened with an aqueous solution of (α)-naphthol, and then with HClAq, turns green in sunlight, and finally reddish brown. Bleaching-powder gives, in a solution of (α)-naphthol, a dark-violet colour, and ultimately violet flakes, which are turned brown by heating, but are decolourised by ammonia. $FeCl_3$ gives a milky pp., soon becoming violet flakes of (α)-dinaphthol. (α)-Naphthol is a powerful antiseptic, more powerful in this respect than (β)-naphthol, although less poisonous (Maximovitch, *C. R.* 106, 366).

Reactions.—1. On boiling in the air, or on heating in sealed tubes at 350°–400°, it yields dinaphthylene oxide $(C_{10}H_6)_2O$ (Merz a. Weith, *B.* 14, 196).—2. Heated to 270° for 8 hours with four times its weight of *ammoniacal* $CaCl_2$ (damp) it yields about 74 p.c. of (α)-naphthylamine. If ammoniacal $ZnCl_2$ is used instead of $CaCl_2$, the product is 60 p.c. of ($\alpha\alpha$)-dinaphthylamine (Benz, *B.* 16, 14; *cf.* Merz a. Weith, *B.* 14, 2344).—3. *Aniline* and $CaCl_2$ yield, on heat-

ing, a little phenyl-naphthyl-amine (M. a. W.).—4. *Ammonium acetate* at 270° yields the acetyl derivative of (α)-naphthylamine (Calm, *B.* 15, 615).—5. *Ammonium formate* at 250° yields CO and (α)-naphthylamine.—6. When (α)-naphthol (2 pts.) is heated with anhydrous oxalic acid (1 pt.) and conc. H_2SO_4 (1 pt.) at 130°, there is formed a compound $C_{22}H_{12}O_2$, crystallising from chloroform in pale rose-coloured leaflets, insol. alcohol and ether, converted by potash-fusion into the acid $C_{22}H_{14}O_3$ (crystallising in golden-green tables), and yielding the halogen derivatives $C_{22}H_{10}Cl_2O_2$ and $C_{22}H_{10}Br_2O_2$, both of which crystallise in the monoclinic system (Hönig, *M.* 1. 251).—7. Boiling with $KClO_3$ and HCl yields di-chloro-naphthoquinone (Wichelhaus, *A.* 152, 301).—8. *Chlorine*, acting on (α)-naphthol dissolved in HOAc, forms $C_{10}H_5Cl_2OH$ [108°] and $C_6H_4<\begin{smallmatrix}CO.CCl_2\\CCl:CH\end{smallmatrix}$ [121°]. When the liquid is kept cold the product is $C_6H_4<\begin{smallmatrix}CO.CCl_2\\CCl_2.CClH\end{smallmatrix}$ [157°] (Zincke a. Kegel, *B.* 21, 1030, 1044).—8. PCl_5 at 100° forms di-naphthyl phosphate. At 150° it yields (α)-chloronaphthalene (Oehler, *B.* 15, 312).—9. Conc. HClAq at 200° yields di-naphthyl-oxide.—10. *Aluminium* and *iodine* yield aluminium-(α)-naphthol (Gladstone a. Tribe, *C. J.* 41, 16). On distillation of this body there is formed a dinaphthyl [189°].—11. *Iodine* and *potash* yield a dark-violet compound (Messinger a. Fortmann, *B.* 22, 2322).—12. Somewhat more readily oxidised by $KMnO_4$ than (β)-naphthol (Dreyfus, *C. R.* 105, 523).—13. H_2SO_4 yields mono- and di- sulphonic acids. In presence of HOAc it also forms oxy-naphthyl methyl ketone. 14. HCl, acting on a mixture of (α)-naphthol and aldehyde below 0° forms $CH_3.CH(C_{10}H_6.OH)_2$ (Claus a. Trainer, *B.* 19, 3004).—15. *Di-chloro-ether* $C_2H_3Cl_2OEt$ yields amorphous $C_{32}H_{24}O_3$ or $C_2H_3(C_{10}H_6OH)_3$ (Wislicenus, *A.* 243, 165).—16. *Benzoic aldehyde* yields $C_6H_5.CH(C_{10}H_6OH)_2$, which turns brown in air (Claisen, *B.* 19, 3316). 17. When boiled with *phthalic anhydride* it yields naphthol-phthaleïn $C_{28}H_{16}O_3$ (Grabowski, *B.* 4, 661, 725; 6, 1065).—18. *Pyromellitic anhydride* (1 mol.), heated with (α)-naphthol (4 mols.), at 300° yields the compounds $C_{50}H_{26}O_6$ and $C_{50}H_{28}O_7$ [265°]. When the two bodies are heated together in other proportions at 250° there are formed the compounds $C_{40}H_{24}O_8$, $C_{40}H_{22}O_7$, and $C_{30}H_{18}O_8$ (Grabowski).—19. *Maleïc anhydride* and $ZnCl_2$ at 160° forms $C_{24}H_{16}O_4$ and an acid $CO_2H.CH:CH.CO.C_{10}H_6OH$ [90°] (Burckhardt, *B.* 18, 2868).—20. *Benzotrichloride* at 100° forms $\{C_6H_5.C(C_{10}H_6OH)_2\}_2O$, a reddish-brown powder, insol. water, sol. alcohol and ether (Doebner, *A.* 257, 58).

Picric acid compound $C_{10}H_8OC_6H_2(NO_2)_3OH$. [190°]. Orange needles (Marchetti, *G.* 12, 503).

Compound with camphor $C_{10}H_8OC_{10}H_{16}O$. S.G. $\frac{9}{}$ 1·0327. $[\alpha]_D = 10·5°$. Syrupy liquid, not solid at −16°. Not sensibly decomposed by water (Léger, *C. R.* 111, 110).

Acetyl derivative $C_{10}H_7.OAc$. [49°]. Formed by heating (α)-naphthol with AcCl (Schaeffer, *B.* 2, 131). Formed also by heating α)-naphthol with HOAc at 200° (Graebe, *A.* 209, 151), or with Ac_2O and NaOAc (Tassinari, *G.* 10, 471). Large crystals, sol. alcohol and ether. Split up into (α)-naphthol and acetic acid by distillation with steam. On oxidation with CrO_3 in cold HOAc it yields *c*-oxy-phthalic acid, and three compounds melting at 114°, 119°, and 121° respectively (Miller, *B.* 14, 1601).

Benzoyl derivative $C_{10}H_7.OBz$. [56°]. Crystals, v. sol. ether (Maikopar, *Z.* 1869, 216).

Methyl ether $C_{10}H_7.OMe$. (270°) (V.); (258°) (S.); (266°) (M.); (265°) (H.); (269° i.V.) (N. a. B.) S.G. $\frac{15}{}$ 1·0974 (S.); $\frac{14}{4}$ 1·0964 (Nasini, *G.* 15, 84). Prepared by the action of MeCl on sodium (α)-naphthol (Vincent, *Bl.* [2] 40, 106) or of MeI (60 g.), KOH (25 g.), and MeOH on (α)-naphthol (60 g.) (Staedel, *A.* 217, 42). Formed also by heating (α)-naphthylamine with methyl alcohol and $ZnCl_2$ at 200° (Hantzsch, *B.* 13, 1347); and by heating MeOH with (α)-naphthol and HCl (Manchetti, *G.* 9, 545). Prepared by boiling (α)-naphthol for several hours with MeOH and $ZnCl_2$ (Green, *priv. com.*). Liquid, smelling like orange-blossom, sol. alcohol, ether, and benzene. With HNO_3 it gives a tri-nitro- derivative [128°]. With picric acid it forms a compound crystallising in red needles, decomposed by alcohol.

Ethyl ether $C_{10}H_7.OEt$. (281° cor.). Formed from (α)-naphthol, KOH, and EtI in alcoholic solution (Schaeffer, *A.* 152, 286); or from (α)-naphthol (25 g.), MeOH (25 g.), and H_2SO_4 (10 g.) at 125° (Gattermann, *A.* 244, 72). Heavy oil. Converted by HNO_3 into a tri-nitro-derivative $C_{10}H_4(NO_2)_3OEt$ [148°] (Staedel, *B.* 14, 899).

Propyl ether $C_{10}H_7.OC_3H_7$. (299° cor.). S.G. $\frac{18·4}{4}$ 1·0447 (Nasini a. Bernheimer, *G.* 15, 84).

Ethylene ether $(C_{10}H_7O)_2C_2H_4$. [126°]. Plates (from alcohol) (Koelle, *B.* 13, 1956).

(α)-*Naphthyl ether* v. DI-NAPHTHYL OXIDE.

Nitroso- derivatives v. *Oxim* of (α)- and (β)- NAPHTHOQUINONE.

(β)-Naphthol $C_{10}H_7.OH$. Mol. w. 144. [123°]. (286°). S.G. $\frac{4}{}$ 1·217 (Schröder, *B.* 12, 1613). R_∞ 76·43 in an 11·18 p.c. alcoholic solution (Kanonnikoff, *J. pr.* [2] 31, 348). S. ·02; S. (20 p.c. alcohol) ·2 (Bouchard, *C. R.* 105, 702). Occurs in coal-tar (K. Schulze, *A.* 227, 150). Formed by the action of nitrous acid on (β)-naphthylamine (Liebermann, *A.* 183, 268). Prepared by fusing sodium naphthalene (β)-sulphonate (1 pt.) with NaOH (2 pts.) at 300° (Schäffer, *A.* 152, 282).

Properties.—Plates or tables, sl. sol. hot water, v. sol. alcohol, ether, chloroform, and benzene. Readily sublimes. May be distilled by superheated steam. Powerfully antiseptic (Bouchard; Maximovitch, *C. R.* 106, 1441). Pine-wood dipped in an aqueous solution of (β)-naphthol and then in HClAq becomes green on exposure to daylight. Bleaching powder colours a solution of (β)-naphthol slightly yellow, but the colour is destroyed by excess of bleaching-powder; on adding ammonia and warming, yellowish flakes separate. $FeCl_3$ colours its solution slightly green, and, after a time, causes deposition of white flakes (of dinaphthol), which become brown on heating. Its solution in NaOHAq yields with mercuric chloride a pp. $(C_{10}H_7O)_2HgHgCl_2·4aq$ (Pouchet, *C. R.* 106, 276). It may be estimated by adding standard iodine

solution to its solution in warm aqueous NaOH (Messinger a. Vortmann, *B.* 23, 2754).

Reactions.—1. Alkaline potassium permanganate *oxidises* it to *o*-carboxy-cinnamic acid $CO_2H.C_6H_4.CH:CH.CO_2H$ [184°], and an acid $C_{20}H_{12}O_4$ [281°] which forms the salts $BaA'_2$7aq and AgA′, an ether EtA′ [123°] and a dihydride $C_{20}H_{14}O_4$ [224°] (Ehrlich a. Benedikt, *M.* 9, 527; 10, 115). When (β)-naphthol is boiled with P_2O_5, or even by itself in presence of air, it forms di-(β)-naphthylene oxide.—2. The dry distillation of calcium (β)-naphthylate $Ca(OC_{10}H_7)_2$ yields di-(β)-naphthylene oxide, naphthalene, (β)-naphthol, and a compound $C_{21}H_{14}O$ (?) [300°–305°] (Niederhäusern, *B.* 15, 1122).—3. *Zinc chloride* forms, on heating, isodinaphthylene oxide.—4. *Chloride of sulphur* in presence of CS_2 or benzene forms $(HO.C_{10}H_6)_2S$ and $(HO.C_{10}H_6)_2S_2$ (Tassinari, *G.* 17, 94; Onufrovitch, *B.* 23, 3356).—5. Boiling with *sulphur* and *caustic soda* solution forms $(HO.C_{10}H_6)_2S_2$ [210°] and a compound melting at 170° (Lange, *B.* 21, 260).—6. By heating (β)-naphthol (150 g.) with *aluminium* (10 g.) as long as hydrogen comes off there is formed a mixture of (β)-naphthol and aluminium (β)-naphthylate, which when distilled yields di-(β)-naphthyl oxide (Gladstone a. Tribe, *C. J.* 41, 15).—7. When heated in sealed tubes with *ammonia*, NH_4Cl, acetamide, ammonium acetate or ammonium formate, it yields (β)-naphthylamine. Heated to 270°–280° for 8 hrs. with four times its weight of ammoniacal $CaCl_2$ (damp) it yields 80 p.c. of (β)-naphthylamine and 12 p.c. of (ββ)-dinaphthylamine. If ammoniacal $ZnCl_2$ is used instead of $CaCl_2$ the product is 4 p.c. of (β)-naphthylamine and 82 p.c. of (ββ)-dinaphthylamine (Benz, *B.* 16, 9).—8. Reacts with *nitroso-dimethyl aniline* forming (β)-naphthol-violet $C_{18}H_{16}N_2O$ (Meldola, *C. J.* 39, 37), which is converted by heat into 'cyanamine,' a blue colouring matter $C_{36}H_{25}N_4O_2$ (Witt, *B.* 23, 2247).—9. *Di-chloro-quinonimide* $C_6H_4(NCl)_2$ forms a red colouring matter $HN:C_6H_3<^{N}_{O}>C_{10}H_6$ which forms a blue solution in conc. H_2SO_4 (Nietzki a. Otto, *B.* 21, 1744). The free base is a yellow pp., v. sol. alcohol and ether, and is converted by heat into a greenish-blue colouring matter, greatly resembling 'cyanamine' (*v. supra*).—10. *Nitrogen iodide* forms iodo-(β)-naphthol, a substance melting at 223°, and an amorphous body (Willgerodt, *J. pr.* [2] 37, 446).—11. *Di-chloro-di-ethyl oxide* $CH_2Cl.CHCl.OEt$ yields $C_{22}H_{15}ClO$ [174°] crystallising in plates, insol. water, sol. alcohol and HOAc (Wislicenus, *A.* 243, 169).—12. When *chlorine* is passed into a solution of (β)-naphthol in HOAc and the product is treated with an excess of $SnCl_2$ there is obtained [1:2] $C_{10}H_6Cl.OH$ [71°] (Zincke, *B.* 21, 3284). This chloro-(β)-naphthol when dissolved in HOAc or chloroform and treated with chlorine yields $C_6H_4<^{CCl_2.CO}_{CH\ :CH}$ (Zincke, *B.* 21, 3540). When (β)-naphthol dissolved in HOAc is treated with excess of chlorine there is formed the compound $C_6H_4<^{CCl_2\ .CO}_{CHCl.CHCl}$ crystallising in plates [103°] or needles [102°] and converted by Na_2CO_3 into chloro-(β)-napthoquinone [172°] (Zincke, *B.* 21, 3550). When chlorine is passed into a well-cooled 10 p.c. solution of (β)-naphthol, there is formed $C_6H_4<^{CCl_2.CO}_{CH\ :CCl}$ which crystallises from hot alcohol in thick yellow needles [96°] (Z.).—13. *Chloroform* in presence of a small quantity of aqueous NaOH forms on boiling crystalline $C_{22}H_{14}O_2$ or $C_{10}H_6<^{C(OH)}_{C_{10}H_6}>C(OH)$, its anhydride $C_{22}H_{12}O$, an aldehyde $C_{10}H_6(OH).CHO$, an alcohol $C_{22}H_{14}O$, and resins (Rousseau, *C. R.* 94, 133; 95, 30, 232).—14. An acetic acid solution of *aldehyde* slowly reacts in the cold forming the di-(β)-naphthyl ether of acetic orthaldehyde $CH_3.CH(OC_{10}H_7)_2$ [201°] (Claisen, *B.* 19, 3318).—15. A few drops of HCl added to a cold solution of *benzoic aldehyde* and (β)-naphthol in HOAc forms $C_6H_5.CH(OC_{10}H_7)_2$ [205°] converted by heating with HOAc and hydrochloric acid solution into $C_6H_5.CH<^{C_{10}H_6}_{C_{10}H_6}>O$ [190°] (Claisen, *B.* 19, 3316). On adding H_2SO_4 (2 pts.) to a solution of benzoic aldehyde (3 pts.) and (β)-naphthol (6 pts.) in alcohol (3 pts.) there is formed $C_{68}H_{46}O_3$ [191° uncor.], a crystalline substance, not affected by boiling Ac_2O, and converted by fuming HNO_3 into $C_{45}H_{17}(NO_2)_7O_2$ (Trzciński, *B.* 17, 499).—16. *Benzotrichloride* at 100° forms $\{C_6H_5C(O.C_{10}H_7)_2\}_2O$ which melts above 350° and may be distilled. It crystallises in white needles, insol. water, alcohol, and ether, sol. nitrobenzene (Doebner, *A.* 257, 59).

Combinations.—With picric acid $C_{10}H_8O.C_6H_2(NO_2)_3OH$. [155°]. Orange-yellow needles (from alcohol), almost insol. cold water (Marchetti, *G.* 12, 504).—With aniline $C_{10}H_8OC_6H_7N$. [82·4°]. Crystalline powder (from ligroïn) (Dyson, *C. J.* 43, 469).—With *p*-toluidine $C_{10}H_8OC_7H_9N$. [80·8°] (D.).

Acetyl derivative $C_{10}H_7OAc$. [70°] (O. Miller, *B.* 14, 1602). Small needles.

Benzoyl derivative $C_{10}H_7OBz$. [107°]. Nodular groups of needles (Maikopar, *Z.* 1869, 216).

Methyl ether $C_{11}H_{10}O$ *i.e.* $C_{10}H_7.OMe$. [72°] (Staedel, *A.* 217, 43); [70·5°] (Vincent, *Bl.* [2] 40, 106). (274°) (Marchetti, *G.* 9, 545). Formed from (β)-naphthol, KOH, MeOH, and MeI or MeCl. Formed also by boiling (β)-naphthol with MeOH and $ZnCl_2$. White plates (from alcohol), insol. cold water, v. sol. ether. Volatile with steam. With HNO_3 (S.G. 1·5) it gives at 0° a tri-nitro- derivative [213°].

Ethyl ether $C_{10}H_7OEt$. [33°]. (275°). Formed from (β)-naphthol, KOH, and EtI (Schäffer; Liebermann, *B.* 15, 1428). Crystalline mass, decomposed in a sealed tube at 310° into ethylene and (β)-naphthol (Bamberger, *B.* 19, 1819).

Bromo-ethyl ether $C_{10}H_7.OC_2H_4Br$. [96°]. Prepared by the action of ethylene bromide and KOH on (β)-naphthol (Koelle, *B.* 13, 1954). Colourless plates; sol. alcohol. Alcoholic ammonia at 100° converts it into amorphous $C_{10}H_7.O.CH_2.CH_2NH_2$, while aniline yields crystalline $C_{10}H_7O.CH_2.CH_2.NHPh$ [75°].

Methylene ether $CH_2(OC_{10}H_7)_2$. [134°].

Ethylene ether $C_2H_4(OC_{10}H_7)_2$. [217°]. S. (benzene) ·5. Plates (from benzene); insol. alcohol and ether.

Ethylidene ether *v.* ALDEHYDE, vol. i. p. 105.

Benzyl ether *v.* BENZYL- NAPHTHYL OXIDE.

Naphthyl ether v. Di-naphthyl oxide.

Nitroso- derivative v. *Oxim* of (β)-Naphthoquinone.

References.—Amido-, Amido-di-imido-, Bromo-, Bromo-nitro-, Chloro-, Iodo-, Iodo-nitro-, and Nitro- naphthols.

(α)-Naphthol tetrahydride $C_{10}H_{12}O$ *i.e.* $\begin{array}{l}CH_2.CH_2.C.CH{=\!=}CH\\ CH_2.CH_2.C.C(OH):CH\end{array}$. *Tetrahydro-(α)-naphthol.* [69°]. (265·5°) at 705 mm. Obtained by reducing (α)-naphthol in amyl-alcoholic solution by sodium. Occurs in the distillate obtained in the preparation of the nitrile of the tetrahydride of (α)-naphthoic acid (Bamberger a. Bordt, *B.* 22, 628; 23, 215). Formed also from the tetrahydride of (α)-naphthylamine by the diazo-reaction (Bamberger a. Althausse, *B.* 21, 1892). Silvery white monoclinic tables, smelling like phenol, and turning red in air; sl. sol. water, v. e. sol. alcohol and ether. Bleaching powder gives only yellowish flakes in its boiling aqueous solution (whereas with (α)-naphthol it gives a deep violet colour). $FeCl_3$ gives no colouration.

Ethyl ether $C_{10}H_{11}OEt$. (259°) at 705 mm. Formed by means of EtOH, KOH, and EtI.

(β)-Naphthol tetrahydride ('aromatic') $\begin{array}{l}CH_2.CH_2.C.CH:COH\\ CH_2.CH_2.C.CH:CH\end{array}$. *ar-Tetrahydro-(β)-naphthol.* [58°]. (275°). Formed by the action of nitrous acid on 'aromatic' (β)-naphthylamine tetrahydride (Bamberger a. Kitschelt, *B.* 23, 884). It is also one of the products of the reduction of (β)-naphthol by sodium (*v. infra*). Flat silvery needles, sl. sol. water, v. sol. alcohol and ether. Smells like creosote. Not etherified by heating with alcohol and H_2SO_4 at 100°. Not affected by heating with conc. H_2SO_4; hot dilute H_2SO_4 appears to form di-naphthyl oxide octohydride $(C_{10}H_{11})_2O$ (Bamberger a. Lengfeld, *B.* 23, 1129). Bleaching-powder added to its aqueous solution forms a white flocculent pp. $FeCl_3$ gives a bluish-green colour, and, on warming, a brownish-yellow flocculent pp. Chloroform and caustic soda give a greenish-yellow colour. $NaNO_2$ added to its solution in conc. H_2SO_4 gives a rose-red colour. Forms a wine-red compound with diazobenzene sulphonic acid. The sodium salt $C_{10}H_{11}ONa$ crystallises in silky scales.

(β)-Naphthol tetrahydride ('alicyclic') $\begin{array}{l}CH:CH.C.CH_2.CH.OH\\ CH:CH.C.CH_2.CH_2\end{array}$, *ac-Tetrahydro-(β)-naphthol.* (178° at 53 mm.); (264°) at 716 mm. Formed by adding sodium to a boiling solution of (β)-naphthol in isoamyl alcohol (Bamberger a. Lodter, *B.* 23, 204), and separated from the accompanying 'aromatic' isomeride by aqueous NaOH, in which it is insoluble (Bamberger a. Kitschelt, *B.* 23, 885). V. sl. sol. water, v. sol. alcohol and ether. On warming with KOH it yields naphthalene dihydride. HI yields an iodide, which readily splits up into HI and naphthalene dihydride. Does not react with diazo- compounds.

Benzoyl derivative $C_{10}H_{11}OBz$. [63°]. (255° at 40 mm.). Formed by heating with HOBz at 170° (Bamberger a. Lodter, *B.* 23, 209). Tables, v. e. sol. warm alcohol and benzene. Split up on distillation into benzoic acid and naphthalene dihydride.

Acetyl derivative $C_{10}H_{11}OAc$. (169° at 34 mm.). Formed by the action of HOAc at 140°–150°. Decomposed at 268°–280° into HOAc and naphthalene dihydride.

NAPHTHO-LACTONE *v. Anhydride* of Oxy-naphthoic acid.

NAPHTHOL ALDEHYDE *v.* Oxy-naphthoic aldehyde.

NAPHTHOL-AZO- compounds *v.* Azo- compounds.

DINAPHTHOL *v.* Di-oxy-dinaphthyl.

(α)-NAPHTHOL BLUE $C_{18}H_{16}N_2O$ *i.e.* $NMe_2.C_6H_4.N\!<\!\begin{array}{c}C_{10}H_6\\ O\end{array}\!>$. *Indophenol.* Formed by the action of nitroso-dimethylaniline on (α)-naphthol, and by the action of dibromo-(α)-naphthol on dimethyl-*p*-phenylene-diamine in alkaline solution. (Köchlin, *Bull. de Mulh.* 52, 532; Witt, *S. C. I.* 1, 255). Obtained also by oxidising a mixture of di-methyl-*p*-phenylene diamine and (α)-naphthol or (α)-naphthylamine with dilute $K_2Cr_2O_7$ and HCl (Pabst, *Bl.* [2] 38, 161; Möhlau, *B.* 16, 2851; 18, 2913). Bluish-violet crystals, with bronze lustre (from alcohol), insol. water. Dissolves in HClAq with yellow colour, being split up into (α)-naphthoquinone and dimethyl-*p*-phenylene-diamine.

NAPHTHOL CARBOXYLIC ACID *v.* Oxy-naphthoic acid.

(α)-NAPHTHOL-GLYCURONIC ACID $C_{16}H_{16}O_7$. [203°]. Occurs in urine after taking (α)-naphthol (Lesnik a. Nencki, *B.* 19, 1537). Long needles, v. sl. sol. chloroform. Split up by dilute HClAq into (α)-naphthol and glycuronic acid. Its aqueous solution is coloured a transient green by H_2SO_4.

(β)-Naphthol-glycuronic acid $C_{16}H_{16}O_7$. [150°]. $[\alpha] = -88°$. Occurs in the urine of dogs dosed with (β)-naphthol, and can be separated through the insolubility of the lead salt (Lesnik a. Nencki, *B.* 19, 1534). Needles (containing 2aq), sl. sol. water, v. sl. sol. chloroform. Conc. H_2SO_4 gives an intense green colour. Split up by HClAq into (β)-naphthol and glycuronic acid. —CaA'_2 4aq.

(α)-NAPHTHOL-MALEÏN $C_{24}H_{16}O_4$ *i.e.* $\begin{array}{l}CH:CH.C(C_{10}H_6.OH)_2\\ CO{-\!-\!-}O\end{array}$. [118°–120°]. Formed, together with a compound $C_{14}H_{10}O_4$, by heating (α)-naphthol with maleic anhydride and $ZnCl_2$. Violet powder, consisting of microscopic four-sided tablets. Dissolves in alcohol to a red solution, which on addition of NH_3 assumes a deep greenish-red fluorescence. Sol. ether, chloroform, and acetic acid, insol. benzene and CS_2 (Burckhardt, *B.* 18, 2867).

NAPHTHOL SULPHIDE *v.* Di-oxy-di-naphthyl sulphide.

(1, 2)-NAPHTHOL SULPHONIC ACID [1:2] $C_{10}H_6(OH)SO_3H$. (α)-*Naphthol 'α'-sulphonic acid.* [101°]. Prepared by heating (α)-naphthol (1 pt.) with conc. H_2SO_4 (2 pts.) on a water-bath (Schaffer, *A.* 152, 293; Claus, *B.* 15, 312; Baum, *G. P.* B 4197 of June 30, 1883; *Monit. Scient.* 1883, 1122). Long, radiating, very deliquescent needles; v. sol. water and alcohol. Dissolves in HNO_3, the solution slowly depositing di-nitro-(α)-naphthol. $FeCl_3$ colours its solution deep blue, changing to green on warming, but becoming blue again on cooling. Gives no colour with bleaching powder. PCl_5 (2 mols.) at 120° yields chloro-naphthol [57°] and di-chloro-naphthalene [94°] (Claus a. Oehler, *B.* 15, 313).

S a l t s.—CaA'_2 3aq. Small laminæ; v. sol. water.—PbA'_2 4aq: needles; v. sol. water.—$PbC_{10}H_6SO_4$ (dried at 100°): minute needles.

Ethyl derivative $C_{10}H_6(OEt).SO_3H$. Obtained from the acid by treatment with alcoholic KOH and EtI (Maikopar, *Z.* 1870, 306).—$KA'\frac{1}{2}$aq: crystalline powder; sl. sol. cold water.

(1, 3?)-**Naphthol sulphonic acid** $C_{10}H_8SO_4$ *i.e.* $C_{10}H_6(OH).SO_3H$. (α)-*Naphthol 'β'-sulphonic acid.* [90° uncor.]. Formed, together with other sulphonic acids by sulphonation of (α)-naphthol in acetic acid solution by means of fuming sulphuric acid (80 p.c. SO_3). It is separated from concomitant products by the sparing solubility of its barium or lead salt. Deliquescent, long, fine needles. Very unstable, being converted into (α)-naphthol and H_2SO_4 by boiling its dilute aqueous or alcoholic solutions. The sodium salt cannot be converted into the chloride by PCl_5, but at once yields di-chloro-(α)-naphthol

$$C_6H_4\left\langle\begin{array}{l}C(OH):CCl\\ \quad\quad\quad\ |\\ CH\quad :CCl\end{array}\right. \quad [90°].$$

S a l t s.—NaA': easily soluble white silvery plates.—×KA': easily solubl eneedles. BaA'_2aq: colourless plates; v. sl. sol. cold water.—PbA'_2aq: small plates; v. sl. sol. cold water (Baum; Claus a. Knyrim, *B.* 18, 2924).

Ethyl derivative $C_{10}H_6(OEt)SO_3H$ [1:3?]. Obtained by heating the ethyl ether of (α)-naphthol (7 pts.) with H_2SO_4 (5 pts.) at 100° (Maikopar).—KA'aq: large glittering plates; sl. sol. cold water.—BaA'_2. [55°–60°]. This acid is perhaps identical with the preceding.

(1, 4)-**Naphthol sulphonic acid** [1:4]$C_{10}H_6(OH)SO_3H$. [170°]. Formed by diazotising the corresponding (α)-naphthylamine sulphonic acid and heating the resulting diazonaphthalene sulphonic acid with dilute H_2SO_4 (Nevile a. Winther, *C. J.* 37, 632; *Monit. Scient.* 1884, 39; Erdmann, *A.* 247, 341). Plates; v. e. sol. water. Converted by dilute HNO_3 into di-nitro-(α)-naphthol. Chromic acid oxidises it to (α)-naphthoquinone. $FeCl_3$ colours its solution greenish-blue, but on warming the colour becomes red. Its s o d i u m s a l t is v. sol. 90 p.c. alcohol, from which it crystallises in needles.

(1, 1')-**Naphthol sulphonic acid** [1:1']$C_{10}H_6(OH).SO_3H$. [107°]. Obtained from the corresponding (α)-naphthylamine *peri*-sulphonic acid by diazotisation, the product being boiled with water. The resulting anhydride (*v. infra*) is heated with alcoholic ammonia for half an hour at 130°, and the ammonium salt thus obtained converted into lead salt, and thence into the free acid (Erdmann, *A.* 247, 346). Deliquescent crystalline mass (containing aq); v. e. sol. water. Gives with $FeCl_3$ a green colour changing to red.

S a l t s.—NH_4A': v. sol. water, but not deliquescent.— KA': plates.— $Na_2C_{10}H_6SO_4$ $1\frac{1}{2}$aq: aggregates of needles.—$PbC_{10}H_6SO_4$ 3aq: white crystalline powder.

Anhydride $C_{10}H_6\left\langle\begin{array}{c}O\\SO_2\end{array}\right\rangle$. *Naphthosultone.* [154°]. Formed as above. Prisms (from benzene); v. sl. sol. CS_2, sl. sol. alcohol, v. sol. chloroform, insol. water. Boils between 360° and 448°. Not attacked by aqueous NH_3, Na_2CO_3, or cold NaOHAq. Boiling NaOHAq converts it into the corresponding acid.

(1, 4')-**Naphthol sulphonic acid** [1:4']$C_{10}H_6(OH)SO_3H$. [110°–120°]. Obtained from the corresponding naphthylamine sulphonic acid by diazotising and boiling the product with H_2SO_4 (1 pt.) diluted with water (4 pts.) (Erdmann, *A.* 247, 343). Hygroscopic crystalline substance.

(1, 2')-**Naphthol sulphonic acid.** Formed by partial hydrolysis of heteronucleal (α)-naphthol disulphonic acid (Liebmann a. Studer, *E. P.* 7812 [1887]). Yields azo- dyes.

(α)-**Naphthol disulphonic acid** (*Heteronucleal*) $C_{10}H_5(OH)(SO_3H)_2$. Obtained, together with the trisulphonic acid, and probably also the (1, 2, 4) disulphonic acid, by heating (α)-naphthol (1 pt.) with H_2SO_4 (containing an additional 20 p.c. of SO_3) (5 pts.) for two hours on a water-bath (Claus a. Mieleke, *B.* 19, 1182). Best prepared by heating (α)-naphthol (1 pt.) with conc. H_2SO_4 (3 to 4 pts.) at 130°. Yields a nitroso- compound $C_{10}H_4(OH)(NO)(SO_3H)_2$ (Seltzer, *G. P.* 20,716; Jan. 30, 1882). Combines with diazo-compounds. On nitration it forms di-nitro-naphthol sulphonic acid.

Chloride $C_{10}H_5(OH)(SO_2Cl)_2$. Liquid; v. sol. ether. Converted by PCl_5 into tri-chloro-naphthalene [82°].

Ethyl derivative $C_{10}H_5(OEt)(SO_3H)_2$. Formed by sulphonating the ethyl ether of (α)-naphthol with fuming H_2SO_4 (10 p.c. additional SO_3) (*G. P.* D 1501, June 7, 1883). Conc. HNO_3 converts it into di-nitro-naphthol sulphonic acid.

(α)-**Naphthol disulphonic acid** (*Homonucleal*) $C_{10}H_5(OH)(SO_3H)_2$ [1:2:4]. Formed by heating (α)-naphthol with H_2SO_4 (4 pts.) at 70°. Differs from the preceding acid in not yielding a nitroso- derivative or forming azo- dyes (Schultze, *Dissertation*, Freiburg, 1883; Bender, *B.* 22, 993). It yields di-nitro-naphthol on nitration.

(1, 1', 4)-(α)-**Naphthol disulphonic acid** [1:1':4] $C_{10}H_5(OH)(SO_3H)_2$. (α)-*Naphthol* (δ)-*sulphonic acid.* Formed from (α)-naphthylamine *peri*-sulphonic acid by sulphonation and diazotisation. Formed also by sulphonating naphthosultone (Bernthsen, *B.* 23, 3088). Readily forms an anhydride.—×Na_2A'': plates, v. sol. water. $FeCl_3$ colours its solution deep blue.—×BaA''.

Anhydride $C_{10}H_5(SO_3H)\left\langle\begin{array}{c}O\\SO_2\end{array}\right\rangle$. S a l t s NaA' 3aq; m. sol. water. Gives no colour with $FeCl_3$.—×BaA'_2: v. sol. water.

Mono-amide $C_{10}H_5(SO_3H)(OH)(SO_2NH_2)$. From the anhydride and NH_3.—NaA'2aq. Plates.

(1, 1', 3)-(α)-**Naphthol disulphonic acid** [1:1':3] $C_{10}H_5(OH)(SO_3H)_2$. (α)-*Naphthol* 'ε'-*disulphonic acid.* Formed from (α)-naphthylamine 'ε'-disulphonic acid by the diazo- reaction (Bernthsen, *B.* 22, 3330; *cf.* Ewer a. Pick, *Monit. Scient.* 1889, 604).—Na_2A'' 6aq: prisms; v. e. sol. water. Its solution is coloured deep-blue by $FeCl_3$.

Anhydride $C_{10}H_5(SO_3H)\left\langle\begin{array}{c}O\\SO_2\end{array}\right\rangle$. *Naphthosultone sulphonic acid.* Formed by boiling diazonaphthalene 'ε'-disulphonic acid with dilute H_2SO_4. Needles (containing aq).

Mono-amide [1:1':3] $C_{10}H_5(OH)(SO_2NH_2)(SO_3H)$. *Naphthol sulphamide sulphonic acid.* Formed by the action of NH_3 on the anhydride. Needles or prisms; m. sol. water.—NaA'aq: needles; v. sol. hot

water.—$NH_3NaA'aq$: crystals; v. e. sol. water.—BaA'_2 5aq: crystals; m. sol. water.

(α)-**Naphthol trisulphonic acid** $C_{10}H_8S_3O_{10}$ *i.e.* $C_{10}H_4(OH)(SO_3H)_3$ [1:2:4':4]. Formed by heating (α)-naphthol with fuming H_2SO_4 (containing 70 p.c. additional SO_3) at 50° (Seltzer, *G. P.* 10,785, Dec. 1879; Caro, *B.* 14, 2028; Claus a. Mielcke, *B.* 19, 1182). Slender needles. Dilute HNO_3 at 50° yields di-nitro-naphthol sulphonic acid. It does not yield azo- dyes or a nitroso-derivative.—$K_4C_{10}H_4S_3O_{10}$; crystals; v. sol. water (Lauterbach, *B.* 14, 2028).

Chloride $C_{10}H_4(OH)(SO_2Cl)_3$. Plates (from chloroform); sl. sol. either; decomposed by fusion. Converted by PCl_5 into tetra-chloro-naphthalene $C_{10}H_4Cl_4$ [140°] and $C_{10}Cl_8$.

(2, 1')-(β)-**Naphthol sulphonic acid** [2:1'] $C_{10}H_6(OH)(SO_3H)$ (Pfitzinger a. Duisberg, *B.* 22, 396; Armstrong a. Wynne, *C. J. Proc.* 1889, 50). (β)-*Naphthol 'α'-sulphonic acid. Bayer's acid. Rumpff's acid.* Formed, together with the isomeric acid of Schäffer, by stirring (β)-naphthol (1 pt.) with conc. H_2SO_4 (2 pts.) at about 50° (Bayer a. Co., *G. P.* 18,027, March 18, 1881). When (β)-naphthyl sulphate $C_{10}H_7O.SO_3H$ (obtained by the action of H_2SO_4 on (β)-naphthol at a low temperature) is mixed with H_2SO_4 at 20° it slowly changes to (β)-naphthol 'α'-sulphonic acid. The two isomeric acids of Schäffer and of Bayer may be separated by means of their lead salts (that of the former acid crystallising well) or by treating their sodium salts with 90 p.c. spirit, which dissolves the salt of Bayer's acid but not that of Schäffer's acid. Formed also from (β)-naphthylamine 'α' sulphonic acid (Badische) by diazotising and heating with dilute H_2SO_4 (Forsling, *B.* 20, 2102).

Reactions.—1. Converted by PCl_5 into chloro-(β)-naphthol [101°] and di-chloro-naphthalene [61°].—2. *Potash-fusion* yields di-oxy-naphthalene [175°].—3. With diazotised xylidine it yields in concentrated, but not in dilute solutions, croceïn scarlet.

Salts.—Forms two series of salts—neutral and basic.—NaA': glistening six-sided plates, v. sol. water, sl. sol. alcohol.—$Na_2C_{10}H_6SO_4$: needles, v. sol. alcohol, v. e. sol. water.—ZnA'_2 2aq: needles. — PbA'_2 2½aq: colourless glistening rhombohedra.—$C_{10}H_6SO_5Pb_2$: small yellow crystals.—$C_{10}H_6SO_4(PbOH)_2$: red crystals (Claus a. Volz, *B.* 18, 3154).

(2, 3')-**Naphthol sulphonic acid** [2:3'] $C_{10}H_6(OH)(SO_3H)$. (β)-*Naphthol 'β'-sulphonic acid. Schäffer's acid.* [125°].

Formation. — 1. By heating (β)-naphthol (1 pt.) with conc. H_2SO_4 (2 pts.) on a water-bath (Schäffer, *A.* 152, 296; Armstrong a. Graham, *C. J.* 39, 135).—2. By fusing naphthalene (β)-disulphonic acid with potash (Ebert a. Merz, *B.* 9, 610; 10, 592).—3. From (β)-naphthylamine sulphonic acid (Brönner's) by the diazo-reaction.

Properties.—Small, non-deliquescent laminæ, v. sol. water and alcohol. $FeCl_3$ turns its solution slightly green and, on warming, brown flakes are deposited. Bleaching-powder gives a yellow colour.

Reactions.—1. *Potash-fusion* yields di-oxy-naphthalene [213°].—2. *Nitrous acid* forms a nitroso- derivative. — 3. *Bromine*-water gives mono- and di-bromo- derivatives. The K salt dissolved in HOAc gives with Br yellow plates of $C_{10}H_4BrSO_6K$, which form a blood-red aqueous solution.—4. Conc. HClAq at 200°–210° splits it up into (β)-naphthol and H_2SO_4.—5. The potassium salt (1 mol.) heated with PCl_5 (2 mols.) at 100° forms gelatinous anhydro- naphthol sulphonic acid $C_{10}H_6(OH).SO_2.O.C_{10}H_6.SO_3H$, sol. water, alcohol, and ether. The K salt of this acid crystallises in colourless plates, and is decomposed by boiling alkalis with reproduction of (β)-naphthol sulphonic acid (Claus a. Zimmermann, *B.* 14, 1481). The K salt (1 mol.) heated with PCl_5 (2 mols.) at 150° forms $(SO_3H.C_{10}H_6.O.SO_2.C_{10}H_6)_2O$, an amorphous mass yielding a gelatinous potassium salt K_2A'' (C. a. Z.). The (β)-naphthol sulphonic acid heated with PCl_5 also yields chloro-(β)-naphthol, and finally ε-di-chloro-naphthalene [135°], both of which bodies yield chloro-phthalic acid [148°] on oxidation (Claus a. Dehne, *B.* 15, 319).

Salts.—KA'$x$aq. S. 2 at 15°.—NH_4A'. S. 3 at 24°. Flat prisms or plates (Meldola, *C. J.* 39, 41).—CaA'_2 5aq: silky laminæ, v. sol. water and alcohol, decomposing at 100°.—BaA'_2 6aq: narrow prisms (from boiling saturated solution).—PbA'_2 6aq: small silvery laminæ, v. sol. water.

Ethyl derivative $C_{10}H_6(OEt)SO_3H$. From the (? impure) acid, KOH, and EtI (Maikopar, *Z.* 1870, 366).—KA': needles, sl. sol. cold water.

(β)-**Naphthol** (γ)-**sulphonic acid** [2:4'] $C_{10}H_6(OH)(SO_3H)$. Formed from the corresponding (β)-naphthylamine sulphonic acid by the diazo- reaction (Reverdin a. Nölting, *Const. de la Naphthaline*). Yields di-oxy-naphthalene [135°] and di-chloro-naphthalene [48°] (Claus, *J. pr.* [2] 39, 315).

(2, 2')-(β)-**Naphthol sulphonic acid** [2:2'] $C_{10}H_6(OH)SO_3H$. (β)-*Naphthol 'δ'-sulphonic acid. Naphthol sulphonic acid* F. [89°]. Formed from (β)-naphthylamine 'δ'-sulphonic acid by the diazo- reaction (Bayer a. Duisberg, *B.* 20, 1431). Formed also, together with Schäffer's acid, by heating (β)-naphthol (100 g.) with H_2SO_4 (70 g.) for 2 or 3 hours at 105° (Green, *B.* 22, 723; *cf.* Armstrong, *B.* 15, 22). It is also a product of the fusion of naphthalene 'α' disulphonic acid with NaOH at 250° (Weinberg, *B.* 20, 2907). Needles (containing aq), v. sol. water and alcohol, insol. ether (W.). PCl_5 (3 pts.) at 165° gives di-chloro-naphthalene [114°], the chief product being a chloro-naphthyl phosphate [215°]. On fusion with potash it yields $C_{10}H_6(OH)_2$ [186°]. Nitrous yields a nitroso- derivative, forming the salt $C_{10}H_5(NO)(OH)SO_3Na$ 2aq crystallising in golden needles.

Salts.—NaA' 2½aq. S. 8 at 15°. Plates.—Ka' aq: crystals, v. sol. water.—MgA'_2 5½aq: plates.—BaA'_2: prisms, sl. sol. water.

(β)-**Naphthol sulphonic acid.** *Ethyl derivative* $C_{10}H_6(OEt).SO_3H$. Formed by warming the ethyl ether of (β)-naphthol with H_2SO_4 (Maikopar, *Z.* 1870, 366).—KA' aq: needles, sl. sol. cold water.—BaA'_2: needles, v. sl. sol. water.

(β)-**Naphthol sulphonic acid.** *Ethyl derivative* $C_{10}H_6(OEt)SO_3H$. Two acids of this formula are obtained by treating the ethyl derivative of (β)-naphthol with $ClSO_3H$ (Amphlett a. Armstrong, *C. J. Proc.* 3, 144). The Ba salt of one acid is insol. water, that of the other is sol. water. One of the acids is doubtless identical with the preceding acid.

(2, 1′ 3′)-Naphthol disulphonic acid [2:1′:3′] $C_{10}H_5(OH)(SO_3H)_2$. (β)-*Naphthol* '*β*'-*disulphonic acid.* (β)-*Naphthol-G-disulphonic acid.* Formed, together with the 'R' isomeride, by heating (β)-naphthol (1 pt.) with conc. or fuming H_2SO_4 (2 or 3 pts.) at 100°–110°, and separated from its isomeride through the greater solubility of its Ba salt (Griess, *B.* 13, 1956).

Properties.—Glistening needles, v. sol. water and alcohol. With diazo- compounds it gives scarlets of a much yellower shade than the (α)-acid. PCl_5 (5 mols.) at 210° forms di-chloro-(β)-naphthol [125°] and tri-chloro-naphthalene [90°]; this $C_{10}H_5Cl_3$, when oxidised with CrO_3, yields a syrupy di-chloro-phthalic acid and a tri-chloro-naphthoquinone, whence aniline forms $C_{10}H_3Cl_2(NPhH)O_2$ melting at 228° (Claus a. Schmidt, *B.* 19, 3173).

Salts.—$^{\times}Na_2A''$: tables or prisms, sol. water and dilute alcohol.—BaA'' 8aq: small prisms, v. sol. water.

(2, 3, 3′)-Naphthol disulphonic acid [2:3:3′] $C_{10}H_5(OH)(SO_3H)_2$. (β)-*Naphthol* '*α*'-*di-sulphonic acid.* (β)-*Naphthol R-disulphonic acid.* Formed as described above (Griess). White glistening needles, v. sol. water and alcohol, insol. ether. Exhibits a bluish-green fluorescence in ammoniacal solution. When heated in a closed vessel with ammonia it yields a naphthylamine disulphonic acid which, on removal of NH_2, gives rise to naphthalene 'α'-disulphonic acid of Ebert and Merz (Pfitzinger a. Duisberg, *B.* 22, 398).

Salts.—$^{\times}Na_2A''$: very small soluble needles. —BaA'' 6aq: needles, sl. sol. cold water, v. sol. hot water, insol. alcohol.

(β)-Naphthol-'δ'-disulphonic acid [2:2′:3] $C_{10}H_5(OH)(SO_3H)_2$. Formed by sulphonating (2, 2′)-naphthol sulphonic acid (Weinberg, *B.* 20, 2911). Solutions of its salts exhibit green fluorescence.—Na_2A'': yellowish powder, v. e. sol. water, sl. sol. 80 p.c. alcohol.—$BaA''2\frac{1}{2}aq$: prisms. S. ·56 in boiling water.

(β)-Naphthol-'γ'-disulphonic acid $C_{10}H_5(OH)(SO_3H)_2$. Formed by the action of $ClSO_3H$ on (β)-naphthol (Armstrong, *B.* 15, 204). The Ba salt crystallises in large prisms.

(β)-Naphthol trisulphonic acid $C_{10}H_4(OH)(SO_3H)_3$. Formed by heating (β)-naphthol (1 pt.) with H_2SO_4 (2 pts.) at 70°–80°, adding H_2SO_4 (2 pts.) and heating at 120°, finally adding fuming H_2SO_4 (40 p.c. additional SO_3) (2 pts.) and heating at 150° (Levinstein, *B.* 16, 462). Gives no colour with diazotised xylidine.

References.—Amido-, and Nitro-naphthol sulphonic acids.

(β)-NAPHTHOL VIOLET $C_{18}H_{16}N_2O$. *Meldola's blue.* Formed from nitroso-dimethyl aniline and (β)-naphthol. Dark flocculent powder, forming a red solution in benzene (Meldola, *C. J.* 39, 38).

Hydrochloride B′HCl *i.e.*

$ClMe_2N.C_6H_3{<}{}^{N}_{O}{>}C_{10}H_6$. Bronzed needles, resembling $KMnO_4$. Sol. water and alcohol. Its aqueous solution is violet, but turned blue by H_2SO_4. Reduces to a leuco-base by taking up H_2. Converted by heat into a blue colouring matter $NMe_2.C_6H_4.N{<}{}^{O}_{C_{10}H_5.N}{<}{}^{NMe_2(OH)}_{C_6H_4}$ (Witt, *B.* 23, 2247).

NAPHTHOL-YELLOW S *v.* Dinitro-(α)-naphthol sulphonic acid.

NAPHTHONITRILE *v.* *Nitrile* of Naphthoic acid.

NAPHTHOPHTHALIC ACID. A name for Naphthalene dicarboxylic acid.

NAPHTHO-OXY-QUINALDINE *v.* Oxy-methyl-naphthoquinoline.

NAPHTHOPHENAZINE $C_{16}H_{10}N_2$ *i.e.*

$C_{10}H_6{<}{}^{N}_{N}{>}C_6H_4$ or $C_6H_4{<}{}^{\overline{C.N}}_{CH:CH.C.N}{>}C_6H_4$.

[142°]. (above 360°). Prepared by boiling sulpho-benzene-azo-phenyl-(β)-naphthylamine with dilute H_2SO_4 (Witt, *B.* 20, 574). Formed by boiling benzene-azo-phenyl-(β)-naphthyl-amine $C_{10}H_6{<}{}^{N.C_6H_5}_{N.NHC_6H_5}$ (?) in acetic acid solution with conc. HCl, aniline being eliminated (Zincke a. Lawson, *B.* 20, 1169). Formed also by treating an alcoholic solution of phenyl-(β)-naphthyl-nitrosamine with HCl (Fischer a. Hepp, *B.* 20, 2473), and by distilling with zinc-dust oxy-naphtho-phenazine, which is itself obtained by heating with conc. HClAq at 190° the amido-naphtho-phenazine which results from the action of phenylene o-diamine on benzene-azo-(α)-naphthylamine hydrochloride (Fischer a. Hepp, *B.* 23, 846). Also got by the action of (β)-naphthoquinone (1 mol.) on o-phenylene-diamine (1 mol.) in 50 p.c. acetic acid solution at 0°, and by oxidising a mixture of *o*-phenylene-diamine and (β)-naphthol with alkaline K_3FeCy_6 (Witt).

Yellowish-white prisms, subliming at about 200° in long flat needles or prisms; v. sol. hot benzene, v. sl. sol. alcohol and ether. Conc. H_2SO_4 dissolves it, forming a brownish-red solution. Its salts are dimorphous. One sulphate crystallises in scarlet needles, the other in garnet-red prisms. One nitrate forms orange needles, the other brick-red needles. One hydrochloride forms long-reddish yellow needles, and changes at 150° into the second form. $SnCl_2$ reduces naphthopheuazine to a hydride, crystallising in violet needles.

α-Amido-naphthophenazine $C_{16}H_{11}N_3$ *i.e.* $C_6H_4{<}{}^{\overline{C.N}}_{C(NH_2):CH.C.N}{>}C_6H_4$. [264°]. Obtained by heating o-phenylene diamine (1 mol.) with benzene-azo-(α)-naphthylamine hydrochloride (1 mol.) in alcohol at 160° (F. a. H.). Golden needles (from alcohol), insol. water, sl. sol. ether and cold alcohol. Its solutions have a yellowish-green fluorescence. Its solution in conc. HClAq or conc. H_2SO_4 is green.—B′HCl.—$B'_2H_2PtCl_6$.—$B'HAuCl_4$.

Acetyl derivative $C_{16}H_{10}AcN_3$. Yellow crystalline powder.

Amido-naphthophenazine $C_{10}H_5(NH_2):N_2C_6H_4$. [191°]. Obtained by reducing the nitro- compound with alcoholic ammonium sulphide (Zaertling, *B.* 23, 176). Brownish-red crystals, sl. sol. alcohol and ether, v. e. sol. boiling aniline.—B′HCl.

Phenylo-chloride of Amido-naphthophenazine $C_{22}H_{16}N_3Cl$ *i.e.*

$C_{10}H_6{<}{}^{N}_{NPhCl}{>}C_6H_3NH_2$. Formed by the action of quinone dichlorimide on phenyl-(β)-naphthylamine (Nietzki a. Otto, *B.* 21, 1600).

Yields a base which is a bluish-violet pp. and a nitrate $C_{22}H_{16}N_3NO_3$ crystallising in slender needles. Yields naphthophenazine on elimination of NH_2 by the diazo- reaction.

Reference.—EURHODINES.

Nitro-naphthophenazine $C_{10}H_5(NO_2):N_2:C_6H_4$ [222°]. Formed by heating nitro-(β)-naphthoquinone with o-phenylene-diamine, HOAc, and NaOAc on the water-bath (Z.). Greenish-yellow prisms, sl. sol. alcohol and ether. Forms a crimson solution in conc. H_2SO_4.—$B'2H_2SO_4$: brown plates.

NAPHTHOPHENAZINE CARBOXYLIC ACID $C_{16}H_9N_2(CO_2H)$. [above 300°]. Obtained by heating its nitrile with KOHAq under pressure at 225° (Brunner a. Witt, *B.* 20, 2663). Needles m. sol. water and most solvents. Conc. H_2SO_4 forms a deep-red solution, becoming yellow on dilution.

Nitrile $C_{16}H_9CyN_2$. [237°]. Formed from sodium naphthophenazine sulphonate and KCy. Forms a cherry-red solution in conc. H_2SO_4, becoming yellow on dilution.

Naphthophenazine sulphonic acid $C_{16}H_9(SO_3H)N_2$. [above 290°]. Formed by sulphonating naphthophenazine with fuming H_2SO_4 (35 p.c.) (Brunner a. Witt, *B.* 20, 2660). Orange-red needles, sol. boiling water and alcohol. KOH yields yellow flakes of a eurhodol. H_2SO_4 forms an orange-red solution.—NaA' 2aq.

NAPHTHOPIASELENOL *v.* SELENIUM ORGANIC COMPOUNDS.

NAPHTHOPIAZTHIOLE $C_{10}H_6<\genfrac{}{}{0pt}{}{N}{N}>S$. [81°]. Formed by heating (αβ)-naphthylene-diamine (2 g.) dissolved in alcohol, with a conc. solution of sodium bisulphite (15 c.c.) at 190° for 7 hours (Hinsberg, *B.* 23, 1393). Long needles (from MeOH), m. sol. water. Pleasant odour. Somewhat volatile with steam. Weak base. Gives a yellow colour with conc. H_2SO_4. Reduced by tin and HCl to H_2S and naphthylene diamine.

NAPHTHOPICRIC ACID, so-called, *v.* TRI-NITRO-α-NAPHTHOL.

NAPHTHO - QUINALDINE *v.* (*Py.* 3)-METHYL-NAPHTHO-QUINOLINE.

(α) - NAPHTHOQUINOLINE $C_{13}H_9N$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{CH:CH.C.CH:CH}{\text{——}C.\ N:CH}$. Formed by heating a mixture of (α)-nitro-naphthalene, (α)-naphthylamine, glycerin, and H_2SO_4 (Skraup, *M.* 2, 162; 4, 460). Formed also by distilling its dicarboxylic acid (Doebner a. Peters, *B.* 23, 1235). White prisms (from ether), insol. water, sol. alcohol, ether, benzene, and dilute acids. Smells like naphthylamine. On oxidation with chromic acid it yields the quinone $C_{13}H_7NO_2$ or $C_6H_4<\genfrac{}{}{0pt}{}{\text{——}C.\ N:CH}{CO.CO.C.CH:CH}$, which forms orange crystals, [205°], sol. alcohol, benzene, ether, and HClAq, insol. water. $KMnO_4$ oxidises it to phenyl-pyridine dicarboxylic acid.

Salts.—Hydrochloride: pale-yellow needles.—$B'_2H_2PtCl_6$ 2aq: bright-yellow prisms, v. sl. sol. water.—$B'H_2SO_4$: yellowish prisms, v. e. sol. water.—$B'H_2Cr_2O_7$ 6aq: needles, sl. sol. cold water.—$B'C_6H_2(NO_2)_3OH$: minute needles.

Methylo-iodide B'MeI 2aq. Needles.

Octohydride $C_{13}H_{17}N$ *i.e.* $\genfrac{}{}{0pt}{}{CH_2.CH_2.C.CH:CH.C.CH_2.CH_2}{CH_2.CH_2.C\text{————}C.NH.\ CH_2}$. Crystals (Bamberger, *B.* 22, 354).

(β)-Naphthoquinoline $C_{13}H_9N$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{CH:CH.C.\ N\ :CH}{\text{————}C.CH:CH}$. [94°] (above 360°). Formed by heating (β)-naphthylamine (28 pts.) with nitro-benzene (13 pts.), glycerin (50 pts.), and conc. H_2SO_4 (40 pts.) at 150°–160° (Skraup a. Cobenzl, *M.* 4, 436). The crude product is neutralised with alkali, extracted with ether, and distilled. In this reaction (1,2)-bromo-(β)-naphthylamine [63°] may be substituted for (β)-naphthylamine, and nitro-phenol may be used instead of nitro-benzene (Lellmann a. Schmidt, *B.* 20, 3154). Formed also by heating (1,2)-nitro-(β)-naphthylamine with glycerin and H_2SO_4 (L. a. S.). Obtained likewise by distilling its carboxylic acids.

Properties.—Colourless crystals, sl. sol. water, sol. ether, alcohol, benzene, and acids. Its alcoholic solution gives a brown colouration with $FeCl_3$, and a green colour with cupric acetate.

Reactions.—1. $KMnO_4$ oxidises it to (β)-phenyl-pyridine dicarboxylic acid.

Salts.—B'HCl 2aq: long needles, v. sol. water, sl. sol. alcohol.—$B'_2H_2PtCl_6$ aq: orange crystalline pp. — $B'_2H_2Cr_2O_7$: short golden prisms.—B'IClHCl. [c. 148°]. Yellow needles, obtained by adding a solution of ICl in HClAq to a solution of the base (Dittmar, *B.* 18, 1616).—Picrate [252°].

Methylo-iodide B'MeI 2aq. [200°–205°]. Light-yellow needles, exhibiting a blue fluorescence in aqueous solution.

Octohydride $C_{13}H_{17}N$ *i.e.* $\genfrac{}{}{0pt}{}{CH_2.CH_2.C.CH:CH.C.NH.CH_2}{CH_2.CH_2.C\text{————}C.CH_2.CH_2}$ [60°]. Obtained by boiling (β)-naphtho-quinoline with isoamyl alcohol, and sodium (Bamberger, *B.* 22, 354). At the same time there is formed an isomeric $C_6H_4<\genfrac{}{}{0pt}{}{CH_2.CH_2.CH.NH.CH_2}{\text{————}CH.CH_2.CH_2}$ [91°].

Reference.—OXY-, OXY-METHYL-, and PHENYL-NAPHTHOQUINOLINE.

(β) - NAPHTHOQUINOLINE CARBOXYLIC ACID $C_{14}H_9NO_2$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{CH:CH.C.\ N\ :CCO_2H}{\text{————}C.CH:CH}$. [187°]. Obtained by oxidising methyl-(β)-naphthoquinoline with $KMnO_4$ and H_2SO_4 (Seitz, *B.* 22, 261). White crystalline powder, insol. water, m. sol. boiling alcohol.—NaA' 2½aq. Crystals, sl. sol. cold water.—BaA'_2 4aq: flocculent pp., becoming crystalline on long boiling; insol. water.—CuA'_2 1½aq: crystalline, insol. water.—B'HCl: yellow needles, v. sl. sol. boiling dilute HClAq.—$B'_2H_2PtCl_6$ 2aq: yellow needles, v. sl. sol. hot dilute HClAq.

(α)-Naphthoquinoline (*Py.* 1, 3)-dicarboxylic acid $C_6H_4<\genfrac{}{}{0pt}{}{CH:CH.C.C(CO_2H)\ CH}{\text{————}C.N\text{——}C.CO_2H}$. [278°]. Formed by oxidising (α)-styryl-(α)-naphthoquinoline carboxylic acid with cold aqueous $KMnO_4$ (Doebner a. Peters, *B.* 23, 1234). Groups of greenish-yellow needles, insol. cold water, sl. sol. hot water, ether, cold alcohol, and dilute HClAq, v. sol. conc. HClAq.

Salts.—The salts of the alkalis and alkaline earths are v. sol. water. The Pb and Cd salts

are white pps.—CuA″2aq: dirty-green pp., sl. sol. water.—Ag_2A'': white flocculent pp.

(β)-Naphthoquinoline-(*Py.* 1, 3)-dicarboxylic acid $C_6H_4\langle\begin{array}{l}CH:CH.C.N{=\!=\!=}C.CO_2H\\ \text{———}C.C(CO_2H):CH\end{array}$ [288°]. Formed by oxidation of (α)-styryl-(β)-naphthoquinoline carboxylic acid by $KMnO_4$ (Doebner a. Peters, *B.* 23, 1240). Very slender light-yellow needles, sl. sol. ether, cold alcohol, and benzene, v. sol. HOAc and alkalis.—BaA'_2aq: white flocculent pp.—Ag_2A'': powder, sl. sol. water.

NAPHTHOQUINOLINE SULPHONIC ACID $C_{13}H_9NSO_3$ *i.e.* $C_4H_3(SO_3H)\langle\begin{array}{l}C.CH:CH.C.N:CH\\ C\text{———}C.CH:CH\end{array}$ Obtained from (β)-naphthylamine sulphonic acid of Forsling (*B.* 20, 2099) by heating with glycerin, H_2SO_4, and nitrobenzene (Immerheiser, *B.* 22, 404; *cf.* Gentil, *B.* 18, 201). Small needles, nearly insol. water. Very dilute solutions of the acid and its salts fluoresce blue.—BaA'_2 4aq. Splendid prisms.

(α)-NAPHTHOQUINONE $C_{10}H_6O_2$ *i.e.* $C_6H_4\langle\begin{array}{l}CO.CH\\ CO.CH\end{array}$ (α)-*Naphthaquinone.* Mol. w. 158. [125°].

Formation.—1. By oxidation of naphthalene by CrO_3 in HOAc (Groves, *C. J.* 26, 209; *cf.* Hermann, *A.* 151, 63).—2. By oxidising with chromic acid the following bodies: naphthylene-*p*-diamine, and its acetyl derivative (Liebermann a. Dittler, *B.* 6, 945), (α)-naphthylamine and its sulphonic acid (Reverdin a. Nölting, *B.* 12, 2305), (α)-amido-(α)-naphthol (Liebermann, *A.* 183, 242), and the acetyl derivative of (α)-naphthol (Miller, *B.* 14, 1600).

Preparation.—1. Naphthalene (10 g.) is dissolved in HOAc (60 g.); to this is slowly added a solution of CrO_3 (30 g.) in water (20 c.c.). The mixture is heated at 100°. Water (30 g.) is added, and the liquid, when cooled to 20°, filtered from naphthalene. From the filtrate water precipitates naphthoquinone. Recrystallised from light petroleum (Japp a. Miller, *C. J.* 39, 220; *cf.* Groves, *C. J.* 26, 209; Plimpton, *C. J.* 37, 634; Miller, *Bl.* [2] 43, 125).—2. (α)-Naphthol-orange (Tropeoline 000 No. 1) is reduced to sulphanilic acid and (1:4) amido-naphthol, the latter is oxidised and the quinone purified by distillation with steam; the yield is 40 p.c.—3. By oxidation of (α)-naphthylamine (1 pt.) with H_2SO_4 (6 pts.), water (25 pts.), and $K_2Cr_2O_7$ ($2\frac{1}{2}$ pts.), in the cold (Monnet, Reverdin, a. Nölting, *B.* 12, 2306).

Properties.—Yellow triclinic needles, which begin to sublime below 100°. Volatile with steam. V. sl. sol. water and ligroïn, v. sol. benzene, CS_2, chloroform, ether, HOAc, conc. H_2SO_4, and boiling alcohol. Smells like quinone. Alkalis form a reddish-brown solution. It is not attacked by SO_2 in the cold. Reacts in alcoholic solution with primary amines forming compounds represented by $C_{10}H_6O_2NR$, which may be considered to be alkyl-amido-(α)-naphthoquinones or more probably as oxy-(β)-naphthoquinone alkylimides. Secondary amines act forming compounds represented by $C_{10}H_5O_2NRR'$; but diphenylamine acts only in presence of HCl. Tertiary amines do not react in this way. Hydro-naphthoquinone may be used instead of naphthoquinone, being oxidised by the air. Salts of amines may be used instead of amines. The compounds crystallise in needles (Plimpton, *C. J.* 37, 633).

Reactions.—1. Naphthoquinone dissolves in aqueous KOH and Na_2CO_3, and on adding acids a red body is ppd. This is also got by oxidising naphthalene with CrO_3 in acetic acid and neutralising the hot liquid with Na_2CO_3 (A. Guyard, *Bl.* [2] 31, 64; Plimpton, *C. J.* 37, 641). It is soluble in benzene and ppd. from it by light petroleum as a dark-red powder. This substance was named c a r m i n a p h t h e by Laurent (*Rev. Scient.* 14, 560), who ascribed to it the formula $C_{18}H_8O_3$.—2. Boiling *nitric acid* oxidises it to phthalic acid.—3. Boiling HIAq and P reduce it to hydronaphthoquinone [176°]. Tin and HCl act in like manner.—4. When boiled with an aqueous solution of an equivalent of *hydronaphthoquinone* there is deposited on cooling dark-purple crystals of naphthoquinhydrone $C_{20}H_{14}O_4$. It is readily converted by oxidising agents into naphthoquinone and by reducing agents into hydronaphthoquinone.—5. *Bromine* in presence of iodine forms di-bromo-naphthoquinone [218°] (Miller, *Bl.* [2] 43, 125).—6. Heated with *benzoic acid* at 160° it forms needles of 'benzonaphthone' $C_{27}H_{12}O_3$? which may be purified by successive boiling with aniline, and alcohol (Japp a. Miller, *C. J.* 39, 221). This body is insoluble in ordinary solvents and in aqueous NaOH. Aqueous $KMnO_4$ oxidises it to phthalic acid. It is not affected by $ZnEt_2$, and therefore contains no hydroxyl.—7. Boiling fuming HClAq forms a green amorphous powder, insol. water, alcohol, and ether, but partially dissolving in HOAc forming a blue solution (Krapp a. Schultz, *A.* 210, 178).—8. *Phenyl-hydrazine* reacts forming benzene-AZO-(α)-naphthol $C_{10}H_6(OH).N_2Ph$.—9. On adding aqueous *ammonia* to alcoholic naphthoquinone the liquid becomes brown and, by precipitation by water, a red-brown amorphous body is formed, probably Laurent's 'carminaphthe' (Plimpton, *C. J.* 37, 641).—10. Yellow *ammonium sulphide* produces a red powder melting with complete decomposition at about 300° (Willgerodt, *B.* 20, 2470).—11. When a solution of *methylamine* (acetate) is added slowly to a small quantity of naphthoquinone dissolved in alcohol, methyl-amido-naphthoquinone $C_{10}H_6O_2NMe$ [232° uncor.], is formed. It crystallises from alcohol in red needles, which are reduced by SO_2 forming a substance crystallising in white needles (Plimpton, *C. J.* 37, 639).—12. When an alcoholic solution of naphthoquinone is mixed with excess of aqueous *dimethylamine* the solution neutralised with acetic acid and the liquid allowed to evaporate spontaneously, there is deposited a substance $C_{10}H_5O_2NMe_2$ which crystallises from alcohol in bright-red needles [118°] (Plimpton, *C. J.* 37, 642).—13. With *ethylamine acetate* in alcoholic solution a brown liquid is formed. If this is boiled with charcoal, filtered and evaporated deposits ethyl-amido-naphthoquinone $C_{10}H_6O_2NEt$ as red needles [140°]. It may be sublimed, and is soluble in benzene, hardly so in light petroleum (Plimpton, *C. J.* 37, 640).—14. *Aniline* in alcoholic solution forms a red liquid. If this solution is heated to boiling and poured into water, the pp. washed with dilute acetic acid and crystallised from alcohol, animal charcoal being used, the product is phenyl-amido-naphthoquinone $C_{10}H_6O_2NPh$ [191°] (Plimpton, *C. J.* 37, 635). It crystallises in red needles, v.

sol. hot alcohol, benzene, and ether. Insol. light petroleum. It forms a crimson solution in conc. H_2SO_4 from which it is ppd. unchanged by water. It forms a purple solution in alcoholic potash. It is not attacked by acetic or benzoic anhydride. It is attacked by conc. HCl at 170° and by aqueous SO_2 at 125°, aniline being among the products (Plimpton, *C. J.* 37, 635; *cf.* Zincke, *B.* 12, 1645; 14, 92).—15. *p-Bromo-aniline* forms, in like manner, when heated with (α)-naphthoquinone or oxy-(α)-naphthoquinone, red needles [266°–269°] (Baltzer, *B.* 14, 1899).—16. *m-Nitro-aniline* yields $C_{10}H_5(NHC_6H_4NO_2)O_2$ [270°] (B.). 17. *p-Nitro-aniline* forms $C_{10}H_5(NHC_6H_4NO_2)O_2$ melting above 270°, which may be reduced to $C_{10}H_5(NH.C_6H_4NH_2)O_2$ [177°] (B.).—18. *Ethyl-aniline* produces $C_{10}H_5(NPhEt)O_2$ crystallising in violet needles [155°] (Elsbach, *B.* 15, 1810).—19. o-*Toluidine* forms $C_{10}H_5(NHC_7H_7)O_2$ crystallising in red needles (Elsbach, *B.* 15, 689).—20. *p-Toluidine* forms $C_{10}H_5(NHC_7H_7)O_2$ crystallising from alcohol in red needles [200°] and forming a crimson solution in conc. H_2SO_4 (Plimpton, *C. J.* 37, 638; Elsbach, *B.* 15, 687).—21. *Diphenyl-amine* forms $C_{10}H_5(NPh_2)O_2$ crystallising from alcohol in needles [164°] (Plimpton).

Oxim $C_6H_4<\begin{array}{l}C(NOH).CH\\CO - - - CH\end{array}$ or $C_6H_4<\begin{array}{l}C(OH):CH\\C(NO):CH\end{array}$. *Nitroso-(α)-naphthol.* Formed, together with a greater quantity of the (β)-oxim of (β)-naphthoquinone, by the action of nitrous acid on (α)-naphthol (Fuchs, *B.* 8, 626). Prepared by the action of hydroxylamine hydrochloride on (α)-naphthoquinone (Goldschmidt, *B.* 17, 2064). Yellowish needles, decomposing at about 190°. V. sol. alcohol and ether, sl. sol. CS_2 and hot benzene. Slightly volatile with steam. Dissolves in alkalis, but is reppd. by CO_2. Does not colour mordants (Kostanecki, *B.* 22, 1347). *Reactions.*—1. *Nitric acid* converts it into di-nitro-(α)-naphthol. — 2. Alcoholic K_3FeCy_6 forms nitro-(α)-naphthol. — 3. PCl_5 forms 'β'-di-chloro-naphthalene [68°]. — 4. *Phenyl cyanate* unites, forming $C_{10}H_5(OH):NO.CO.NHPh$, which crystallises in yellow prisms [170°] (Goldschmidt a. Strauss, *B.* 22, 3106).—5. Boiling with *aniline* and HOAc yields phenyl-(β)-amido-(α)-naphtho-quinone anilide $C_{10}H_5(NHPh)<\begin{array}{l}O\\NPh\end{array}$ [187° cor.] (Brömme, *B.* 21, 393).—6. *p*-Toluidine forms, in like manner, *p*-tolyl-amido-(α)-naphthoquinone *p*-toluide [183° cor.] (B.).—7. *ψ-Cumidine* forms ψ-cumyl-amido-(α)-naphthoquinone ψ-cumidide [181° cor.].—8. *Naphthylamine* forms (α)-naphthyl-amido-(α)-naphthoquinone-(α)-naphthalide [178° cor.].—9. *Bromine* in HOAe forms di-bromo-(α)-naphthoquinone oxim $C_{10}H_4Br_2<\begin{array}{l}O\\NOH\end{array}$ [175°] (Brömme, *B.* 21, 391). *Methyl ether* A'Me. [100°]. Yellow crystals; v. sol. alcohol, ether, and benzene, insol. water; dissolves in H_2SO_4 with a yellow colour (Ilinski, *B.* 17, 2589).

Di-oxim $C_{10}H_6(NOH)_2$[1:4]. [207°]. Formed by boiling tho mono-oxim for two days with hydroxylamine and alcohol (Nietzki a. Guitermann, *B.* 21, 433). Slender colourless needles, sol. alcohol and ether; decomposed by melting. With Ac_2O it yields $C_{10}H_6(NOAc)_2$ [160°]. Tin and HCl reduco it to naphthyleno-diamine. Alkaline $KMnO_4$ oxidises it to di-nitroso-naphthalene $C_{10}H_6(NO)_2$, a yellow powder, exploding at 120°.

Di-chloro-di-imide $C_{10}H_6(NCl)_2$. [137°]. Formed from naphthylene-*p*-diamine hydrochloride and a cold solution of bleaching powder (Friedländer a. Böckmann, *B.* 22, 591). Yellow needles (from alcohol and xylene), smelling strongly like quinone. Reconverted by reducing agents to naphthylene-diamine. Conc. HClAq in HOAc converts it into di-chloro-(α)-naphthoquinone [190°].

Di-phenyl-di-imide $C_{10}H_6(NPh)_2$. [187°]. Formed by heating benzene-azo-(α)-naphthylamine with aniline at 150° (Fischer a. Hepp, *A.* 256, 264). Golden plates, sl. sol. alcohol.

Tetrahydride $\begin{array}{l}CH_2.CH_2.C.CO.CH\\CH_2.CH_2.C.CO.CH\end{array}$. [55·5°]. Obtained by oxidising (α)-naphthylamine tetrahydride with $Na_2Cr_2O_7$ and H_2SO_4 (Bamberger a. Lengfeld, *B.* 23, 1131).

(β)-Naphthoquinone $C_6H_4<\begin{array}{l}CO.CO\\CH:CH\end{array}$. *Formation.*—By oxidation of amido-(β)-naphthol, which is got by reducing its (α)-oxim (nitroso-(β)-naphthol) (Stenhouse a. Groves, *C. J.* 32, 47; 33, 415; *A.* 189, 153; 194, 202; Liebermann a. Jacobson, *A.* 211, 40). The amido-(β)-naphthol may also be obtained by reducing (β)-naphthol orange (*v.* Azo- COMPOUNDS).

Preparation.—Amido-(β)-naphthol hydrochloride (1 pt.) is dissolved in saturated aqueous SO_2, and when cold the solution is poured into ferric chloride solution (12 pts., containing 1·2 pts. Fe_2O_3). The quinone is deposited as golden needles (Groves, *C. J.* 45, 298).

Properties.—Orange needles (from alcohol) or red needles (from ether). Softens and decomposes at 115°–120°. Has no smell. Is not volatile with steam. Dissolves in alkalis, forming a yellow solution, which absorbs oxygen from the air.

Reactions.—1. Boiling *nitric acid* forms phthalic acid.—2. SO_2 *reduces* it to hydro-(β)-naphthoquinone. HIAq acts in like manner (S. a. G.). Tin and HClAq reduce it to 'di-naphthyl dihydroquinone' $C_{20}H_{14}O_4$ crystallising in colourless needles [178°] (Korn, *B.* 17, 3024). 3. Dilute H_2SO_4 forms, on warming, 'di-naphthyl-diquinhydrone' $C_{20}H_{12}O_4$, a black insoluble powder (S. a. G.).—4. *Chlorine* passed into its solution in HOAc forms chloro-naphthoquinone and the compound $C_6H_4<\begin{array}{l}CO.CO\\CHCl.CCl_2\end{array}>$ which crystallises in monoclinic needles (containing 2aq) [112°], and, when anhydrous, melts at 128° (Zincke, *B.* 20, 2892).—5. An alcoholic solution of *aniline* forms the anilide $C_{16}H_{11}NO_2$, probably oxy-(α)-naphthoquinone anilide $C_{10}H_6(OH)<\begin{array}{l}O\\NPh\end{array}$ (Liebermann a. Jacobson, *A.* 211, 75; Zincke, *B.* 14, 1494). This substance crystallises in red or yellow needles melting above 240°, insol. water, sl. sol. alcohol and hot benzene. It is split up by boiling acids into aniline and oxy-(α)-naphthoquinone. Boiling HOAc converts it into phenyl-amido-(α)-naphthoquinone. With NaOEt and alkyl bromides it gives the compounds $C_{10}H_5(OMe)O(NPh)$ [151°], $C_{16}H_{10}EtNO_2$ [104°], $C_{16}H_{10}PrNO_2$ [100°], and $C_{16}H_{10}PrNO_2$ [104°] (Zincke, *B.* 15, 279). The so-called dianilide of

(β)-naphthoquinone, which is formed by heating di-bromo-(α)-naphthol with aniline, is probably the anilide of phenyl-amido-(β)-naphthoquinone $C_{10}H_5(NPhH)\Big\langle\begin{matrix}O\\NPh\end{matrix}$. It crystallises in orange-red needles [179°] (Meldola, *C. J.* 45, 157; *cf.* Zincke, *B.* 15, 481). This body has also been described as di-phenyl-di-imido-naphthol $C_{10}H_5(OH)(NPh)_2$ (Griess, *B.* 13, 123). The corresponding di-*p*-toluide [c. 175°] and di-(β)-naphthalide [247°], prepared by the same reaction from di-bromo-(α)-naphthol, are probably constituted in a similar manner.—6. *Ethyl-aniline* forms phenyl-ethyl-amido-(β)-naphthoquinone $C_{10}H_5(NPhEt)O_2$? which crystallises in thick red needles [165°], insol. NaOHAq, and is resolved by dilute HClAq into ethyl-aniline and (β)-oxy-(α)-naphthoquinone (Elsbach, *B.* 15, 691).—7. o-*Toluidine* forms $C_{17}H_{13}NO_2$, probably $C_{10}H_5(OH)\Big\langle\begin{matrix}O\\NC_7H_7\end{matrix}$, which crystallises in red needles, sol. NaOHAq. It is not affected by HOAc at 150°. Boiling dilute HClAq splits it up into o-toluidine and (β)-oxy-(α)-naphthoquinone (Elsbach, *B.* 15, 689).—8. *p-Toluidine* forms the *p*-toluide $C_{17}H_{13}NO_2$, probably $C_{10}H_5(OH)\Big\langle\begin{matrix}O\\N.C_6H_4Me\end{matrix}$, which crystallises in red needles [246°], sol. NaOHAq. On heating with dilute HClAq at 130° it forms (β)-oxy-(α)-naphthoquinone, and this body is probably an intermediate product in the conversion of (β)-naphthoquinone *p*-toluide into (α)-naphthoquinone *p*-toluide, which takes place on heating with acetic acid at 150° (Elsbach, *B.* 15, 686). It gives the following ethers:—$C_{17}H_{12}MeNO_2$ [150°], $C_{17}H_{12}EtNO_2$ [137°], and $C_{17}H_{12}PrNO_2$ [139°] (Zincke a. Brauns, *B.* 15, 1969).—9. Boiling with ammonium acetate forms (β)-naphthazine.

Phenyl hydrazide $C_{10}H_6\Big\langle\begin{matrix}O\\N_2HC_6H_5\end{matrix}$. *Benzene*-o-*azo*-($\alpha$)-*naphthol*. [138°]. Formed by the action of phenyl-hydrazine hydrochloride upon (β)-naphthoquinone suspended in acetic acid (Zincke a. Bindewald, *B.* 17, 3030). Long red needles, sol. hot alcohol and hot HOAc, insol. water. Does not combine with acids or bases. Yields amido-naphthol on reduction with $SnCl_2$. Bromine in HOAc forms $C_{16}H_{10}Br_2N_2O$ [215°–219°].

o-*Tolyl-hydrazide* $C_{17}H_{14}N_2O$ *i.e.* $C_{10}H_6\Big\langle\begin{matrix}O\\N.NHC_7H_7\end{matrix}$. [156°]. Red plates, with golden lustre, v. e. sol. alcohol. Reduced by $SnCl_2$ to amido-naphthol. Nitric acid oxidises it to di-nitro-naphthol. Bromine forms $C_{17}H_{12}Br_2N_2O$ [254°].

p-Tolyl-hydrazide $C_{17}H_{14}N_2O$ *i.e.* $C_{10}H_6\Big\langle\begin{matrix}O\\N.NHC_7H_7\end{matrix}$. [145°]. Red needles (Zincke a. Rathgen, *B.* 19, 2491). Forms $C_{17}H_{12}Br_2N_2O$ [136°].

(α)-*Oxim* $C_6H_4\Big\langle\begin{matrix}C(NOH).CO\\CH{=\!=}CH\end{matrix}$. ($\alpha$)-*Nitroso*-($\beta$)-*naphthol*. [109·5°]. S. (alcohol) 2·4 at 13°. Prepared by adding a concentrated aqueous solution of $NaNO_2$ (50 pts.) to a boiling solution of (β)-naphthol (100 pts.) and $ZnCl_2$ (75 pts.) in spirit (600 pts.). After cooling, and standing for some hours, the brown zinc salt which separates is washed with alcohol, suspended in water (1000 pts.), and digested for a short time with NaOH (90 pts.). After cooling, the sodium salt is filtered off, washed with a little water, and decomposed by cold HCl. The yield is 110 p.c. of the naphthol (Henriques a. Ilinski, *B.* 18, 704; *cf.* Groves, *C. J.* 45, 295; Stenhouse a. Groves, *C. J.* 32, 47; *A.* 189, 146; Fuchs, *B.* 8, 1026). *Properties*.—Thin plates or short thick orange prisms. V. sl. sol. boiling water, sl. sol. ligroïn, v. e. sol. ether, benzene, and HOAc. Volatile with steam (when pure). *Reactions*.—1. Aqueous *ammonia* at 100° forms a compound $C_{10}H_8N_2O$, probably the oxim of naphthoquinonimide $C_{10}H_6\Big\langle\begin{matrix}NH\\N.OH\end{matrix}$, which crystallises from alcohol in green needles [152°], soluble in alcohol, ether, acids, and alkalis. It is converted by nitrous acid into an unstable nitrosamine $C_{10}H_6\Big\langle\begin{matrix}N(NO)\\NOH\end{matrix}$ [244°], which forms the salts $KC_{10}H_6N_3O_2$ and $AgC_{10}H_6N_3O_2$. Naphthoquinonimide-oxim is reduced by ammonium sulphide to a base $C_{10}H_8N_2$ [92°–95°]. Naphthoquinonimide-oxim forms the salts $KC_{10}H_7N_2O$, a red powder; $C_{10}H_8N_2OHCl$, yellow plates; $(C_{10}H_8N_2O)_2H_2PtCl_6$ 2aq, orange needles, and $C_{10}H_8N_2OHNO_3$.—2. Dilute *nitric acid* forms nitro-naphthol.—3. *Ammonium sulphide* reduces it to amido-naphthol.—4. *Chlorine* passed into a cold solution of the oxim in chloroform yields $C_6H_4\Big\langle\begin{matrix}C(NOH).CO\\CH{=\!=}CCl\end{matrix}$, crystallising in yellowish-red needles (Zincke a. Schmunk, *A.* 257, 133). This body takes up more chlorine, forming $C_6H_4\Big\langle\begin{matrix}C(NOH).CO\\CCl_2{-\!-}CHCl\end{matrix}$, which crystallises in white needles [186°], and when treated with potash changes to the di-chloro- derivative $C_6H_4\Big\langle\begin{matrix}C(NOH).CO\\CCl{=\!=}CCl\end{matrix}$ [166°].—5. *Bromine* added to its solution in chloroform unites forming $C_{10}H_7NO_2Br_2$ crystallising in colourless needles [131°], which dissolve in alkalis, changing to $C_6H_4\Big\langle\begin{matrix}C(NOH).CO\\CH{=\!=}CBr\end{matrix}$, crystallising in yellow needles [172°]. The last body is also formed by adding bromine to a solution of (β)-naphthoquinone (α)-oxim in cold HOAc. Bromine added to a hot solution in HOAc forms a bromo-naphthoquinone [201°] (Brömme, *B.* 21, 386).—6. *Phenyl cyanate* forms $C_{10}H_6\Big\langle\begin{matrix}O\\NO.CO.NHPh\end{matrix}$, crystallising in felted needles [128°] (Goldschmidt a. Strauss, *B.* 22, 3106).—7. SO_2 or $NaHSO_3$ acting on its alcoholic solution form amido-naphthol sulphonic acid (Schmidt, *J. pr.* [2] 42, 156).—8. *Aniline* in HOAc forms the same phenyl-amido-naphthoquinone anilide as it forms with the two other naphthoquinone-oxims (Brömme, *B.* 21, 393). Salts.—NaA′: green pp. (from alcoholic solution), sl. sol. water.—KA′: lustrous green plates, sol. water and alcohol.—NH_4A': green plates.—CoA'_2: brownish-red pp.—CoA'_3: purple-red pp., soluble without alteration in alcohol, aniline, phenol, conc. H_2SO_4, and HNO_3; it is very stable towards acids, alkalis, oxidising agents, and reducing agents (Ilinski a. Knorr, *B.* 18, 699).—NiA'_2: brownish-yellow pp., sl. sol. water and alcohol, easily decomposed by acids (difference from the cobalt salt).—FeA'_3: black pp., insol. water, v. sol. aniline, forming a

dark-brown solution.—CuA'_2; lustrous brown pp., sol. dilute HClAq and 50 p.c. acetic acid.—AgA': reddish-brown powder, insol. water and alcohol. $Ag(NH_4)A'_2$; slender green needles, insol. water and alcohol.—$AgHA'_2$; microcrystalline brown pp., sol. alcohol (Ilinski, *B.* 17, 2581; 18, 2728).

Methyl ether of the (α)-*oxim* $C_6H_4<\begin{matrix}C(NOMe).CO\\CH{=\!=\!=}CH\end{matrix}$. [75°]. Long yellow needles, v. sol. alcohol, ether, and benzene, m. sol. hot water, sl. sol. cold ligroïn. Forms a deep-red solution in H_2SO_4. Yields (α)-amido-(β)-naphthol on reduction with tin and HClAq (Goldschmidt a. Schmid, *B.* 18, 571).

Ethyl ether of the (α)-*oxim* $C_{10}H_6O(NOEt)$. [50°–60°]. Needles (from alcohol-ligroïn) (Ilinski, *B.* 19, 341).

Benzoyl derivative $C_{10}H_6O(NOBz)$. [114°].

(β)-*Oxim* $C_6H_4<\begin{matrix}CO.C(NOH)\\CH:CH\end{matrix}$. (β)-*Nitroso*-(α)-*naphthol.* [148°] (W.); [152°] (G.). This is the chief product of the action of nitrous acid on (α)-naphthol (Fuchs, *B.* 8, 626). It may be separated from the oxim of (α)-naphthoquinone (*v. supra*), which accompanies it by means of their sodium salts (Worms, *B.* 15, 1816). It is also obtained by boiling (β)-naphthoquinone with hydroxylamine hydrochloride for half an hour (Goldschmidt, *B.* 17, 215). Yellow needles (from benzene), almost insol. cold water, m. sol. ether, v. sol. alcohol. Somewhat volatile with steam. Conc. H_2SO_4 forms a deep-red solution. Not decomposed by boiling alcoholic potash.

Reactions.—1. *Bromine* acting on its solution in chloroform unites forming a dibromide $C_{10}H_7NO_2Br_2$, crystallising in grey leaflets [155°] (Brömme, *B.* 21, 390). Bromine acting on its solution in HOAc yields the bromo- derivative $C_{10}H_6BrNO_2$, separating from alcohol in yellow crystals [175°] (B.).—2. Alkaline K_3FeCy_6 oxidises it to (β)-nitro-(α)-naphthol.—3. *Nitric acid* forms di-nitro-(α)-naphthol and phthalic acid.—4. *Phenyl cyanate* unites with it, forming $C_{10}H_6<\begin{matrix}O\\NO.CO.NHPh\end{matrix}$, crystallising from benzene in greenish-yellow prisms (containing benzene) [120°] (Goldschmidt a. Strauss, *B.* 22, 3106).—5. *Aniline* in HOAc forms the same phenyl-amido-naphthoquinone anilide as with the other two isomeric oxims (Brömme).

Salts.—NH_4A': lustrous green needles.—NaA' (dried at 110°): reddish-brown powder, insol. conc. NaOHAq, m. sol. water and alcohol.—KA': lustrous green plates.—BaA'_2 2aq: bronzed plates.—PbA'_2: dark-brown scales, insol. water.—AgA': brownish-red pp.

Methyl ether of the (β)-*oxim* $C_6H_4<\begin{matrix}CO.C(NOMe)\\CH:CH\end{matrix}$. [98°]. From the Ag salt and MeI (Fuchs). Formed also by heating (β)-naphthoquinone with the hydrochloride of the methyl ether of hydroxylamine (Goldschmidt a. Schmid, *B.* 18, 571, 2224). Yellowish-green needles, v. sol. alcohol. Reduced by tin and HCl to (β)-amido-(α)-naphthol.

Ethyl ether $C_{10}H_6O(NOEt)$. [101°]. Flat greenish-yellow needles.

Benzoyl derivative $C_{10}H_6O(NOBz)$. [162°].

Di-oxim $C_{10}H_6(NOH)_2$. [149°] (G. a. S.); [166°] (B.); [181°] (K. a. M.). Formed by warming either the (α)- or the (β)- oxim in concentrated methyl-alcoholic solution with hydroxylamine hydrochloride at 100° (Goldschmidt a. Schmid, *B.* 17, 2066; Brömme, *B.* 21, 392). Formed also by adding an alkaline solution of hydroxylamine to a cold solution of the (α)-oxim in caustic soda (Kehrmann a. Messinger, *B.* 23, 2816). Yellow needles, forming a reddish-yellow solution in alkalis, and a dark-red solution in H_2SO_4. On warming with dilute H_2SO_4 or with alkalis it is converted into an anhydride. Phenyl cyanate also brings about this change (Goldschmidt a. Strauss, *B.* 22, 3107). Phenyl hydrazine combines, forming $C_{16}H_{16}N_4O_2$, which crystallises from alcohol in tufts of long needles [105°–138°] (Polonovsky, *B.* 21, 182). Stannous chloride reduces it to naphthylene-(1, 2)-diamine. Alkaline K_3FeCy_6 oxidises it to di-nitroso-naphthalene $C_{10}H_{16}(NO)_2$, which crystallises in needles [127°]; insol. water and alkalis, v. sol. alcohol (Leuckart, *B.* 19, 174, 349). The dioxim colours iron and cobalt solutions brown.—$KC_{10}H_7N_2O_2$: brownish-red amorphous pp., obtained by adding ether to an alcoholic solution of the dioxim and KOEt (Ilinski, *B.* 19, 342).—$AgC_{10}H_7N_2O_2$: dark-red pp., obtained by adding ammoniacal $AgNO_3$ to an alcoholic solution of the dioxim.

(α)-*Methyl ether of the dioxim* $C_6H_4<\begin{matrix}C(NOMe).C(NOH)\\CH{=\!=\!=}CH\end{matrix}$. [159°]. Formed by action of hydroxylamine on the methyl ether of the (α)-oxim. Insol. water, sol. alkalis.

(β)-*Methyl ether of the dioxim* $C_6H_4<\begin{matrix}C(NOH).C(NOMe)\\CH{=\!=\!=}CH\end{matrix}$. Formed from the silver salt of the dioxim and MeI; and also by the action of hydroxylamine on the methyl ether of the (β)-oxim. Yellow oil, turning brown in air. Sol. alkalis.

(α)-*Ethyl ether of the dioxim* $C_6H_4<\begin{matrix}C(NOEt):C(NOH)\\CH{=\!=\!=}CH\end{matrix}$. [153°]. Formed by warming an alcoholic solution of the ethyl ether of the (α)-oxim with hydroxylamine hydrochloride. Green needles (from alcohol); insol. water.—$KC_{12}H_{11}N_2O_2$: brown needles.

Anhydride of the dioxim $C_{10}H_6<\begin{matrix}N\\N\end{matrix}>O$. [78°]. Formed from the dioxim by the action of AcCl, alkalis, or acids. Formed also by heating the (α)- or (β)-oxim with an alcoholic solution of hydroxylamine hydrochloride at 150° (Goldschmidt, *B.* 17, 216, 801). Long colourless monoclinic needles (from ligroïn). Insol. alkalis.

***Peri*-Naphthoquinone** $C_{10}H_6O_2$ *i.e.*
$$\begin{matrix}\ulcorner O{-}O\\ CH:C{-}C{-}C:CH\\ CH:CH.C.CH:CH\end{matrix}$$
Occurs in small quantity in the product of the oxidation of di-bromo-(α)-naphthol by fuming nitric acid (Meldola a. Hughes, *C. J.* 57, 632). Slender, pale-yellow needles; no definite melting-point observed. Blackens and decomposes above 220°. Sl. sol. boiling dilute NaOH. Gives an azo- compound with phenyl hydrazine. Not reduced by cold aqueous SO_2. Zinc-dust and HOAc reduces it to the corresponding dioxynaphthalene, which blackens at 205° and forms a diacetyl derivative melting at 227°.

References. — Amido-, Amido-oxy-, Bromo-,

BROMO-AMIDO-, CHLORO-, NITRO-, and OXY-NAPHTHOQUINONE.

NAPHTHOQUINONE-PHENAZINE $C_6H_4<\begin{smallmatrix}CO.C.N\\CO.C.N\end{smallmatrix}>C_6H_4$. Formed by heating o-nitro-phenyl-amido-naphthoquinone with alcoholic ammonium sulphide (Leicester, *B.* 23, 2797). Green plates (from alcohol). Its alcoholic solution is brown with green fluorescence.

NAPHTHOQUINONE PHENYL-HYDRAZIDE *v. Benzene-AZO-naphthol.*

NAPHTHOQUINONE-TOLAZINE $C_6H_4<\begin{smallmatrix}CO.C.N.C.CH:CH\\CO.C.N.C.CH:CMe\end{smallmatrix}$. Formed by reduction of o-nitro-tolyl-amido-(α)-naphthoquinone with alcoholic ammonium sulphide (Leicester, *B.* 23, 2797). Steel-blue plates with green lustre, forming a green powder. Conc. H_2SO_4 forms a green solution. Its solutions in alcohol or HOAc are greenish-yellow with faint moss-green fluorescence.

NAPHTHOQUINONE TOLYL HYDRAZIDE *v. Toluene-AZO-naphthol.*

NAPHTHOQUINOXALINE $C_{12}H_8N_2$ *i.e.* $C_6H_4<\begin{smallmatrix}C.N:CH\\CH:CH.C.N:CH\end{smallmatrix}$. [62°]. Formed by warming naphthylene-($\alpha\beta$)-diamine with the bisulphite compound of glyoxal in presence of some HOAc (Hinsberg, *B.* 23, 1394). Small colourless needles; v. sol. alcohol and ether, sl. sol. hot water. Volatile with steam. Conc. H_2SO_4 gives a deep-red colour, turned yellow by addition of water.—The sulphate crystallises well. The platinochloride is sl. sol. water.

NAPHTHOQUINOXIM *v. Oxim* of NAPHTHOQUINONE.

NAPHTHOSTYRIL *v. Lactone* of *peri*-AMIDO-NAPHTHOIC ACID.

NAPHTHOTOLAZINE *v.* TOLUNAPHTHAZINE.

(α)-NAPHTHOXINDOLE $C_{12}H_9NO$ *i.e.* $C_{10}H_6<\begin{smallmatrix}NH\\CH_2\end{smallmatrix}>CO$. [245°]. Formed by the action of mineral acids on the sodium salt of (α)-naphthindole sulphonic acid (Hinsberg, *B.* 21, 116). Colourless needles (from alcohol). Yields a nitroso- derivative, which on reduction and subsequent oxidation forms (α)-naphthisatin.

(β) - Naphthoxindole $C_{10}H_6<\begin{smallmatrix}NH\\CH_2\end{smallmatrix}>CO$. [234°]. Formed by the action of mineral acids on (β)-naphthindole sulphonic acid (Hinsberg, *B.* 21, 114). Faint greenish needles. Sl. sol. water, v. sol. alcohol, ether, HOAc. Not attacked by *mineral acids.* Conc. KOHAq dissolves it without change. Baryta-water at 150° in sealed tubes yields the Ba salt of a strong acid. $NaNO_2$ in HOAc solution gives a nitroso- derivative [c. 240°], crystallising in yellowish-red needles. M. sol. alcohol, ether, HOAc, sl. sol. water.

NAPHTHOXY-ACETIC ACID *v. Naphthyl derivative* of GLYCOLLIC ACID, vol. ii. p. 639.

NAPHTHOYL-BENZOIC ACID $C_{18}H_{12}O_3$ *i.e.* $C_{10}H_7.CO.C_6H_4.CO_2H$ [173·5°]. Formed by the action of phthalic anhydride on naphthalene in presence of $AlCl_3$ (Ador a. Crafts, *C. R.* 88, 1355). Small white prisms (from dilute alcohol). Its Ba salt crystallises from alcohol in very hygroscopic needles. Conc. H_2SO_4 converts it into naphthanthraquinone $C_{10}H_6<\begin{smallmatrix}CO\\CO\end{smallmatrix}>C_6H_4$ (Elbs, *B.* 19, 2209).

NAPHTHOYL-CYANIDE *v. Nitrile* of NAPHTHYL-GLYOXYLIC ACID.

NAPHTHOYL-FORMIC ACID *v.* NAPHTHYL-GLYOXYLIC ACID.

($\alpha\alpha$)-DINAPHTHYL $C_{20}H_{14}$ *i.e.* $(C_{10}H_7)_2$. Mol. w. 254. [154°]. (above 360°). V.D. 8·67 (calc. 8·77).

Formation.—1. Together with phthalic acid and other bodies by heating naphthalene with MnO_4 and dilute H_2SO_4 (Lossen, *A.* 144, 77).—2. By distilling ($\beta\beta$)-dioxy-dinaphthyl (1 pt.) with zinc-dust (12 pts.), the yield being 65 p.c. of the theoretical (Walder, *B.* 15, 2170; Julius, *B.* 19, 2549).—3. By distilling (β)-'dinaphthyl diquinone' $C_{20}H_{10}O_4$ with zinc-dust (Korn, *B.* 17, 3019).—4. By diazotising di-amido-dinaphthyl (naphthidine), and boiling the tetra-azo-dinaphthyl sulphate with alcohol (Nietzki a. Groll, *B.* 18, 3256).

Preparation.—Naphthalene is boiled with MnO_2 and H_2SO_4 (diluted with more than its own bulk of water). The product is boiled with water, filtered, and the residue extracted with alcohol, the alcohol boiled off (in a current of air), and the residue distilled. The fraction coming over above 360° is boiled with light petroleum and animal charcoal, filtered, and allowed to crystallise (Watson Smith, *C. J.* 35, 225). No $\beta\beta$ compound is formed.

Properties.—Colourless plates (by sublimation), v. sol. benzene, CS_2, HOAc, and ether, m. sol. alcohol. Its solutions exhibit blue fluorescence (K.).

Picric acid compound $C_{20}H_{14}2C_6H_2(NO_2)_3OH$. [145°]. Reddish-brown needles.

($\alpha\beta$)-Dinaphthyl $C_{20}H_{14}$. [76°] (S.); [80°] (W.). V.D. 8·78 (calc. 8·77). Formed, together with a larger quantity of the ($\beta\beta$)- and a very little of the ($\alpha\alpha$)-isomerides, by passing the vapour of naphthalene, mixed with $SbCl_3$, through a red-hot tube (Watson Smith, *C. J.* 32, 559). Small six-sided tables, m. sol. alcohol, ether, and benzene than the ($\beta\beta$)-isomeride.

Picrate $C_{20}H_{14}.C_6H_2(NO_2)_3OH$. [156°] (Wegscheider, *B.* 23, 3199).

($\beta\beta$)-Dinaphthyl $C_{20}H_{14}$. *Isodinaphthyl* [187°] (S.); [189°] (G. a. T.). V.D. 8·73 (calc. 8·77).

Formation.—1. By passing naphthalene through a red-hot tube (Watson Smith, *C. J.* 24, 1184).—2. By passing naphthalene and CCl_4 through a tube at dull-red heat $4C_{10}H_8 + CCl_4 = 2C_{20}H_{14} + 4HCl + C$ (Watson Smith, *C. J.* 35, 229).—3. By passing through a red-hot tube, naphthalene with chloroform, (α)-bromo-naphthalene, $SbCl_3$ or $SnCl_4$.—4. By heating to redness (α)-bromo-naphthalene with naphthalene and soda lime (S.).—5. By passing $C_{10}H_8$ and $C_{10}H_7Br$ through a red-hot tube packed with Fe_2O_3 (S.).—6. By distilling aluminium (β)-naphthol (Gladstone a. Tribe, *C. J.* 41, 16).—7. By dropping isoamyl chloride upon naphthalene (100 g.) and $AlCl_3$ (25 g.) at 120°; pentane being also formed (Roux, *Bl.* [2] 41, 379).

Properties.—Plates (from benzene), with slight blue fluorescence. Much less sol. alcohol, ether, and benzene than either of its isomerides. On oxidation with $KMnO_4$ or dilute HNO_3 at 160° it yields phthalic acid. CrO_3 in HOAc produces a quinone $C_{20}H_{10}O_4$.

Picric acid compound $C_{20}H_{11}2C_6H_2(NO_2)_3OH$. [184°]. Orange prisms (Wegscheider, *B.* 23, 3200).

(ββ)-**Dinaphthyl sulphonic acid** $C_{20}H_{14}SO_3$ *i.e.* $C_{10}H_7.C_{10}H_6SO_3H$. Prepared by heating (ββ)-dinaphthyl (15 g.) with conc. H_2SO_4 (3 g.) for 5 hours at 200° (Watson Smith a. Takamatsu, *C. J.* 39, 552).—CaA'_2 2aq: white needles, m. sol. hot water, insol. alcohol, ether, and benzene.—BaA'_2 2aq?

(ββ)-**Dinaphthyl disulphonic acid** $C_{10}H_7(SO_3H).C_{10}H_7(SO_3H)$. Two isomeric acids of this formula are formed by heating (ββ)-dinaphthyl (10 g.) with conc. H_2SO_4 (7 g.) at 190° for 5 hours (S. a. T.) One gives an insoluble barium salt, the other forms $BaA''x$aq, v. sol. water, and $PbA''x$aq, a yellowish-white crystalline powder.

(ββ)-**Dinaphthyl tetrasulphonic acid** $C_{10}H_5(SO_3H)_2.C_{10}H_5(SO_3H)_2$. Formed by heating (ββ)-dinaphthyl with an excess of Nordhausen sulphuric acid (S. a. T.).—Pb_2A^{iv} 6aq: v. sol. water, insol. alcohol, ether, and benzene.

References.—Di-amido-, Di-bromo-, Tetra-chloro-, and Nitro- dinaphthyl.

NAPHTHYL-ACETAMIDINE $C_{12}H_{12}N_2$ *i.e.* $CH_3.C(NH).NHC_{10}H_7$. (α)-*Naphthyl-ethenyl-amidine.* Prepared by the action of (α)-naphthylamine hydrochloride on acetonitrile at 165° (Bernthsen a. Trompetter, *B.* 11, 1758).—B'HCl: soluble prisms.—$B'_2H_2PtCl_6$: small yellow tables.—$B'H_2C_2O_4$: small crystals.—$B'_2H_2SO_4$: white crystals.—$B'HNO_3$: oil.

Di-(α)-naphthyl-acetamidine $C_{22}H_{18}N_2$ *i.e.* $CH_3.C(NC_{10}H_7).NHC_{10}H_7$. Formed from (α)-naphthylamine (6 mols.), AcCl (3 mols.), and PCl_3 (Hofmann, *J.* 1865, 415). Resinous.

Di-(β)-naphthyl acetamidine $CH_3.C(NC_{10}H_7).NHC_{10}H_7$. [168°]. Formed by heating (β)-naphthylamine (6 mols.) with AcCl (3 mols.) and PCl_3 (1 mol.) at 150° (Maschke, *C. C.* 1886, 824).

(α)-**NAPHTHYL-ACETIC ACID** $C_{12}H_{10}O_2$ *i.e.* $C_{10}H_7.CH_2.CO_2H$. [131°]. Prepared by heating (α)-naphthyl-glyoxylic acid with HI and P (Boessneck, *B.* 16, 641). Long silky needles. Sol. alcohol, ether, acetic acid, benzene, and hot water, sl. sol. cold water.

Amide $C_{10}H_7.CH_2.CO.NH_2$. [181°] (B.); [154°] (W.). Formed from the acid (B.) and perhaps also by the action of yellow ammonium sulphide on (α)-naphthyl methyl ketone (Willgerodt, *B.* 21, 534). Colourless needles, sol. benzene, acetic acid, ether, CS_2, and hot water.

Nitrile $C_{10}H_7.CH_2.CN$. (above 300°). Formed from the amide and P_2O_5. Oil.

DI-NAPHTHYL-ACETYLENE $C_{10}H_7.C⁝C.C_{10}H_7$. [225°]. (above 360°). Obtained by distilling *exo*-di-chloro-di-naphthyl-ethylene or *exo*-tri-chloro-di-naphthyl-ethane (1 pt.) with soda-lime (10 pts.) (Grobowski, *B.* 11, 301). Long silky needles (from alcohol).

(α)-**NAPHTHYL-ACRYLIC ACID** $C_{13}H_{10}O_2$ *i.e.* $C_{10}H_7.CH:CH.CO_2H$. (α)-*Naphthoeinnamic acid.* [207°] (L.); [212°] (B.). S. ·014. Obtained by heating naphthoic aldehyde (2 pts.) with sodium acetate (1 pt.) and Ac_2O (20 pts.) at 170° (Lugli, *G.* 11, 394; Brandis, *B.* 22, 2155). Needles, m. sol. hot water, v. sol. alcohol and ether. Oxidised by $KMnO_4$ to naphthoic aldehyde and naphthoic acid. Combines with bromine forming $C_{10}H_7.CHBr.CHBr.CO_2H$ [189°]. HBr at 100° yields $C_{10}H_7.CHBr.CH_2.CO_2H$ [216°].—CaA'_2: plates.—BaA'_2: needles.—CuA'_2.—AgA': white pp., blackening on exposure.

NAPHTHYL-ALLYL-THIO-UREA $C_{14}H_{14}N_2S$ *i.e.* $C_{10}H_7NH.CS.NHC_3H_5$. [145°]. Formed from (α)-naphthylamine and oil of mustard (Zinin, *A.* 84, 346; Prager, *B.* 22, 3000). Crystals, insol. water, v. sol. alcohol and ether.

Dinaphthyl-allyl-ψ-thiourea *v.* Di-naphthyl-imido-thio-carbamic ether.

(α)-**NAPHTHYL-AMIDO-ACETIC ACID** $C_{12}H_{11}NO_2$ *i.e.* $C_{10}H_7.NH.CH_2.CO_2H$. *Naphthyl-glycocoll.* [199°] (B. a. N.); [198°] (J.); [192°] (M.). Formed from (α)-naphthylamine, chloroacetic acid, and NaOAc at 100° (Bischoff a. Nastvogel, *B.* 22, 1808; Jolles, *B.* 22, 2372; Mauthner, *M.* 10, 251; Forte, *G.* 19, 361). Needles, insol. water, almost insol. ether, sl. sol. alcohol, v. sol. acetone. Forms a platinochloride and a nitrosamine. The Ca salt distilled with calcium formate gives a product crystallising in colourless plates [163°].—CaA'_2 3aq: tufts of needles.—BaA'_2 2aq.—CuA'_2: small plates.—AgA'aq: silvery plates.

Anhydride $(C_{10}H_7.NH.CH_2.CO)_2O$. [269°]. Formed by heating the acid at 230°. Scales, insol. ether, sol. alcohol.

Acetyl derivative [154°].—BaA'_2 5aq.

(β)-**Naphthyl-amido-acetic acid** $C_{10}H_7.NH.CH_2.CO_2H$. [135°]. Formed by heating (β)-naphthylamine (2 mols.) with a solution of chloro-acetic acid (1 mol.) at 100° (Jolles, *B.* 22, 2372; Bischoff, *B.* 23, 2005). Minute crystals (from water), v. sol. alcohol, ether, and HOAc. Yields a nitrosamine $C_{10}H_7.N(NO).CH_2.CO_2H$ crystallising from MeOH in reddish plates [126°].

Salts.—The Ag salt decomposes on drying in the air. (β)-Naphthylamine salt $C_{10}H_7NH_2HA'$. [116°]. Needles.

(α)-**NAPHTHYL-AMIDO-CROTONIC ACID.** *Ethyl ether* $C_{10}H_7NH.C(Me).CH.CO_2Et$. [45°]. Formed by the action of acetoacetic ether on (α)-naphthylamine (Conrad a. Limpach, *B.* 21, 531). White silky needles, sol. ether and benzene. Yields on heating to 240° (*Py.* 1:3)-oxy-methyl-(α)-naphthoquinoline, with elimination of alcohol.

(β)-**Naphthyl-amido-crotonic acid** *Ethyl ether* $C_{10}H_7NH.C(Me).CH.CO_2Et$. [66°]. Formed by the action of acetoacetic ether on (β)-naphthylamine at 100° (Conrad a. Limpach, *B.* 21, 532). Large prisms (from alcohol). Yields (*Py.* 1:3)-Oxy-methyl-(β)-naphthoquinoline on heating to 240°.

(β)-**NAPHTHYL AMIDO-ETHYL OXIDE** $C_{12}H_{13}NO$ *i.e.* $C_{10}H_7.O.C_2H_4NH_2$. Formed by the action of alcoholic ammonia on the chloro-ethyl ether of (β)-naphthol (Koelle, *B.* 13, 1955). Amorphous mass. — B'HCl aq: needles. — $B'_2H_2PtCl_6$: needles.

(α)-**NAPHTHYL-AMIDO-METHYL-MALON-AMIC ACID** $CH_3.C(NHC_{10}H_7)(CO_2H)(CONH_2)$. *Ethyl ether* A'Et. [159°] Formed by dissolving α-cyano-α-(α)-naphthyl-amido-propionic ether (*q.v.*) in conc. H_2SO_4 (Gerson, *B.* 19, 2969). Long white needles; sl. sol. cold water, more easily in hot water with a beautiful green fluorescence, v. sol. alcohol and ether.

(α) - **NAPHTHYLAMIDO - (β) - NAPHTHOQUINONE** (α)-*naphthylamide* $C_{30}H_{20}N_2O$ *i.e.* $C_{10}H_5(NHC_{10}H_7)<^{O}_{NC_{10}H_7}$. [178° cor.]. Formed from (α)-naphthoquinone oxim and (α)-naphthylamine (Brömme, *B.* 21, 394). Forms a violet solution in alcohol and a blue solution in conc. H_2SO_4. Gives a green colour on heating with H_2SO_4.

(β)-Naphthyl-amido-(β)-naphthoquinone (β)-*naphthylamide* $C_{10}H_5(NHC_{10}H_7)<^{O}_{NC_{10}H_7}$. [247°]. Formed by heating di-bromo-(α)-naphthol with (β)-naphthylamine (Meldola, *C. J.* 45, 160). Dull, reddish, fibrous needles. Feebly basic. Insol. alcohol, but dissolves when boiled with alcohol and HCl, forming a violet solution. Dissolves in hot toluene or chloroform, giving a reddish-brown liquid.

DI-(α)-NAPHTHYL-DI-AMIDO-OIAZTHIOLE $C_{22}H_{16}N_4S$ *i.e.* $S<^{C(NHC_{10}H_7):N}_{C(NHC_{10}H_7):N}>$. [136°]. Obtained by oxidising (α)-naphthyl-thio-urea with hydrogen peroxide and dilute HClAq (Hector, *B.* 23, 359). Crystallises from alcohol in white needles containing HOEt (1 mol.) and melting at 104°. Insol. water. Cyanogen, passed into its warm solution, forms $C_{22}H_{16}N_4SC_4N_4$ [203°].

Salts. — $B'_2H_2PtCl_6$. [225°]. — Picrate $B'C_6H_2(NO_2)_3OH\ \frac{1}{2}EtOH$. [below 100°]. Small yellow grains.—$B'AgNO_3$. Pp.; insol. alcohol.

Acetyl derivative $C_{22}H_{15}AcN_4S$. [263°]. Needles (from alcohol).

Benzoyl derivative $C_{22}H_{15}BzN_4S$. [270°].

Di-(β)-naphthyl-di-amido-oiazthiole $C_{22}H_{16}N_4S$. [100°–117°]. Prepared from (β)-naphthyl-thio-urea and H_2O_2. Grey powder (from alcohol); more sol. alcohol than the (α)-isomeride. Cyanogen passed into its warm alcoholic solution forms $C_{22}H_{16}N_4SCy_4$ [200°].—$B'_2H_2PtCl_6$. Begins to decompose at 236°–240°. —$B'C_6H_2(NO_2)_3OH$. [178°]. Yellow powder, sl. sol. alcohol.—$B'AgNO_3$: white pp.

Acetyl derivative $C_{22}H_{15}AcN_4S$. [203°]. Needles (from alcohol).

Benzoyl derivative $C_{22}H_{15}BzN_4S$. [247°].

(β)-**NAPHTHYL PHENYL-AMIDO-ETHYL OXIDE** $C_{18}H_{17}NO$ *i.e.* $C_{10}H_7.O.C_2H_4.NHC_6H_5$. [75°]. Formed by the action of aniline on the chloro-ethyl ether of (β)-naphthol (Koelle, *B.* 13, 1955).

TRI - (β) - NAPHTHYL - TRI - AMIDO - TRI - PHENYL-CARBINOL $(C_{10}H_7.NH.C_6H_4)_3C.OH$. Formed by heating para-rosaniline with (β)-naphthylamine (Meldola, *C. N.* 47, 133, 147). Dyes wool or silk blue.

TRI - NAPHTHYL - TRI - AMIDO - TRI - PHENYL-CARBINYL CHLORIDE $C_{49}H_{36}N_3Cl$ *i.e.* $(C_{10}H_7.NH.C_6H_4)_2C.C_6H_4NHCl.C_{10}H_7$. *Phenyl-(α)-naphthyl-amine blue.* Formed by heating phenyl-(α)-naphthylamine with oxalic acid (Hausdörfer, *B.* 23, 1965). Dark brown powder, v. sol. hot aniline, sl. sol. cold alcohol, insol. ether and benzene.

NAPHTHYL-AMIDO-ISOSUCCINAMIC ACID *v.* NAPHTHYL-AMIDO-METHYL-MALONAMIC ACID.

(α)-**NAPHTHYLAMINE** $C_{10}H_9N$ *i.e.* $C_6H_4<^{C(NH_2):CH}_{CH=\!=CH}$. *Naphthalidine. Naphthalamine.* Mol. w. 143. [50°]. (300°). V.D. (at 194°) 72·6 (calc. 71·5) (Eykman, *B.* 22, 2757). S. ·167 in the cold (Ballo, *B.* 3, 675).

Formation.—1. By reduction of nitro-naphthalene by alcoholic ammonium sulphide (Zinin, *J. pr.* 27, 143), by iron and acetic acid (Béchamp, *A. Ch.* [3] 42, 186; Schützenberger a. Willm, *C. R.* 47, 82; Ballo, *B.* 3, 288, 673), or by tin or zinc and HClAq (Böttger, *D. P. J.* 173, 480).—2. By heating (α)-naphthol with four times its weight of ammoniacal $CaCl_2$ to 270° for 8 hours, the yield being 74 p.c. (Benz, *B.* 16, 14; *cf.* Calm, *B.* 15, 616).

Preparation.—Granulated nitronaphthalene (600 kilos.) is slowly added to a warm mixture of iron borings (800 kilos.), hydrochloric acid (40 kilos.), and some water. The mixture is agitated and kept at about 50° by blowing in steam for 7 hours, after which milk of lime (containing 50 kilos. of CaO) is added. The mixture is distilled in a current of superheated steam (Witt, *Chem. Industrie*, 10, 215).

Properties.—White silky needles, with powerful odour. May be sublimed. V. e. sol. alcohol and ether. Colours pine-wood yellow. When not quite pure it rapidly becomes coloured in the air. Does not turn red litmus blue. Aqueous solutions of its salts give a blue pp. with $FeCl_3$, $AgNO_3$, auric chloride, platinic chloride, $SnCl_4$, $HgCl_2$, chromic acid, H_2O_2, and other oxidising agents (Piria, *A. Ch.* [3] 31, 217; 78, 64; Schiff, *A.* 101, 92; Wurster, *B.* 22, 1910). This blue pp., 'oxynaphthylamine' $C_{10}H_9NO$, is amorphous, v. sol. chloroform, and not reduced by SO_2 (Schiff, *A.* 129, 255). If to a solution of (α)-naphthylamine in alcohol or HOAc there be added a small quantity of nitrous acid and a little HClAq an intense purple colour is produced (Liebermann, *A.* 183, 265).

Reactions.—1. *Heated* with $ZnCl_2$ or $CaCl_2$ at 280° it splits up to some extent into NH_3 and dinaphthylamine.—2. Distillation over PbO yields naphthazine.—3. Boiling *chromic acid mixture* oxidises it to naphthoquinone, phthalic acid, and other products (Reverdin a. Nölting, *B.* 12, 2306).—4. Heated with *nitro-naphthalene* and some HClAq at 200° it yields 'tri-naphthylene-diamine' $C_{30}H_{18}N_2$ (Salzmann a. Wichelhaus, *B.* 9, 1107).—5. *Urea* (1 pt.) heated with (α)-naphthylamine (2 pts.) at 120° forms only di-naphthyl-urea; but both mono- and di-naphthyl-urea are formed on heating (α)-naphthylamine hydrochloride with urea at 160° (Pagliani, *G.* 9, 28).—6. *Cyanic acid* forms (α)-naphthyl-urea.—7. *Alkyl thio-carbimides* form alkyl-naphthyl-thio-ureas.—8. Alcoholic CS_2 forms di-naphthyl-thio-urea.—9. MeOH and $ZnCl_2$ at 190° form the methyl ether of (α)-naphthol (Hantzsch, *B.* 13, 1347).—10. (α)-naphthylamine hydrochloride heated with *o*-amido-azo- compounds yields azine colouring matters (eurhodines).—11. Readily converted into naphthalene by diazotising, and pouring the alkaline solution of the diazo- compound into a solution of $SnCl_2$ in aqueous NaOH (Friedländer, *B.* 22, 587).—12. SiF_4 in benzene solution forms minute crystals of $Si(NHC_{10}H_7)_4$ (Reynolds, *C. J.* 55, 482).—13. The bisulphite warmed with *benzoic aldehyde* forms $C_6H_5.CH:NC_{10}H_7$, a yellow powder (Papasogli, *A.* 171, 138).—14. *Benzoic aldehyde* and *pyruvic acid* form the compound $C_{10}H_6<^{N:CPh}_{C(CO_2H)}>CH$ crystallising in yellow

needles [300°] (Doebner a. Kuntze, *A.* 249, 109). 15. *Benzil* reacts on heating, forming the compounds $C_6H_5.C(NC_{10}H_7).CO.C_6H_5$ [139°] and $C_6H_5.C(NC_{10}H_7).C(NC_{10}H_7).C_6H_5$ [219°] both crystallising in yellow needles (Bandrovsky, *M.* 9, 685). — 16. A conc. boiling aqueous solution of *alloxan* forms a compound $C_{14}H_{11}N_3O_4$, which separates in transparent white needles, insol. water, and coloured green by H_2SO_4. Alkalis convert it into a crystalline acid $C_{14}H_{10}N_2O_5$ (Pellizari, *G.* 17, 409).—17. *Cyanuric chloride* forms $N_3C_3Cl_2(NHC_{10}H_7)$ [149°], $N_3C_3Cl(NHC_{10}H_7)_2$ [215°], or $N_3C_3(NHC_{10}H_7)_3$ [223°], according to the proportions used (Fries, *B.* 19, 242; *C. J.* 49, 314).—18. *Citraconic acid* at 145° forms $C_{10}H_7N:C_5H_4O_2$ [143°] (360°) (Morawski a. Gläser, *M.* 9, 284).—19. *Itaconic acid* heated with (α)-naphthylamine in aqueous solution forms $C_{10}H_7N\langle{}^{CH_2.CH.CO_2H}_{CO\ .CH_2}$, a white crystalline powder [206°], m. sol. hot alcohol (Scharfenberger, *A.* 254, 151).—20. *Chloro-acetic ether* in ethereal solution forms $C_{16}H_{16}NO_2Cl$, crystallising in prisms [75°] (Bender, *B.* 20, 2750).

Salts.—B'HCl. Needles (by sublimation) or scales (from alcohol); v. e. sol. water, alcohol, and ether.—$B'_2H_2PtCl_6$: yellow pp., sl. sol. water. — B'HBr. — $B'_2H_2SO_4$. — $B'_2H_2SO_4$ 2aq.— $B'HNO_3$: scales.—$B'_2H_2C_2O_4$: stellar groups of small laminæ.—$B'H_2C_2O_4$: nodules. Yields on distillation $C_2O_2(NHC_{10}H_7)_2$ and the formyl derivative $CHO.NHC_{10}H_7$ (Zinin, *A.* 108, 228).— $B'_2H_2PtCy_4$: crystals (Scholtz, *M.* 1, 905).— $B'H_2SO_3$: pearly rosettes. — Citraconate [99°]. Formed by mixing solutions of (α)-naphthylamine and citraconic acid in benzene (Morawski a. Gläser, *M.* 9, 285).—Phenate $B'C_6H_5OH$. [30·1°]. Formed by heating phenol with (α)-naphthylamine (Dyson, *C. J.* 43, 468). Needles (from light petroleum).—Benzene sulphonate [225°] (Norton a. Westenhof, *Am.* 10, 129).—Toluene *p*-sulphonate [239°] (Norton a. Otten, *Am.* 10, 140).

Formyl derivative $C_{10}H_7NH(COH)$. [139°]. White silky needles (Tobias, *B.* 15, 2447).

Acetyl derivative $C_{10}H_7NHAc$. [159°]. Formed from the base by treatment with AcCl, Ac_2O, or HOAc (Rother, *B.* 4, 850; Tommasi, *C. R.* 76, 1267; Liebermann, *A.* 183, 229). Formed also by heating (α)-naphthol with ammonium acetate. White silky needles; sl. sol. boiling water, v. sol. alcohol. On heating with sulphur the products are ethenyl-amido-naphthyl mercaptan and $C_{10}H_6\langle{}^{N}_{S}\rangle C.C\langle{}^{N}_{S}\rangle C_{10}H_6$, which crystallises in yellow plates [above 300°] (Hofmann, *B.* 20, 1801). The only products of the nitration of acetyl-(α)-naphthylamine are the o- and *p*-nitro- derivatives of melting-points [199°] and [190°] respectively; the supposed isomeride of melting-point [170°] is a molecular compound of the o- and *p*- bodies, and the so-called 'β- and δ-nitracetnaphthalides' are diacetyl derivatives of the same two nitro-(α)-naphthylamines (Lellmann a. Remy, *B.* 19, 796). Chlorine passed into its solution in HOAc forms $C_{10}H_5Cl_2NHAc$ [214°] (Cleve, *B.* 20, 448).

Chloro-acetyl derivative $C_{12}H_{10}NClO$ *i.e.* $C_{10}H_7NH.COCH_2Cl$. [121°]. Formed from naphthylamine and chloro-acetyl chloride (Tommasi, *Bl.* [2] 20, 21; Abenius, *J. pr.* [2] 40, 437). Silky needles.

Thioacetyl derivative $C_{10}H_7NH.CS.CH_3$ [96°] (B. a. T.); [111°] (*J.*). Formed by heating (α)-naphthyl-acetamidine with CS_2 for several hours at 100° (Bernthsen a. Trompetter, *B.* 11, 1760). Formed also by heating acetyl-(α)-naphthylamine with P_2S_5 (Jacobsen, *B.* 20, 1897). White tables. Gives $C_{10}H_7NH.CH_2.CH_3$ on reduction. Oxidised by K_3FeCy_6 to ethenyl-amido-naphthyl mercaptan $C_{10}H_6\langle{}^{N}_{S}\rangle C.CH_3$.

Benzoyl derivative $C_{10}H_7.NHBz$ [156°] (W.); [162°] (Kühn, *B.* 18, 1477); [160°] (Hofmann, *B.* 20, 1798). Colourless needles; v. sol. dilute alcohol, sl. sol. absolute alcohol and water (Ebell, *B.* 7, 1317; 8, 562; Worms, *B.* 15, 1814). Yields on nitration $C_{10}H_6(NO_2)NHBz$ [224°]. PCl_5 converts it into $C_{10}H_7N:CClC_6H_5$ [60°] (Just, *B.* 19, 984).

Thiobenzoyl derivative $C_{10}H_7NH.CS.C_6H_5$. [148°]. Formed from the benzoyl derivative by heating with P_2S_5; or from (α)-naphthyl-acetamidine by heating with CS_2 (B. a. T.; *J.*). Yellowish needles or plates. Oxidised by K_3FeCy_6 to benzenyl-amido-naphthyl mercaptan.

(α)-Naphthylamine *ar*-tetrahydride $C_{10}H_{11}NH_2$ *i.e.* $\begin{matrix} CH_2.CH_2.C.C(NH_2):CH \\ CH_2.CH_2.C.CH \text{——} CH \end{matrix}$ (275°) at 712 mm. S.G. $\frac{16}{}$ 1·0625. Formed by the action of sodium on a solution of (α)-naphthylamine in isoamyl alcohol (Bamberger, *B.* 20, 2916; 21, 1789). Thick colourless oil, sl. sol. water, v. sol. alcohol and ether, insol. NaOHAq. Less basic than the (β)-isomeride. Reduces Ag from hot solutions, but does not reduce Fehling's solution. Readily diazotised. Aqueous $NaNO_2$ (1 mol.) acting on its hydrochloride (1 mol.) at 0° forms $C_{10}H_{11}.N_2.C_{10}H_{10}NH_2$ (Bamberger a. Lengfeld, *B.* 23, 1134). Yields dyes with diazo-compounds. $KMnO_4$ oxidises it to adipic acid.

Salts.—B'HCl: dimetric plates, v. sol. water and alcohol.—$B'HClHgCl_2$: flat white plates, sl. sol. cold, v. sol. hot water.—$B'_2H_2SO_4$ ½aq.— Picrate: yellow needles.

Acetyl derivative $C_{10}H_{11}NHAc$. [158°]. Needles, v. sol. ether, chloroform, and alcohol.

(α)-Naphthylamine *ac*-tetrahydride $C_6H_4\langle{}^{CH(NH_2).CH_2}_{CH_2 \text{——} CH_2}$ (246·5°) at 714 mm. Formed by adding a 10 p.c. solution of $CuSO_4$ slowly at 100° to a solution of amido-naphthyl-hydrazine tetrahydride derived from (1,4')-naphthylene diamine (Bamberger a. Bammann, *B.* 22, 963). Liquid, sol. cold water, v. sol. hot water, alcohol, and ether. Unlike its 'aromatic' isomeride it turns red litmus blue. It cannot be diazotised. Does not yield dyes with diazo-compounds. $FeCl_3$ has no effect in the cold, but on warming produces a reddish-brown colour. $K_2Cr_2O_7$ and H_2SO_4 give no colour. $KMnO_4$ oxidises it, in cold dilute solution, to *o*-carboxy-β-phenyl-propionic acid [166°]. — B'HCl: needles, v. e. sol. water.—$B'_2H_2PtCl_6$ 2aq. [190°]. Orange prisms, sol. water.—$B'HNO_3$. [139°]. Needles, v. e. sol. water.—$B'H_2CO_3$: needles.—Picrate: needles, sol. hot water.

Acetyl derivative $C_{10}H_{11}.NHAc$. [149°]. Prisms or needles, sl. sol. cold water.

(β)-Naphthylamine $C_{10}H_9N$ *i.e.* $C_6H_4<{CH:C.NH_2 \atop CH:CH}$. [112°]. (294°) (Liebermann a. Jacobson, *A.* 211, 41).

Formation.—1. From the acetyl derivative of (α)-naphthylamine by successive bromination, nitration, elimination of Ac, removal of NH_2 by the diazo- reaction, and reduction of the resulting bromo-nitro-naphthalene by tin and HClAq (Liebermann a. Scheiding, *A.* 183, 258).—2. By heating (β)-naphthol with ammonia-zinc-chloride at 200°, di-(β)-naphthylamine being also formed (Merz a. Weith, *B.* 13, 1300).—3. By passing dry ammonia over strongly heated (β)-naphthol (Graebe, *B.* 13, 1850).—4. By heating (β)-naphthol with four times its weight of ammoniacal $CaCl_2$ (prepared by passing NH_3 over ordinary granulated $CaCl_2$ containing about 18 p.c. of H_2O) for 8 hours at 270°–280°; the yield being 80 p.c. on the naphthol, together with 12 p.c. of ($\beta\beta$)-dinaphthylamine (Benz, *B.* 16, 8).—5. In small quantity, together with a large quantity of dinaphthylamine, by heating (β)-naphthol with ammoniacal $ZnCl_2$ (*B.*).

Preparation.—1. By passing NH_3 under pressure into (β)-naphthol at 150°–160°.—2. By heating (β)-naphthol (10 pts.) with NaOH (4 pts.) and NH_4Cl (4 pts.) (*G. P.* 14,612 [1880]).

Properties.—White plates (from water) without odour. Volatile with steam. Gives no colouration with $FeCl_3$, chromic acid, or bleaching powder. Its alcoholic solution is not coloured by nitrous acid and HCl.

Reactions.—1. Heated with PbO it gives azo-naphthalene (Volodkevitch, *Bl.* [2] 45, 178).—2. $SiCl_4$ forms $SiCl_2(NHC_{10}H_7)_2$ (Horden, *C. J.* 51, 40). A benzene solution of $SiCl_4$ forms $Si(NH.C_{10}H_7)_4$ (Reynolds, *C. J.* 55, 481).—3. With *paraldehyde*, *acetone*, and HCl it gives dimethyl-(β)-naphthoquinoline (Reed, *J. pr.* [2] 35, 298).—4. With *methylal*, *acetone*, and HCl it forms methyl-(β)-naphthoquinoline, (β)-naphthoacridine and a base, $C_{24}H_{20}N_2$, which is probably methyl-amido-naphthyl-naphthoquinoline dihydride $C_{10}H_6<{CMe:CH \atop NH.CH.C_{10}H_6NH_2}$. This base [203° uncor.] forms the following derivatives: $B''C_6H_2(NO_2)_3OH$. — $B''Et_2I_2$. — $C_{24}H_{20}N_4O_3$ [c. 238°]. (R.).—5. *Cyanuric chloride* forms $C_3N_3Cl_2(NHC_{10}H_7)$ [154°], $C_3N_3Cl(NHC_{10}H_7)_2$ [278°], and $C_3N_3(NHC_{10}H_7)_3$ [209°] (Fries, *B.* 19, 2056).—6. *Benzoic aldehyde* in hot alcoholic solution forms $C_6H_5CH:NC_{10}H_7$ [103°] which may be reduced by sodium amalgam to $C_6H_5CH_2.NHC_{10}H_7$ [68°] which forms a nitrosamine $C_6H_5CH_2.N(NO)C_{10}H_7$ [112°] (Claisen, *A.* 237, 272; Kohler, *A.* 241, 360).—7. *Benzil* at 215° forms $C_6H_5.CH(OH).C(NC_{10}H_7).C_6H_5$ crystallising from alcohol in yellow prisms [130°] (Voigt, *J. pr.* [2] 34, 22).—8. The compound of *glyoxal* with $KHSO_3$ yields $C_{12}H_8NSO_3K$ crystallising in white plates (Hinsberg, *B.* 21, 110).—9. *Malic acid* reacts on heating, forming the compounds $C_2H_4O(CO.NHC_{10}H_7)_2$ [263°] and $C_{10}H_7N<{CO.CH.OH \atop CO.CH_2}$ [193°] (Bischoff, *B.* 23, 2046).—10. *Pyruvic acid* and *benzoic aldehyde* form ${N.C_{10}H_6 \atop CPh.CH}>C.CO_2H$ (Doebner, *A.* 249, 109). 11. *Quinone chlorimide* acts on an alcoholic solution forming a eurhodine of the formula $C_{10}H_6<{N \atop N}>C_6H_3NH_2$ (Nietzki a. Otto, *B.* 21, 1598).—12. *Chloro-acetic acid* forms $C_{10}H_7NH.CH_2.CO.NHC_{10}H_7$ [170°] (Cosiner, *B.* 14, 60).

Salts.—B'HCl: colourless plates, v. e. sol. water and alcohol, sl. sol. HClAq.—$B'_2H_2PtCl_6$: yellow plates, sol. water.—$B'_2H_2SO_4$: plates, m. sol. cold water.—$B'HNO_3$: colourless plates, sl. sol. cold water.—Picrate. [195°]. Long yellow needles, v. sol. alcohol.—Citrate $B'C_6H_8O_7$. [89°] (Hecht, *B.* 19, 2616).—Citraconate. [173°]. Yellow needles (from acetone) (Morawski a. Gläser, *M.* 9, 285).

Compounds with metallic salts. B'_2CuSO_4 (Lachovitch, *M.* 9, 516). Forms also a compound with mercuric chloride.

Formyl derivative $C_{10}H_7.NH.CHO$. [120°] (C.; Tobias, *B.* 15, 2447). [129°] (L. a. J.). Formed by heating (β)-naphthylamine with formic ether and alcohol (Cosiner, *B.* 14, 58), or with formic acid (Liebermann a. Jacobson, *A.* 211, 42). Small plates, sl. sol. hot water.

Acetyl derivative $C_{10}H_7.NHAc$. [132°]. Long needles or plates, sol. hot water (Merz a. Weith, *B.* 13, 1300; 14, 2343). On heating with sulphur it yields $C_{10}H_6<{N \atop S}>C.C<{N \atop S}>C_{10}H_6$, crystallising in yellow plates, insol. most solvents, sol. nitrobenzene (Hofmann, *B.* 20, 1804). Bromine in HOAc forms $C_{10}H_6Br.NHAc$ [140°] (Lellmann a. Schmidt, *B.* 20, 3154).

Thio-acetyl derivative $C_{12}H_{11}NS$ *i.e.* $C_{10}H_7.NH.CSCH_3$. [146°]. Formed by heating the acetyl derivative with P_2S_5 (Jacobson, *B.* 21, 2627). Needles or plates (from alcohol). Oxidised by K_3FeCy_6 to ethenyl-amido-naphthyl-mercaptan $C_{10}H_6<{N \atop S}>CMe$ [81°].

Valeryl derivative $C_{10}H_7.NH.COC_4H_9$. [138·5°] (Bamberger a. Müller, *B.* 21, 1112).

Benzoyl derivative $C_{10}H_7NHBz$. [143°] (Cosiner, *B.* 14, 58); [157°] (Hofmann, *B.* 20, 1803). Minute needles, sol. ether, benzene, and hot alcohol. PCl_5 converts it into the compound $C_{10}H_7N:CClC_6H_5$ [68°] (Just, *B.* 19, 983).

(β)-Naphthylamine *ar*-tetrahydride $C_{10}H_{13}N$ *i.e.* ${CH_2.CH_2.C.CH:CNH_2 \atop CH_2.CH_2.C.CH:CH}$. [38°]. (276°) at 713mm. Formed to the extent of 3 or 4 p.c. in the preparation of the alicyclic isomeride by reduction of (β)-naphthylamine (Bamberger a. Kitschelt, *B.* 23, 882). Neutral in reaction. Its salts are acid in reaction. May be diazotised. Yields adipic acid on oxidation.

(β)-Naphthylamine *ac*-tetrahydride $C_6H_4<{CH_2.CHNH_2 \atop CH_2.CH_2}$. (162°) at 36 mm.; (249·5 cor.) at 710 mm. S.G. $\frac{18}{}$ 1·031. Formed by reducing (β)-naphthylamine with sodium and isoamyl alcohol (Bamberger a. Müller, 20, 2916; *B.* 21, 850, 1115; Bamberger a. Kitschelt, *B.* 23, 877). Purified by dissolving in ligroïn and ppg. by CO_2. The carbonate is then dissolved in acetic acid, which leaves a brown oil. Colourless liquid, smelling like piperidine; sl. sol. cold, m. sol. hot water, v. sol. alcohol and ether. Powerful base with alkaline reaction, displacing ammonia from its salts. Absorbs CO_2 from the air. Possesses no reducing power. Carbon disulphide at 0° forms tetrahydronaphthyl-ammo-

nium tetrahydronaphthyl thio-carbamate $C_{10}H_{11}NH_3.S.CS.NHC_{10}H_{11}$ [142°]. Phenyl cyanate forms $PhNH.CO.NHC_{10}H_{11}$ [166·5°]. Does not yield colouring matters with diazo- compounds. Powerful midriatic poison. $KMnO_4$ oxidises it to *o*-carboxy-phenyl-propionic acid and phthalic acid. Benzoic aldehyde forms $C_6H_5.CH{:}NC_{10}H_{11}$ [52°]. HBrAq at 150° forms naphthalene.

Salts.—$B'_2H_2CO_3$ and $B'H_2CO_3$ are white crystalline pps., giving off CO_2 in the air.—B'HCl. [237°]. Plates, v. e. sol. water and alcohol.—$B'_2H_2PtCl_6$.—$B'HAuCl_4$.—$B'HClHgCl_2$ (?) [241°]. Prisms, sol. hot water.—$B'_2H_2SO_4$.—$B'_2H_2Cr_2O_7$.—$B'HNO_3$. [212°]. White satiny tables, sl. sol. cold water, v. sol. conc. HNO_3. At 220° it dissociates with explosive violence.—$B'HNO_2$. [c. 160°]. Needles (from water), v. e. sol. water, insol. ether. Not decomposed by boiling water.—B'HOAc. [156°]. Thick monoclinic crystals, v. sol. alcohol, sl. sol. ether.

Acetyl derivative $C_{10}H_{11}NHAc$. [107°]. Prisms, v. e. sol. chloroform and benzene, v. sol. hot water, m. sol. ether, insol. petroleum-ether. Not attacked by bromine in the cold.

Benzoyl derivative $C_{10}H_{11}NHBz$. [151°]. Needles, v. sl. sol. water, v. sol. benzene.

Di-(α)-naphthylamine $C_{20}H_{15}N$ *i.e.* $(C_{10}H_7)_2NH$. [111° uncor.]. (L.); [113°]. (G. a. V.). (313°) at 15 mm.

Formation.—1. By heating (α)-naphthylamine hydrochloride with (α)-naphthylamine (Girard a. Vogt, *Bl.* [2] 19, 68).—2. A product in the preparation of methyl-(α)-naphthylamine from (α)-naphthylamine and MeCl (Landshoff, *B.* 11, 638).—3. By heating (α)-naphthol with four times its weight of ammoniacal $ZnCl_2$ to 260°; the yield being about 60 p.c. (Benz, *B.* 16, 15).—4. By heating a mixture of (α)-naphthylamine, (α)-naphthol, and $CaCl_2$ to 260°; the yield being 22 p.c. (B.).—5. In small quantities by heating (α)-naphthylamine with $CaCl_2$ or $ZnCl_2$.

Properties.—Dimetric leaflets (from alcohol), m. sol. alcohol, v. e. sol. ether. $FeCl_3$ gives a green pp. in its alcoholic solution.

Picric acid compound $NH(C_{10}H_7)_2 2C_6H_2(NO_2)_3OH$. [169°]. Small glistening black needles.

Acetyl derivative $NAc(C_{10}H_7)_2$. [217°].

Nitrosamine $(C_{10}H_7)_2N.NO$. [262°]. Formed by adding rather more than the theoretical quantity of powdered $NaNO_2$ to a solution of dinaphthylamine in HOAc (L.; Wacker, *A.* 243, 300). Yellow crystalline powder, v. sl. sol. alcohol and HOAc. On adding alcoholic HCl to its ethereal solution it is changed to the isomeric nitroso-dinaphthyl-amine $C_{10}H_6(NO).NH.C_{10}H_7$ or $C_{10}H_6{<}\genfrac{}{}{0pt}{}{NH(C_{10}H_7)}{N\rule{3em}{0.4pt}}{>}O$ [169°] (Fischer a. Hepp, *B.* 20, 1248).

(αβ)-Di-naphthyl-amine $NH{<}\genfrac{}{}{0pt}{}{C_{10}H_{7\alpha}}{C_{10}H_{7\beta}}$ [111°]. Formed by heating a mixture of (β)-naphthol and (α)-naphthylamine with $CaCl_2$ or $ZnCl_2$.

Preparation.—A mixture of (β)-naphthol (100 pts.), (α)-naphthylamine (100 pts.), and $CaCl_2$ (200 pts.), is heated for 8 hours to 280°; the yield is 70 pts. (Benz, *B.* 16, 17). Long colourless prisms. Soluble in benzene, alcohol, and ether, sparingly soluble in petroleum-ether.

Picric acid compound $NH(C_{10}H_7)_2 2(C_6H_2(NO_2)_3OH)$: [173°], small dark-brown needles.

Acetyl derivative $NAc(C_{10}H_7)_2$. [125°].

Di-(β)-naphthyl-amine $NH(C_{10}H_7)_2$. [171°]. (471°) (Ris, *B.* 20, 2619).

Formation.—1. Together with (β)-naphthylamine by heating (β)-naphthol with ammonia-zinc-chloride at 200° (Merz a. Weith, *B.* 13, 1300).—2. In small quantity by heating (β)-naphthol with ammoniacal $CaCl_2$.—3. By heating (β)-naphthylamine with $CaCl_2$ or $ZnCl_2$.

Preparation.—1. By heating a mixture of (β)-naphthylamine (100 pts.), (β)-naphthol (100 pts.), and damp $CaCl_2$ (200 pts.) for 8 hours at 275°; the yield being good (130 pts.) (Benz, *B.* 16, 9).—2. By passing HCl into fused (β)-naphthylamine at 180°; the yield being quantitative (Klopsch, *B.* 18, 1585).

Properties.—White silvery leaflets, sol. benzene and HOAc, sl. sol. hot alcohol. Its solutions exhibit blue fluorescence.

Reactions.—1. Conc. HClAq at 150° has no action, but at 200° it forms (β)-naphthol and (β)-naphthylamine (Ris, *B.* 19, 2016).—2. Ammoniacal $ZnCl_2$ and NH_4Cl at 370° forms (β)-naphthylamine: $(C_{10}H_7)_2NH + NH_3 = 2C_{10}H_7NH_2$.—3. *Bromine* in HOAc forms a tetra-bromo- derivative $C_{20}H_{11}Br_4N$ [246°]. Bromine and $AlBr_3$ form $C_{20}H_7Br_8N$ [over 300°] (Ris, *B.* 20, 2621).—4. S_2Cl_2, acting on its benzene solution at 35°, forms two isomeric imido-di-naphthyl disulphides $NH{<}\genfrac{}{}{0pt}{}{C_{10}H_6}{C_{10}H_6}{>}S_2$, one crystallising from benzene in plates [205°], and the other in needles [220°] (Kym, *B.* 21, 2807).—5. *Phosgene* acts in the cold, forming $(C_{10}H_7)_2N.COCl$ [173°] (Kühn a. Landau, *B.* 23, 811; *cf.* Kym, *B.* 23, 427). This chloro-formyl derivative is v. sl. sol. cold alcohol, v. sol. benzene, and reconverted into di-(β)-naphthylamine by alcoholic potash.

Salts.—B'HCl; white crystalline pp.—$B'2C_6H_2(NO_2)_3OH$. [165°]. Brown needles.

Acetyl derivative $(C_{10}H_7)_2NAc$. [115°]. Small colourless needles.

Benzoyl derivative $(C_{10}H_7)_2NBz$. [157°]. Large needles (Klopsch, *B.* 18, 1585).

Nitrosamine $(C_{10}H_7)_2N.NO$. [140°]. Needles, m. sol. alcohol and ether, v. sol. benzene (Ris, *B.* 20, 2622).

References.—Bromo-, Bromo-nitro-, Chloro-, Iodo-, Iodo-nitro-, and Nitro-naphthylamine.

(α)-NAPHTHYLAMINE (α)-SULPHONIC ACID $C_{10}H_9NSO_3$ *i.e.* $C_{10}H_6(NH_2)(SO_3H)$ [1:4]. *Naphthionic acid.* S. ·022 at 15°.

Formation.—1. By boiling nitro-naphthalene (1 pt.) with alcohol (5 pts.) and aqueous ammonium sulphite (5 pts. of S.G. 1·24), and maintaining an alkaline reaction by frequent addition of ammonium carbonate (Piria, *A. Ch.* [3] 31, 217; *A.* 78, 31).—2. By heating the acid sulphate of (α)-naphthylamine (Nevile a. Winther, *C. J.* 37, 632; Witt, *B.* 19, 55).—3. By heating (α)-naphthylamine (1 pt. with H_2SO_4 (4 pts.) at 120° for an hour (Schaal a. Schmidt, *B.* 7, 1368; Erdmann, *A.* 247, 313).—4. By heating (α)-naphthylamine with $KHSO_4$ at 230° (Bischoff, *B.* 23, 1913).—5. By reducing the corresponding nitro-naphthalene sulphonic acid by ammonium sulphide (Cleve, *B.* 23, 961).

Properties.—Small needles (containing ½aq)

(from hot water); blackened by heat without melting. V. sl. sol. alcohol, almost insol. water. Not affected by boiling aqueous acids or alkalis. Dilute solutions of its salts exhibit violet fluorescence. The azo- colouring matters (*e.g.* Congo red), formed by its combination with diazo- compounds give on reduction *o*-naphthylene-di-amine-sulphonic acid, proving that they are *ortho*-azo- compounds, and hence that the HSO_3 group occupies the *para*- position to the NH_2 (Witt, *B.* 19, 1719).

Reactions.—1. Split up by *water* at 160° into naphthylamine and H_2SO_4 (N. a. W.).—2. *Chromic acid mixture* forms a brown resinous product.—3. *Benzoic aldehyde*, acting on its sodium salt forms $C_6H_5.CH:N.C_{10}H_6.SO_3Na$, crystallising in yellow plates, v. sl. sol. cold water (Erdmann, *A.* 247, 325).—4. *Succinic acid* heated with its K salt at 170° forms $C_2H_4:C_2O_2:N.C_{10}H_6.SO_3K$, crystallising from water or dilute alcohol in small needles (containing 2aq) (Pellizari, *A.* 248, 157).—5. *Phthalic anhydride* heated with the K salt at 160° forms $C_6H_4:C_2O_2:NC_{10}H_6SO_3K$, crystallising from hot water in small needles (containing 3aq) (P.).—6. On displacing NH_2 by Cl, and distilling the resulting chloro-naphthalene sulphonic acid with PCl_5, there is formed (1,4)-di-chloro-naphthalene.

S a l t s.—KA′: small micaceous laminæ, v. sol. water and alcohol, sl. sol. KOHAq.—NaA′4aq: monoclinic prisms.—BaA'_2 8aq.—CaA'_2 8aq; monoclinic crystals, v. sol. water, almost insol. alcohol.—MgA'_2 8aq: monoclinic prisms.—MgA'_2 10aq.—PbA'_2 2aq; needles, sl. sol. water.—ZnA'_2 *x*aq.—CuA'_2.—AgA′aq: crystalline grains.—$AgA'N_2H_6$ 2aq.

Amide $C_{10}H_6(NH_2).SO_2NH_2$. [206°]. Formed by reducing the amide of (1,4)-nitro-naphthalene sulphonic acid with HI in HOAc and P (Cleve, *B.* 23, 961). Needles (from alcohol).—B′HCl: colourless needles, v. sl. sol. water.

Acetyl derivative of the amide $C_6H_4(NHAc).SO_2NH_2$. [241°]. Small needles.

(α)-Naphthylamine (α′)-sulphonic acid $C_{10}H_6(NH_2)(SO_3H)$ [1:4′]. S. ·1064 at 15°.

Formation.—1. By reducing (α)-nitro-naphthalene sulphonic acid by ammonium sulphide (Laurent; Cleve, *Bl.* [2] 24, 511).—2. Together with naphthionic acid by adding (α)-naphthylamine hydrochloride (1 pt.) at 0° to (2 pts. of) fuming H_2SO_4 (containing 25 p.c. additional SO_3) (Witt, *B.* 19, 578; Mauzelius, *B.* 20, 3401). 3. Together with a small quantity of the (1,4) acid from the acetyl derivative of (α)-naphthylamine and fuming H_2SO_4 (Erdmann, *A.* 247, 315; G. Schultz, *B.* 20, 3161; *cf.* Lange, *B.* 20, 2940).

Properties.—Needles. Solutions of its salts exhibit green fluorescence, and reduce $AgNO_3$ on warming. Auric chloride, $FeCl_3$, and $CuSO_4$ colour its solution red, and suffer reduction. By boiling its diazo- compound with HCl a chloro-naphthalene sulphonic acid is obtained, the K salt of which on distillation with PCl_5 yields (γ)-di-chloro-naphthalene [107°] (M.). Benzoic aldehyde, acting on its sodium salt, forms $C_6H_5CH:N.C_{10}H_6.SO_3Na$, crystallising in pearly plates, decomposed by boiling water (Erdmann, *A.* 247, 326).

S a l t s.—KA′aq: needles or prisms, v. e. sol. water.—NaA′aq: plates (C.) or needles (M.).—NaA′5aq: plates (W.).—BaA'_2 8aq (W.).—BaA'_2 6aq (C.; M.).—CaA'_2 6aq (W.): pearly plates, v. e. sol. water.—CaA'_2 9aq (C.; M.): tables, v. sol. hot water.—MgA'_2 8aq: plates, v. sol. water.—PbA'_2 4aq: nodules.—ZnA'_2 9aq: needles, m. sol. cold water.—AgA′.

Amide. [260°]. Tables. Yields an acetyl derivative [232°] and a diacetyl derivative [200°] (Ekborn, *B.* 23, 1119).—B′HCl.—$B'H_2SO_4$.

(α)-Naphthylamine *peri*-sulphonic acid $C_{10}H_6(NH_2)(SO_3H)$ [1:1′]. *Naphthylamine sulphonic acid* S. S. ·42 at 100°; ·0207 at 21°. Formed, together with the (1,4′) acid from naphthalene (α)-sulphonic acid by nitration and reduction (Mensching, *Schöllkopf's Aniline Co., G. P.* 40,571; G. Schultz, *B.* 20, 3162). Formed also, together with the (1,4′) acid, from (α)-nitro-naphthalene by sulphonation and reduction (Cleve, *B.* 20, 1535). White needles (from water) or tufts of needles (from HOAc). Its sodium salt is less soluble than that of the preceding isomeride. $FeCl_3$ colours its cold aqueous solution violet. The diazo- compound treated with PCl_5 gives $C_{10}H_5ClSO_3$, crystallising in yellow needles [175°].—NaA′. S. 2·67 at 100°; 1·13 at 24°.—KA′. Plates. S. 14·9 at 100°; 3·56 at 19° (Erdmann, *A.* 247, 306).

Anhydride $C_{10}H_6{<}{\substack{SO_2\\NH}}{>}$. [167°]. Small crystals, v. sl. sol. water (Cleve).

(α)-Naphthylamine (δ)-sulphonic acid $C_{10}H_6(NH_2)(SO_3H)$ [1:2′ or 3′]. S. ·2 at 15°; ·7 at 100°. Obtained by heating (α)-naphthylamine (1 pt.) with conc. H_2SO_4 (5 pts.) at 125°–130° for 8 hours until the naphthionic acid at first formed has disappeared (Hirsch, *B.* 21, 2370). Plates, sl. sol. water and alcohol, insol. ether and benzene. The K salt is crystalline, and sl. sol. cold water. Gives, on treatment with HNO_2 and HNO_3, di-nitro-naphthol sulphonic acid isomeric with naphthol yellow S.

(α)-Naphthylamine 'β'-sulphonic acid $C_{10}H_6(NH_2)(SO_3H)$ [1:3′]. Formed, together with its (γ) and (θ) isomerides, from naphthalene (β)-sulphonic acid by successive nitration and reduction (Cleve, *Bl.* [2] 26, 447; *B.* 20, 1535). Slender needles (containing 2aq) or anhydrous tables; sl. sol. cold, v. sol. hot, water.—NaA′4aq: thin tables.—KA′aq: needles.—MgA'_2 10aq: rhombohedra.—BaA'_2 aq: flat needles, m. sol. water.—CaA'_2 7aq: rhombohedra.

Anhydride $C_{10}H_6{<}{\substack{NH\\SO_2}}{>}$. [180°]. Formed by treating the chloride of 'β' nitro-naphthalene (β)-sulphonic acid with HI and HOAc. Yellow needles, v. sl. sol. HOAc.

(α)-Naphthylamine (γ)-sulphonic acid $C_{10}H_6(NH_2)(SO_3H)$ [1:3]. Formed, with isomerides, from naphthalene (β)-sulphonic acid by nitration and reduction (Cleve, *B.* 19, 2181; 21, 3271). Small needles, sl. sol. water. Gives rise to a di-chloro-naphthalene [61°].

S a l t s.—NaA′: scales, v. sol. water.—BaA'_2 aq: thin plates, v. sol. water.—PbA'_2: prisms.—AgA′aq: minute needles.

Amide $C_{10}H_6(NH_2).SO_2NH_2$ aq. [131°]. Needles.—B′HCl: prisms, sl. sol. cold water. With potassium cyanate it forms $NH_2.CO.NH.C_{10}H_6.SO_2.NH.CO.NH_2$ [273°].

Acetyl derivative of the amide $C_{10}H_6(NHAc).SO_2NH_2$. [221°].

Anhydride $C_{10}H_6<\genfrac{}{}{0pt}{}{NH}{SO_2}>$. [124°]. Formed from (γ)-nitro-naphthalene (β)-sulphonic chloride, HOAc, and HI (Cleve, *B.* 20, 1536). Lemon-yellow needles, v. sl. sol. HOAc and alcohol.

(α)-Naphthylamine (θ)-sulphonic acid $C_{10}H_6(NH_2)(SO_3H)$ [1:2']. Formed, with isomerides, from naphthalene (β)-sulphonic acid by nitration and reduction (Cleve, *Bl.* [2] 29, 415; *B.* 21, 3264). Crystals (containing aq). Gives rise to di-chloro-naphthalene [61°]. Its alcoholic solution yields with nitrous acid a deep violet dye $SO_3H.C_{10}H_6.N_2.C_{10}H_5(NH_2)SO_3H$ $2\frac{1}{2}$aq.

Salts.—NaA' $\frac{1}{2}$aq: thin needles, v. sol. water.—CaA'$_2$ 2aq: powder, v. sol. water, turning red in air.—BaA'$_2$: flat needles.—ZnA'$_2$ 4aq: needles.

Amide $C_{10}H_6(NH_2).SO_2NH_2$. [181°]. Needles. B'HCl aq.—B'HI aq. Yields the urea derivative $NH_2.CO.NH.C_{10}H_6.SO_2.NH.CO.NH_2$ [225°].

Acetyl derivative of the amide $C_{10}H_6(NHAc).SO_2NH_2$. [213°].

Anhydride $C_{10}H_6<\genfrac{}{}{0pt}{}{NH}{SO_2}>$. [173°]. Formed from (θ)-nitro-naphthalene (β)-sulphonic chloride, HOAc, and HI (Cleve, *B.* 20, 1536). Yellow needles, sol. boiling Ac_2O.

(β)-Naphthylamine 'α'-sulphonic acid $C_{10}H_6(NH_2)(SO_3H)$ [2:1']. '*Badische acid.*' S. ·059 (Forsling).

Formation.—1. By heating (β)-naphthylamine (1 pt.) with conc. H_2SO_4 ($3\frac{1}{2}$ pts.) at 100°–105° for 5 or 6 hours there is obtained a mixture of the 'α,' 'β,' (γ), and (δ) sulphonic acids of (β)-naphthylamine in the proportion of about 50 p.c. of the 'α' acid, 40 p.c. of the 'β' acid, 5 p.c. of the (γ)-acid, and 5 p.c. of the (δ)-acid (Green, *C. J.* 55, 35; *cf.* Badische Anilinfabrik, *G.P.* 14,612, 20,760; Dahl, *G.P.* 29,084, 32,271, 32,276). The same mixture heated at 120° gives a greater quantity of the 'β' acid, and less of the 'α' acid. Fuming sulphuric acid (20 p.c. SO_3 extra) at 70°–80° gives 30 p.c. of the 'α' and 70 p.c. of the (γ)-acid. (β)-Naphthylamine sulphate, shaken with conc. H_2SO_4 for three days in the cold, yields a similar mixture (Dahl); but on heating (β)-naphthylamine with conc. H_2SO_4 for an hour at 160° the 'β' and (δ) acid are formed in about equal quantities (Bayer a. Duisberg, *B.* 20, 1426; G. Schultz, *B.* 20, 1358).—2. By heating the (β)-naphthol 'α'-sulphonic acid (of Bayer) with ammonia in a closed vessel (Pfitzinger a. Duisberg, *B.* 22, 396; *cf.* Landshoff, *B.* 16, 1931).

Properties.—Needles or broad tables, v. sl. sol. water, insol. alcohol. Solutions of its salts exhibit blue fluorescence.

Reactions.—1. Yields naphthalene (α)-sulphonic acid when its amido- group is removed by the diazo- reaction (P. a D.; Nietzki a. Zübelen, *B.* 22, 453).—2. Yields by Sandmeyer's method a bromo-naphthalene sulphonic acid which can be converted into di-bromo-naphthalene [75°] (Forsling, *B.* 22, 619).—3. Yields by Skraup's method (β)-naphthaquinoline sulphonic acid, which may be oxidised to $<\genfrac{}{}{0pt}{}{CO\ —}{C_5NH_3}>C_6H_3.SO_3H$, showing that the naphthylamine sulphonic acid is heteronuclear (Immerheiser, *B*, 22, 402, 412; *cf.* Armstrong a. Wynne, *C. J. Proc.* 4, 103; 5, 49).—4. Heating with H_2SO_4 (3 pts.) at 160° for $1\frac{1}{2}$ hours converts it into a mixture of the 'β' and (δ) isomerides (Weinberg, *B.* 20, 3353).—5. Reacts with diazobenzene sulphonic acid, forming a yellow diazo-amido- and not an azo- compound (Witt, *B.* 21, 3483).—6. On conversion into the corresponding chloro-naphthalene sulphonic acid and treatment of this with PCl_5 there is formed di-chloro-naphthalene [61·5°].

Salts (Forsling, *B.* 20, 2099).—NaA': plates, v. sol. water, insol. alcohol.—KA' $\frac{1}{2}$aq: tables, v. sol. water.—^{x}NH$_4$A': large prisms, v. sol. water.—BaA'$_2$ 4aq: columns, v. e. sol. warm water. S. 4·35 in the cold.—CaA'$_2$ 6aq: tables. S. 9·09 in the cold.—MgA'$_2$ $3\frac{1}{2}$aq: nodules, v. e. sol. water. — ZnA'$_2$ 6aq: columns. — PbA'$_2$: needles.—CuA'$_2$: crystalline powder.—AgA'.

(β)-Naphthylamine 'β'-sulphonic acid $C_{10}H_6(NH_2)(SO_3H)$ [2:3']. '*Brönner's acid.*'

Formation.—1. By heating the corresponding (Schäffer's) (β)-naphthol sulphonic acid with ammonia under pressure (Farbfabrik vormals Brönner, *G. P.* 22,547), or by passing a current of ammonia over the potassium (β)-naphthol sulphonate at 200°–250° (Landshoff, *B.* 16, 1931; Green, *B.* 22, 723).—2. Together with the 'α,' (γ), and (δ) isomerides by heating (β)-naphthylamine (1 pt.) with conc. H_2SO_4 (3 pts.) at 105° (Bayer a. Duisberg, *B.* 20, 1426; Green, *C. J.* 55, 35).—3. By heating (β)-naphthylamine with $KHSO_4$ at 230°; the yield being 60 p.c. of the theoretical (Bischoff, *B.* 23, 1914). 4. The chief product obtained by heating (β)-naphthylamine acid sulphate at 200°.

Properties.—Plates or flat needles, sl. sol. warm water (Schultz, *B.* 20, 3158). According to Forsling the laminar crystals contain aq. Its solution exhibits blue fluorescence. Yields, by conversion into diazo-naphthalene sulphonic acid and application of Sandmeyer's reaction, a chloro-naphthalene sulphonic acid whence PCl_5 forms $C_{10}H_6Cl_2$ [136°].

Salts (Forsling, *B.* 20, 76).—NH$_4$A'aq: large thin plates, v. sl. sol. water, forming a solution exhibiting violet fluorescence (Green).—NaA' 2aq: flat needles. S. 2·5 at 15°.—KA' aq: long needles. S. 2·4.—BaA'$_2$ 6aq: needles. S. ·22 at 15°.—CaA'$_2$ 6aq: laminæ. S. ·44 in the cold.—MgA'$_2$ 6aq: laminæ or broad needles.—PbA'$_2$ 2aq: v. sl. sol. water. — ZnA'$_2$ 4aq. — CuA'$_2$ 4aq: sl. sol. water.—AgA' aq: powder.

(β)-Naphthylamine (γ)-sulphonic acid $C_{10}H_6(NH_2)(SO_3H)$ [2:4']. *Dahl's acid.* S. ·077 in the cold (F.). Formed by sulphonating (β)-naphthylamine, and is the chief product when the sulphonation is carried out at 15° to 20° (Dahl, *G. P.* 32,276; Forsling, *B.* 20, 2099; Claus, *J. pr.* [2] 39, 315). Small plates or needles, insol. alcohol. Its solutions show blue fluorescence. May be converted into di-chloro-naphthalene [48°]. Conc. H_2SO_4 (3 pts.) at 160° converts it into a mixture of the 'β' and (δ) isomerides (Weinberg, *B.* 20, 3353).

Salts.—^{x}NH$_4$A': exceedingly soluble tables. KA' aq: rhombohedra, v. e. sol. water.—NaA' 5aq: tables, v. e. sol. water.—BaA'$_2$ $2\frac{1}{2}$aq: nodules, v. e. sol. water.—CaA'$_2$ 11aq: needles. S. 9·09 in the cold.—AgA'$_2$ 8aq: crystalline.

(β)-Naphthylamine (δ)-sulphonic acid $C_{10}H_6(NH_2)(SO_3H)$ [2:2']. (β)-*Naphthylamine sulphonic acid F. Bayer's acid.* S. ·2857.

Formation.—1. Together with the 'β' isomeride, by heating (β)-naphthylamine with H_2SO_4 at 160°–170° (Bayer a. Duisberg, *B.* 20, 1426, 3158; Schultz, *B.* 20, 1358, 3161). It is also formed when the sulphonation is conducted at temperatures between 105° and 160°, the quantity increasing with the temperature (Green, *C. J.* 55, 36).—2. By heating the corresponding (β)-naphthol sulphonic acid with ammonia at 200° (Weinberg, *B.* 20, 2908; Erdmann, *B.* 21, 637), or by heating naphthalene 'α' disulphonic acid with NaOH at 250°, and afterwards with NH_4Cl (Weinberg, *B.* 20, 2906, 3353).—3. By heating the 'α' or (γ)-isomeride with H_2SO_4 at 160° (B. a. D.).

Properties.—Long silky needles (containing aq), m. sol. hot water nearly insol. cold water. On boiling with water the needles change to an almost insoluble crystalline powder. With tetrazo-diphenyl it gives a yellowish-red colouring matter (δ-purpurin). Yields by the diazo- reaction the (β)-naphthol sulphonic acid of Weinberg, which by fusion with NaOH is converted into dioxynaphthalene [129°]. Gives rise to (δ)-di-chloro-naphthalene [114°].

Salts.—KA′: needles, v. sol. water.—NaA′4aq: white needles (from water) or plates (from hot 90 p.c. alcohol), v. e. sol. hot water, S. 1·4 in cold water, v. sol. hot spirit (90 p.c.) (difference from 'α' isomeride).—×NH_4A': small plates, m. sol. water.—BaA'_2 $4\frac{1}{2}$aq: plates, sl. sol. cold water (difference from (γ)-isomeride).—MgA'_2 aq: white needles (B. a. D.).—MgA'_2 5aq (W.).—CaA'_2 6aq: plates, with blue fluorescence. S. ·38 at 15°.

(α)-Naphthylamine ν-sulphonic acid $C_{10}H_7.NHSO_3H$. *Thionaphthamic acid.* Formed, together with the (1,4) acid, by the action of ammonium sulphite on (α)-nitro-naphthalene (Piria, *A.* 78, 54). The free acid, liberated from its salts, splits up at once into naphthylamine and H_2SO_4.—KA′: pearly plates, v. sol. water, sl. sol. KOHAq.—×NH_4A': plates, sol. water and alcohol.—$BaA'_2$3aq: plates.—PbA′(OAc).

(α)-Naphthylamine 'α' disulphonic acid $C_{10}H_9NS_2O_6$ *i.e.* $C_{10}H_5(NH_2)(SO_3H)_2$ [1:3:3′]. Formed by reducing (α)-nitro-naphthalene 'α'-disulphonic acid by ammonium sulphide (Alén, *Bn.* 2, 407). Crystals, v. e. sol. water and alcohol, insol. ether and benzene. Yields (α)-naphthylamine on treatment with sodium-amalgam. — NH_4HA'' 2aq (?): slender needles. — KHA′ 3aq: needles, m. sol. hot water.—CaA″ 5aq.—BaA″ 4aq: tables, m. sol. water.—PbA″ 4aq (?).

(α)-Naphthylamine 'β' disulphonic acid $C_{10}H_5(NH_2)(SO_3H)_2$ [1:3:2′]. Obtained by reducing (α)-nitro-naphthalene 'β' disulphonic acid (Alén). Small needles (from water), v. sol. water, sl. sol. alcohol. Yields (α)-naphthylamine on treatment with sodium-amalgam.—NH_4HA'': needles, m. sol. hot water.—KHA″: needles.—CaA″ 2aq.—BaA″ aq: minute needles, sl. sol. water.—PbA″.

(α)-Naphthylamine (δ)-disulphonic acid $C_{10}H_5(NH_2)(SO_3H)_2$ [1:1′:4]. *Naphthylamine disulphonic acid S.* (Schöllkopf's *G. P.* 40,571). Formed by sulphonating (1, 1′)-naphthylamine sulphonic acid. — Na_2A''2aq: long needles (Bernthsen, *B.* 23, 3090).

(α)-Naphthylamine (ϵ)-disulphonic acid $C_{10}H_5(NH_2)(SO_3H)_2$ [1:3:1′]. Formed by heating naphthalene with conc. H_2SO_4 at 90° and fuming H_2SO_4 at 100°–120°, then nitrating, and reducing the product (*G. P.* 45,776, 46,953; Bernthsen, *B.* 22, 3328). Formed also from naphthalene ($\alpha\beta$)-disulphonic acid (corresponding to $C_{10}H_6Cl_2$ [48°]) by nitration and reduction (Ewer a. Pick, *Monit. scient.* 1889, 604; *cf.* Armstrong a. Wynne, *C. N.* 54, 255). Colourless scales (containing 3aq), v. e. sol. warm water.—NaHA″ 2aq: needles or thin prisms, sl. sol. cold water.—Na_2A'' 6aq: needles or prisms, v. e. sol. water.—BaA″ 3aq.—BaA″ 4aq: flat needles, v. sol. hot, m. sol. cold, water.—$Ba(HA'')_2$ 5aq: minute needles, sl. sol. cold water.

(α)-Naphthylamine disulphonic acid $C_{10}H_5(NH_2)(SO_3H)_2$ [1:4:2′]. S. ·7 at 20°; 5 at 100°. Formed, together with two isomeric acids, by sulphonating (α)-naphthylamine (1 pt.) with H_2SO_4 (containing 25 p.c. SO_3 extra) (5 pts.) at 120°. The acids are separated by treatment of the lime salts with dilute alcohol, which dissolves the salts of the two isomeric acids (Dahl & Co., *G. P.* 41,957; Armstrong a. Wynne, *C. J. Proc.* 6, 125). Formed, together with a smaller quantity of the following acid, by treating (α)-naphthylamine 'α'-sulphonic acid (1 pt.) with H_2SO_4 containing SO_3 ($1\frac{1}{2}$ pts.) at 30°. Groups of needles, insol. 85 p.c. alcohol. Its solutions and those of its salts exhibit blue fluorescence.

Salts.—K_2A'' 3aq.—Na_2A'' 3aq: v. sol. water. CaA'_2 aq: v. sl. sol. water.

(α)-Naphthylamine disulphonic acid $C_{10}H_5(NH_2)(SO_3H)_2$ [1:4:3′]. S. 17 at 20°. Formed in the preparation of the preceding, from which it may be separated by extracting the mixed calcium salts with dilute alcohol. Alcohol of 90 p.c. extracts the salt of a third isomeride, subsequent treatment with alcohol of 85 p.c. extracts the present acid. Needles, insol. alcohol, v. sol. boiling alcohol of 85 p.c. The calcium salt is v. sol. water, insol. alcohol of 90 p.c. The K and Na salts are v. sol. water. Solutions of the acid and its salts exhibit blue fluorescence.

(β)-Naphthylamine 'α' disulphonic acid $C_{10}H_5(NH_2)(SO_3H)_2$ [2:3:3′]. (β)-*Naphthylamine R-disulphonic acid.* Formed by heating the corresponding (β)-naphthol R-disulphonic acid with ammonia. Readily yields dyes with diazo- salts.

(β)-Naphthylamine (γ)-disulphonic acid $C_{10}H_5(NH_2)(SO_3H)_2$ [2:1′:3′]. (β)-*Naphthylamine G-disulphonic acid.* Formed by heating the corresponding (β)-naphthol G-disulphonic acid with ammonia. Formed also by heating (β)-naphthylamine sulphate (10 kilos.) with H_2SO_4 (30 kilos. containing 25 p.c. SO_3 extra) at 110°–140° (Gans a. Co., *G. P.* 35,019). V. sol. water, m. sol. alcohol. Does not react with diazo- compounds (G. Schultz, *B.* 21, 3487). The salts are v. sol. water.

(β)-Naphthylamine disulphonic acid $C_{10}H_5(NH_2)(SO_3H)_2$ [2:1:3′]. Formed, together with the (2, 1′, 3′) acid, from (2, 3′)-naphthylamine sulphonic acid and H_2SO_4 (with 20 p.c. SO_3) at 20° (Armstrong a. Wynne, *C. J. Proc.* 6, 130). Needles. Yields $C_{10}H_5Cl_3$ [92°].

(β)-Naphthylamine disulphonic acid $C_{10}H_5(NH_2)(SO_3H)_2$ [2:3′:x]. Formed by heating (Brönner's) (β)-naphthylamine 'β'-sulphonic acid at 160° to remove water of crystallisation, adding fuming H_2SO_4 (4 pts.) and heating at 110° (Forsling, *B.* 21, 3495). Possibly identical with the preceding acid. White needles, v. e.

sol. water, sl. sol. alcohol. Its dilute aqueous solution fluoresces blue. It gives rise to a tri-chloro-naphthalene [91°].

Salts.—$K_2A''2aq$: large needles, v. sol. water.—KHA'' aq : needles, sl. sol. cold water.—$NaHA''2aq$.—Na_2A'': long needles.—$(NH_4)_2A''aq$: monoclinic crystals.—NH_4HA''.—×CaA'': plates.

(β)-Naphthylamine disulphonic acid $C_{10}H_5(NH_2)(SO_3H)_2$ [2:1:4′]. Formed, together with a greater quantity of the (2, 2′, 4′)-isomeride from (2, 4′)-naphthylamine sulphonic acid and H_2SO_4 (with 20 p.c. SO_3) at 20° (A. a. W.). Yields $C_{10}H_5Cl_3$ [78°].

(β)-Naphthylamine disulphonic acid $C_{10}H_5(NH_2)(SO_3H)_2$ [2:2′:4′]. Formed as above. Yields $C_{10}H_5Cl_3$ [80°].

(β)-Naphthylamine disulphonic acid $C_{10}H_5(NH_2)(SO_3H)_2$ [2:3:2′]. Formed from the corresponding naphthol disulphonic acid.

Di-NAPHTHYL-ANTHRYLENE $C_{22}H_{12}$ *i.e.*
$C_{10}H_6.C$
| ||| (?). [270°]. Formed by distilling di-
$C_{10}H_6.C$
naphthyl-acetylene, or by distilling (β)-di-naphthyl-tri-chloro-ethane (1 pt.) with ZnO (15 pts.) (Grabowski, *B.* 11, 302). Large leaflets (by sublimation).—$C_{22}H_{12}C_6H_2(NO_2)_3OH$: crystals (from chloroform).

NAPHTHYL-ARSENIOUS ACID. Described as *Naphthalene arsonic acid*, vol. i. p. 322.

NAPHTHYL-BENZAMIDINE $C_{17}H_{14}N_2$ *i.e.* $C_6H_5C(NH).NHC_{10}H_7$. [141°] Formed by heating (α)-naphthylamine hydrochloride with benzonitrile at 200° (Bernthsen a. Trompetter, *B.* 11, 1757). Tables (from alcohol); may be sublimed.—B′HCl: white prisms.—$B'_2H_2PtCl_6$: yellow needles.—$B'H_2C_2O_4$: prisms, sl. sol. water.—Chromate: yellow pp.

(α)-NAPHTHYL-BENZYL-AMINE $C_{17}H_{15}N$ *i.e.* $C_{10}H_7.NH.CH_2Ph$. [67°]. Formed from (α)-naphthylamine and benzyl chloride (Froté a. Tommasi, *Bl.* [2] 20, 67).

(β)-Naphthyl-benzyl-amine $C_{10}H_7.NH.CH_2Ph$. [68°]. Formed by reducing $C_{10}H_7.N{:}CHPh$ (Kohler, *A.* 241, 358). Prisms.

Nitrosamine $C_{10}H_7.N(NO).CH_2Ph$. [112°]. Yellow needles, sol. alcohol and ether.

(α)-NAPHTHYL - BENZYLIDENE - AMINE $C_{10}H_7N{:}CHPh$. [73°]. Formed from (α)-naphthylamine and benzoic aldehyde or hydrobenzamide (Lachovitch, *M.* 9, 695; *cf.* Papasogli, *A.* 171, 138). Yellow needles (from alcohol).

(β)-Naphthyl-benzylidene-amine. [101°]. Resembles the preceding in preparation and properties (Claisen, *A.* 237, 261).

NAPHTHYL BENZYL KETONE *v.* BENZYL NAPHTHYL KETONE.

NAPHTHYL BENZYL OXIDE *v.* BENZYL NAPHTHYL OXIDE.

NAPHTHYL BROMO-METHYL KETONE $C_{12}H_9BrO$ *i.e.* $C_{10}H_7.CO.CH_2Br$. Obtained by adding bromine (9·5 g.) to a solution of naphthyl methyl ketone (10 g.) in CS_2 (Pampel a. Schmidt, *B.* 19, 2898). Pungent oil.

(α)-NAPHTHYL-CARBAMATE $C_{11}H_9NO_2$ *i.e.* $C_{10}H_7.O.CO.NH_2$. [158°]. Formed from (α)-naphthol and $ClCO.NH_2$ (Gattermann, *A.* 244, 43). Needles (from alcohol).

(β)-Naphthyl carbamate. [187°]. From (β)-naphthol and $ClCONH_2$ (G.). Long needles, almost insol. water, v. sol. alcohol and ether.

(α)-NAPHTHYL-CARBAMIC ACID. *Ethyl ether* $C_{13}H_{13}NO_2$ *i.e.* $C_{10}H_7NH.CO_2Et$. [79°]. Formed from (α)-naphthylamine and $ClCO_2Et$ (Hofmann, *B.* 3, 657). Needles, insol. water.

Isopropyl ether $C_{10}H_7NH.CO_2Pr$. [78°]. From (α)-naphthylamine and $ClCO_2Pr$ (Spica, *G.* 17, 168). Groups of needles, sl. sol. water.

(β)-Naphthyl-carbamic acid. *Ethyl ether* $C_{10}H_7NH.CO_2Et$. [73°]. Formed from (β)-naphthylamine and $ClCO_2Et$ (Cosiner, *B.* 14, 60). Needles, insol. hot water, v. sol. alcohol.

Isopropyl ether $C_{10}H_7NH.CO_2Pr$. [70°]. Needles, sol. alcohol and ether (S.).

Di-(β)-naphthyl carbamate. *Methyl ether* $(C_{10}H_7)_2N.CO_2Me$. [114°]. Formed from di-(β)-naphthylamine and $ClCO_2Me$ at 155° (Ris, *B.* 20, 2620). Needles (from alcohol and ether), v. sol. cold alcohol and ether.

(α)-NAPHTHYL-CARBAMINE $C_{11}H_7N$ *i.e.* $C_{10}H_7.NC$. Formed from (α)-naphthylamine, chloroform, and alcoholic KOH (Liebermann, *B.* 16, 1640). Solid, v. sol. alcohol.

(β)-Naphthyl-carbamine $C_{10}H_7.NC$. [54°]. Formed from (β)-naphthylamine, chloroform, and alcoholic potash (Liebermann, *B.* 16, 1640). Needles, sol. alcohol, ether, and benzene.

(α)-NAPHTHYL-*semi*-CARBAZIDE $C_{11}H_{11}N_3O$ *i.e.* $C_{10}H_7.NH.NH.CO.NH_2$. [231°]. Formed by heating (α)-naphthylamine hydrochloride with urea at 140° (Pinner, *B.* 21, 1219). Thin plates (from boiling isoamyl alcohol), insol. water and ether, sl. sol. dilute alkalis.

(β)-Naphthyl-*semi*-carbazide. [225°] (P.); [221°] (H.). Formed like its isomeride, and also by mixing equivalent quantities of (β)-naphthylamine hydrochloride and potassium cyanate in aqueous solution (Pinner, *B.* 21, 1223; Hillringhaus, *B.* 22, 2657; Hauff, *A.* 253, 28). Silky plates, sl. sol. hot water, v. sol. hot alcohol. Reduces Fehling's solution. With HClAq at 140° it yields a naphthazine.

DINAPHTHYL-CARBAZOLE, so-called, is described as IMIDO-DINAPHTHYL.

(α)-NAPHTHYL-CARBINOL $C_{11}H_{10}O$ *i.e.* $C_{10}H_7.CH_2OH$. *Naphthobenzyl alcohol.* [60°]. (301° cor.) at 715 mm. Formed by warming (α)-naphthyl-carbinylamine hydrochloride with aqueous $NaNO_2$ (Bamberger a. Lodter, *B.* 21, 258). Long needles, v. e. sol. ether and alcohol, v. sl. sol. cold water. Yields (α)-naphthoic aldehyde on oxidation with chromic acid mixture.

(β)-Naphthyl-carbinol $C_{10}H_7.CH_2OH$. [80·5°]. Resembles the preceding in mode of preparation and properties (Bamberger, *B.* 20, 1118).

Tri-naphthyl-carbinol $C_{31}H_{22}O$ *i.e.* $(C_{10}H_7)_3C.OH$. Formed from naphthalene, $C(NO_2)Cl_3$, and $AlCl_3$, the product being boiled with water (Elbs, *B.* 16, 1275). Crystalline powder (from acetone), melting below 278°; v. sol. benzene, sl. sol. ether, almost insol. alcohol.

(α)-NAPHTHYL-CARBINYLAMINE $C_{11}H_{11}N$ *i.e.* $C_{10}H_7.CH_2NH_2$. *Menaphthylamine. Naphthobenzylamine.* (292°). Formed, together with s-di-naphthyl-ethane, by reducing the amide of thionaphthoic acid in alcoholic solution with zinc and HClAq (Hofmann, *B.* 1, 101; Bamberger a. Lodter, *B.* 21, 256). Caustic liquid, absorbing CO_2 from the air. Reduced in alcoholic solution by Na to the tetrahydride.—B′HCl: long needles, sl. sol. water.—$B'_2H_2PtCl_6$: crystalline pp.—$B'HNO_2$: prisms [148·5°].

Tetrahydride $C_{10}H_{11}CH_2.NH_2$. (270°) at 722 mm. Obtained by reducing the nitrile of (α)-naphthoic acid $C_{10}H_7.CN$ in alcoholic solution by sodium (Bamberger a. Lodter, *B.* 20, 1707).—$B'HCl$: white needles, v. e. sol. hot water.—$B'_2H_2PtCl_6$: yellow needles, sl. sol. cold water.—$B'C_6H_2(NO_2)_3OH$: needles, v. sol. hot water.

(β)-Naphthyl-carbinylamine $C_{10}H_7.CH_2NH_2$. [60°]. Formed from the amide of thio-(β)-naphthoic acid $C_{10}H_7.CS.NH_2$ by treating its alcoholic solution with zinc and HCl at 35° (Bamberger a. Lodter, *B.* 21, 1117). Prisms, sl. sol. cold water, v. sol. alcohol. It is a powerful base, ppg. the hydroxides from solutions of salts of copper, zinc, and lead.

Salts.—$B'HCl$. [260°–270°]. Prisms, v. sol. alcohol and water, insol. ether.—$B'_2H_2PtCl_6$: yellow needles. — $B'C_6H_2(OH)(NO_2)_3$: golden-yellow needles, v. sol. hot water.

Tetrahydride $C_{10}H_{11}.CH_2NH_2$. (270° cor.) at 729 mm. Formed by adding sodium to a hot alcoholic solution of (β)-naphthonitrile (Bamberger a. Boekmann, *B.* 20, 1711). Yields an acetyl derivative [65°] (Bamberger a. Helwig, *B.* 22, 1915). Carbon disulphide reacts forming $C_{10}H_{11}CH_2.NH.CS.SHNH_2.CH_2.C_{10}H_{11}$ [128°], which on boiling with alcohol gives rise to $CS(NH.CH_2C_{10}H_7)_2$ [143°].—$B'HCl$. [229°]. Needles, v. sol. water and alcohol. With potassium cyanate it gives $CO(NH.CH_2C_{10}H_7)_2$ [226°] and $CO(NH_2)(NHCH_2C_{10}H_7)$ [135°].—$B'_2H_2PtCl_6$. Needles.—$B'H_2CO_3$: white needles.—$B'_2H_2SO_4$. Prisms, v. e. sol. water.—$B'C_6H_2(NO_2)_3(OH)$. Yellow prisms, sl. sol. water.

DI-NAPHTHYL-TRI-CHLORO-ETHANE *v.* Tri-chloro-di-naphthyl-ethane.

(α)-**NAPHTHYL-CYANAMIDE** $C_{10}H_7NH.CN$. [133°]. Formed by heating a solution of oxy-(α)-naphthyl-thio-urea $C_{10}H_7NH.CS.NH.OH$ (Tiemann, *B.* 22, 1940).

Di-(α)-naphthyl-cyanamide $C_{21}H_{14}N_2$ *i.e.* $H_7C_{10}.N{:}C{:}N.C_{10}H_7$. *Di-(α)-naphthyl-carbimide. Carbo-di-(α)-naphthyl-imide.* [94°]. Obtained by adding HgO to a boiling solution of di-(α)-naphthyl-thio-urea in dry benzene; the yield being c. 30 p.c. of the theoretical (Huhn, *B.* 19, 2405). Large prisms. V. sol. benzene, sl. sol. cold ether and petroleum-ether. By heating with dilute alcohol it is converted into di-(α)-naphthyl-urea. H_2S passed into the boiling solution in dry benzene converts it into di-(α)-naphthyl-thio-urea. Heated with CS_2 at 200° it yields (α)-naphthyl-thiocarbimide.

Di-(β)-naphthyl-cyanamide $H_7C_{10}.N{:}C{:}N.C_{10}H_7$. *Di-(β)-naphthyl-carbimide.* [146°]. Obtained by adding HgO to a boiling solution of di-(β)-naphthyl-thio-urea in dry benzene; the yield being 25 p.c. of the theoretical (Huhn, *B.* 19, 2406). White granular crystals. V. sol. hot benzene, sl. sol. ether and petroleum-ether. By boiling with dilute alcohol it is converted into di-(β)-naphthyl-urea. If H_2S is passed into its solution in dry boiling cumene, di-(β)-naphthyl-thio-urea is regenerated. With CS_2 at 200° it yields (β)-naphthyl-thio-carbimide.

(α) - **NAPHTHYL - CYANATE** $C_{10}H_7N{:}CO$. (270°). Formed in small quantity by heating di-naphthyl-urea with P_2O_5, and in larger quantity by the like treatment of naphthyl-carbamic ether (Hall, *Pr.* 9, 366; Hofmann, *Pr.* 19, 108; *C. R.* 47, 425). Pungent liquid. With oxy-azo-benzene it forms $C_6H_5.N_2.C_6H_4O.CO.NHC_{10}H_7$ [149°] (Goldschmidt a. Rosell, *B.* 23, 492).

NAPHTHYL CYANIDE *v.* Nitrile of naphthoic acid.

NAPHTHYL CYANURIC ACID *v. Cyanuric acid* in the article Cyanic acids.

TRI-NAPHTHYL-CYANURATES $(C_{10}H_7)_3C_3N_3O_3$. Formed from cyanuric chloride and sodium-naphthyl dissolved in naphthol (Otto, *B.* 20, 2239). The (α)- compound decomposes between 160° and 225°, the (β)- compound begins to decompose at 220°. Both are powders, sl. sol. hot water and alcohol, m. sol. benzene.

NAPHTHYLENE-ACETAMIDINE *v.* Naphthylene-ethenyl-amidine.

o-**NAPHTHYLENE-DIAMINE** $C_{10}H_{10}N_2$ *i.e.* $C_{10}H_6(NH_2)_2$ [1:2]. *Di-amido-naphthalene. Amido-naphthylamine.* Mol. w. 158. [95°].

Formation.—1. By reduction of *p*-sulphobenzene-azo-(β)-naphthylamine with tin and HCl (Griess, *B.* 15, 2193; Witt, *B.* 21, 3482).—2. By reduction of benzene-azo-(β)-naphthylamine, of (β)-naphthalene-azo-(β)-naphthylamine, of the dioxim of (β)-naphthoquinone, of (2,1)-nitro-(α)-naphthylamine, or of (1,2)-nitro-(β)-naphthylamine (Lawson, *B.* 18, 800, 2423; Leuckart, *B.* 19, 174; Lellmann a. Remy, *B.* 19, 803; Bamberger a. Schieffelin, *B.* 22, 1376).

Properties.—Silvery trimetric plates (from hot water), sl. sol. water, sol. alcohol and ether. Its ethereal solution quickly turns brown. $FeCl_3$ colours its solution green.

Reactions.—1. *Phenanthraquinone* yields naphthophenanthrazine which forms yellowish-white crystals giving a scarlet solution in H_2SO_4. 2. *Phenyl cyanate* in benzene solution reacts forming $C_6H_5NH.CO.NH.C_{10}H_6NH_2$ [335°] and $(C_6H_5.NH.CO.NH)_2C_{10}H_6$.—3. *Phenyl thiocarbimide* unites forming $(C_6H_5NH.CS.NH)_2C_{10}H_6$ [355°–360°].—4. On heating with excess of *oil of mustard* in alcoholic solution it yields, in like manner, silky needles of $C_{10}H_6(NH.CS.NHC_3H_5)_2$, which decompose at 170°–200° into naphthylene-thio-urea and di-allyl-thio-urea (Lellmann, *B.* 19, 808).—5. An alcoholic solution of benzil reacts forming di-phenyl-naphthoquinoxaline $C_{10}H_6\!<\!\begin{array}{l}N{:}CC_6H_5\\N{:}CC_6H_5\end{array}$ [148°] (Leuckart, *B.* 19, 174). 6. o-*Aldehydo-benzoic acid* $CHO.C_6H_4.CO_2H$ forms $C_{10}H_0\!<\!\begin{array}{c}N\\NH\end{array}\!\!>\!C.C_6H_4.CO_2H$, which decomposes at 280° (Bistrezycki, *B.* 23, 1044).

Salts.—$B''H_2Cl_2$. [90°]. Prisms or plates, v. sol. water.—$B''H_2SO_4$: white plates, sl. sol. water.—Picrate: nearly insoluble powder.

Acetyl derivative $C_{10}H_6(NHAc)_2$. [234°]. White needles.

Propionyl derivative $C_{10}H_6(NHC_3H_5O)_2$. [192°]. Formed from the base and propionic anhydride. Prisms (from alcohol), insol. ether.

Benzoyl derivative $C_{10}H_6(NHBz)_2$. [291°]. Plates, sl. sol. alcohol and HOAc (Hinsberg, *A.* 254, 256).

ar-Tetrahydride $C_{10}H_{14}N_2$ *i.e.* $\begin{array}{l}CH_2.CH_2.C.C(NH_2){:}C(NH_2)\\CH_2.CH_2.C.CH{=\!=}CH\end{array}$. [84°]. (220°) at 81 mm. Formed, together with a smaller quantity of the alicyclic isomeride, by reducing naphthylene-o-diamine with sodium (Bamberger a. Schieffelin, *B.* 22, 1377). Needles, v. sol. alcohol, ether, and hot water. Reduces $AgNO_3$. Gives

a red colour with cold aqueous $FeCl_3$. $KMnO_4$ oxidises it to adipic acid.

Salts.—$B''H_2Cl_2$. [c. 260°]. Tables, v. sol. water.—$B''2HNO_3$. [201°]. Plates, m. sol. water.

Acetyl derivative of the tetrahydride $C_{10}H_6(NHAc)_2$. [245°]. Needles, v. e. sol. alcohol, sl. sol. ether and cold water.

ac-Tetrahydride $\begin{matrix}CH{:}CH.C.CH(NH_2).CH(NH_2)\\ CH{:}CH.C.CH_2\text{———}CH_2\end{matrix}$. Formed as above (B. a. S.). Its hydrochloride and platinochloride crystallise in needles.

Naphthylene-*p*-diamine $C_{10}H_6(NH_2)_2$ [1:4]. [120°] (G.); [118°] (B. a. S.).

Formation.—1. By reduction of naphthalene-azo-(α)-naphthylamine by tin and HCl (Perkin, *C. J.* 18, 173; *A.* 137, 359; Friedländer, *B.* 22, 587).—2. By reduction of *p*-sulpho-benzene-azo-(α)-naphthylamine with tin and HCl (Griess, *B.* 15, 2192).—3. By reduction of (α)-nitro-(α)-naphthylamine (Liebermann, *A.* 183, 238).—4. By boiling benzene-azo-(α)-naphthylamine with zinc-dust and water (Bamberger a. Schieffelin, *B.* 22, 1381).

Properties.—Colourless prisms or needles, sl. sol. water, sol. alcohol and ether. Yields (α)-naphthoquinone on oxidation with $FeCl_3$.

Salts.—$B''H_2Cl_2$: white soluble four-sided plates, nearly insol. HClAq.—$B''H_2SO_4$: needles.

Mono-acetyl derivative $C_{10}H_6(NH_2)(NHAc)$. Formed by reducing the acetyl derivative of (α)-nitro-naphthylamine with tin and HCl (Liebermann).—$B''HCl$: long needles.—$B''_2H_2Cr_2O_7$.—$B''C_6H_2(NO_2)_3OH$: yellow needles.

Di-acetyl derivative $C_{10}H_6(NHAc)_2$. [205°]. Formed from the base or its mono-acetyl derivative and Ac_2O (Kleemann, *B.* 19, 334; B. a. S.). Needles, sl. sol. alcohol, nearly insol. water and ether.

Mono-benzoyl derivative $C_{10}H_6(NH_2)(NHBz)$. [186°]. Formed by reducing $C_{10}H_6(NO_2)(NHBz)$ (Ebell, *A.* 208, 326).—Needles.—$B''HCl$.—$B''HNO_3$.—$B''H_2SO_4$.

ar-Tetrahydride $\begin{matrix}CH_2.CH_2.C.C(NH_2){:}CH\\ CH_2.CH_2.C.C(NH_2){:}CH\end{matrix}$. The sole product of the reduction of *p*-naphthylene-diamine by sodium (Bamberger a. Schieffelin, *B.* 22, 1382). Needles, resinified on exposure to air. Yields adipic acid on oxidation with $KMnO_4$.—$B''H_2Cl_2$: crystalline powder.

Acetyl derivative of the tetrahydride $C_{10}H_{10}(NHAc)_2$. [285°]. Needles, v. sl. sol. cold water, m. sol. boiling alcohol. Reduces ammoniacal $AgNO_3$. $FeCl_3$ colours a solution of its hydrochloride green, changing to brown.

***Peri*-naphthylene-diamine** $C_{10}H_6(NH_2)_2$ [1:1']. [67°].

Formation.—1. By reduction of *peri*-di-nitro-naphthalene with iodide of phosphorus and water (De Aguiar, *B.* 3, 27; 7, 307; Beilstein a. Kuhlberg, *A.* 169, 90; Ladenburg, *B.* 9, 1651).—2. By reducing di-nitro-(α)-naphthoic acid [265°] with tin and HCl (Ekstrand, *B.* 20, 1353; *J. pr.* [2] 38, 263).—3. By the action of ammonia on *peri*-di-oxy-naphthalene at 150°–300° (Erdmann, *A.* 247, 363).

Properties.—Needles (from dilute alcohol), m. sol. water. Gives a reddish-brown colour and pp. with $FeCl_3$. $NaNO_2$ added to a solution of the sulphate ppts. red needles of the azimide. By the diazo- reaction it yields di-chloro-naphthalene [84°]. Benzoic aldehyde forms $C_{10}H_6\langle\begin{matrix}N{=}CPh\\ N(CH_2Ph)\end{matrix}\rangle$ (Hinsberg, *B.* 22, 861). Phenanthraquinone does not yield an azine. Oxalic ether at 100° yields $C_{14}H_{12}N_2O_2$, crystallising from chloroform in red needles, carbonised at 195° (Aguiar).

Salts.—$B''H_2Cl_2$. [c. 280°]. Small plates.—$B''H_2I_2$.—$B''H_2SO_4$.—$B''H_2C_2O_4$.

(1,4')-Naphthylene-diamine $C_{10}H_6(NH_2)_2$ [1:4']. [190°]. Formed by reducing the corresponding di-nitro-naphthalene in alcoholic solution with tin and HCl (Erdmann, *A.* 247, 361; *cf.* Zinin, *A.* 52, 362; 85, 329; Hollemann, *Z.* [2] 1, 555; De Aguiar, *B.* 3, 33; 7, 307). Formed also by heating the corresponding di-oxy-naphthalene with ammonia at 150°–180°, and finally at 250°–300° (E.). Thin white needles, which may be sublimed, sl. sol. cold water, v. sol. alcohol. $FeCl_3$ colours its solution bluish-violet. Converted by the diazo- reaction into di-chloro-naphthalene [107°]. — $B''H_2Cl_2$. — $B''H_2I_2$. — $B''H_2SO_4$.—$B''H_2C_2O_4$.

Tetrahydride $\begin{matrix}CH{:}CH\text{——}C.CH(NH_2).CH_2\\ CH{:}C(NH_2).C\text{-}CH_2\text{——}CH_2\end{matrix}$. [77°]. (264°) at 60 mm. Formed by the action of sodium on a solution of the base in isoamyl alcohol (Bamberger a. Hoskyns-Abrahall, *B.* 22, 944). Prisms (from ether) or needles (from ligroïn), sl. sol. hot water, v. sol. alcohol. $FeCl_3$ gives a deep reddish-brown colour in its hot solution, but no colour in the cold. Boiling $K_2Cr_2O_7$ gives a claret-colour. Gives off NH_3 when heated. This base can be separated into dextro- and lævo-rotatory varieties by crystallisation of the bitartrate, for on adding a crystal of dextro-rotatory coniine tartrate, the lævo-rotatory tetrahydro-naphthylene-diamine tartrate crystallises out, while the mother-liquor deposits the dextro-rotatory compound after long standing (Bamberger, *B.* 23, 291). The rotatory powers of the two hydrochlorides, $[\alpha]_D$ are $-7°\ 30'$ and $+8°\ 9'$ respectively. *Reactions.* 1. *Nitrous acid* at 0° forms a diazo- compound which when boiled with water yields $\begin{matrix}CH{:}CH\text{——}C.CH(NH_2).CH_2\\ CH{:}C(OH).C\text{-}CH_2\text{——}CH_2\end{matrix}$, the di-acetyl derivative of which crystallises in needles [152°] (Bamberger a. Bammann, *B.* 22, 960).—2. *Diazotisation* and *reduction* by $SnCl_2$ and HCl yields the hydrazine $\begin{matrix}CH{:}CH\text{——}C.CH(NH_2){:}CH_2\\ CH{:}C(N_2H_3).C\text{——}CH_2\text{—}CH_2\end{matrix}$. — 3. A dilute ethereal solution of CS_2 forms $C_{10}H_{10}(NH_2).NH_3S.CS.NH.C_{10}H_{10}NH_2$ [145°], the alicyclic amidogen entering into reaction. By treatment with PbO this substance is converted into the urea $CO(NH.C_{10}H_{10}.NH_2)_2$. Boiling with alcohol yields $CS(NH.C_{10}H_{10}.NH_2)_2$ [155°].—4. A warm alcoholic solution of CS_2 forms $C_{10}H_{10}\langle\begin{matrix}NH.CS.NH\\ NH.CS.NH\end{matrix}\rangle C_{10}H_{10}$ [175°], both amidogens taking part in the reaction. Salts. $B''H_2Cl_2$: trimetric prisms, $a{:}b{:}c = {\cdot}574{:}1{:}{\cdot}906$, v. sol. water, v. sl. sol. alcohol.—$B''H_2PtCl_6$ aq: prisms. — $B''_2H_2PtCl_6$: crystalline solid. — $B''H_2SO_4$ 2aq: triclinic prisms. *Acetyl derivative* $C_{10}H_{10}(NHAc)_2$. [262° cor.]. Prisms (from alcohol), sol. ether, sl. sol. boiling water.

(2,2')-Naphthylene-diamine $C_{10}H_6(NH_2)_2$ [2:2']. [159°] (B. a. S.); [161°] (L.). Formed by heat-

ing the corresponding di-oxy-naphthalene [186°] of Ebert and Merz with ammoniacal $CaCl_2$ at 265° (Lange, *B.* 21, Ref. 839; Bamberger a. Schieffelin, *B.* 22, 1384). Plates (from water), v. sol. boiling water, alcohol, and ether.

(2,3′)-Naphthylene - diamine $C_{10}H_6(NH_2)_2$. [218°]. Formed from di-oxy-naphthalene [213°], by heating with ammonia and NH_4Cl at 200°–250° (Lange, *B.* 21, Ref. 839). Its salts are more soluble than those of the (2,2′)-isomeride.

***m*-Naphthylene-diamine** $C_{10}H_6(NH_2)_2$ [1:3]. Obtained by reducing di-nitro-naphthalene [144°] with tin and HCl (Urban, *B.* 20, 973). A solution of its hydrochloride is coloured yellow by nitrous acid.—$B''H_2Cl_2$: v. e. sol. water, m. sol. alcohol, insol. ether.

Acetyl derivative $C_{10}H_6(NHAc)_2$. [156°]. Prisms, v. sol. benzene.

Dinaphthylene-amine $C_{20}H_{13}N$ *i.e.* $\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}\!\!>\!NH$ (?) [159° cor.]. Formed by heating $(\beta\beta)$-dioxy-dinaphthyl with ammoniacal-zinc chloride (Walder, *B.* 15, 2173). White trimetric plates or needles. V. sol. ether, benzene, or acetone, insol. dilute acids.

Picric acid compound $C_{20}H_{13}N\ 2(C_6H_2(NO_2)_3OH)$: [219° cor.]: blue-black needles.

Acetyl derivative $C_{20}H_{12}NAc$. [144° uncor.]; fine white needles, v. sol. ether, less sol. alcohol.

Tri-naphthylene-diamine $C_{30}H_{18}N_2$ *i.e.* $(C_{10}H_6)_3N_2$ (?). Formed by heating a mixture of naphthylamine, naphthylamine hydrochloride, and nitro-naphthalene in molecular proportions for 3 hours at 190°–220° (Salzmann a. Wichelhaus, *B.* 9, 1107). Amorphous blue-black powder (containing aq), insol. water and ether, forming a red solution in warm benzene. Begins to decompose at 180°.—$B'HCl$: amorphous violet powder.

References. — Bromo-, Di-chloro-, and Ethenyl-naphthylene-diamine.

***o*-NAPHTHYLENE-DIAMINE-'α'-SULPHONIC ACID**

$C_{10}H_{10}N_2SO_3$ *i.e.* $C_6H_4\!\!<\!\!\begin{array}{l}C(NH_2)\ :C(NH_2)\\ \qquad\qquad\quad\ |\\ C(SO_3H):CH\end{array}$. Formed, together with benzidine, by reduction of Congo-red. Not isolated (Witt, *B.* 19, 1719).

***o*-Naphthylene-diamine 'β'-sulphonic acid** $\begin{array}{l}\ CH:CH.C.C(NH_2):C(NH_2)\\ SO_3HC{=}CH.C\text{-}CH{=\!=}CH\end{array}$. Obtained by reducing 'gold-brown,' an azo-dye obtained from Brönner's (β)-naphthylamine sulphonic acid, and diazobenzene (Witt, *B.* 21, 3484). Yellowish-white crystals (from alcohol or ether), v. sl. sol. water. Quickly turns brown in air. K_3FeCy_6 turns its solution first brown, then yellow. $FeCl_3$ colours its aqueous solution dirty-green. Phenanthraquinone bisulphite yields, in presence of NaOAc and HOAc, naphthophenanthrazine sulphonic acid, which dissolves in H_2SO_4 with reddish-violet colour, and which is converted by potash-fusion into a eurhodol, forming in H_2SO_4 a solution coloured a pure ultramarine, turned cherry-red by water. Naphthylene-diamine 'α'-sulphonic acid acts in the same way, but the compound formed by phenanthraquinone dissolves in H_2SO_4 with bluish-violet colour, and the eurhodol with indigo-blue colour, the sulphate being ppd. as a crimson crystalline powder.

***o*-Naphthylene-diamine (γ)-sulphonic acid** $\begin{array}{l}CH:CH{-\!-\!-}C.C(NH_2):C(NH_2)\\ CH:C(SO_3H).C.CH{=\!=}CH\end{array}$. Formed by reduction of azo-dyes prepared from (β)-naphthylamine (γ)-sulphonic acid (of Dahl) (Witt, *B.* 21, 3486). Plates, sl. sol. water (more soluble than the 'β'-isomeride). $FeCl_3$ colours its solution emerald-green. The corresponding azines are rendered violet by H_2SO_4, becoming orange on dilution. The eurhodol gives a dark-violet solution in H_2SO_4, becoming cherry-red on dilution, the eurhodol sulphate being deposited in dirty-red flakes.

***o*-Naphthylene-diamine (δ)-sulphonic acid** $\begin{array}{l}SO_3H.C{=}CH.C.C(NH_2):C(NH_2)\\ \qquad\quad CH:CH.C.CH{=\!=}CH\end{array}$. Obtained by reducing azo-dyes prepared from (β)-naphthylamine (δ)-sulphonic acid (W.). Grey powder, more soluble in water than the 'β'-isomeride. Occurs also in a gelatinous (? hydrated) condition, v. e. sol. water. It resembles the 'β'-isomeride in its reactions with $FeCl_3$, with K_3FeCy_6, and with phenanthraquinone.

***o*-Naphthylene-diamine 'α'-disulphonic acid** $C_{10}H_4(NH_2)_2(SO_3H)_2$ [1:2:1′ or 4′:3′]. Obtained by reducing benzene-azo-(β)-naphthylamine 'α'-disulphonic acid formed from (β)-naphthylamine R disulphonic acid (Witt, *B.* 21, 3487).—$NaHA''$: sandy crystalline powder, v. sol. water, forming a solution with green fluorescence. $FeCl_3$ gives a green colour. Yields lemon-yellow sodium naphtho-phenanthrazine disulphonate, which forms a bluish-magenta solution in H_2SO_4. The eurhodol yields a deep greenish-blue solution in H_2SO_4, becoming claret-red on dilution.

Naphthylene-diamine disulphonic acid $C_{10}H_4(NH_2)_2(SO_3H)_2$. Formed by reducing di-nitro-naphthalene disulphonic acid (Alén, *Bn.* 3, 1025).—KHA'' 3aq: needles, m. sol. hot water.—$Ba(HA'')_2$ 6aq.

NAPHTHYLENE-BENZAMIDINE *v.* Benzenyl-naphthylene-amidine.

NAPHTHYLENE-ETHENYL-AMIDINE

$C_{12}H_{10}N_2$ *i.e.* [2:3] $C_{10}H_6\!\!<\!\!\begin{array}{c}NH\\N\end{array}\!\!>\!C.CH_3$. [168°]. Formed by the action of cold conc. alcoholic HCl upon (β)-naphthyl-ethyl-nitrosamine (Fischer a. Hepp, *B.* 20, 1248). Nodules (from water). Crystallises from methyl alcohol in prisms (containing MeOH) [75°]. Sl. sol. hot water.—$B'HCl\ \tfrac{1}{2}aq$: colourless needles, sl. sol. water, m. sol. alcohol. — $B'_2H_2PtCl_6$ 3aq. — $B'H_2SO_4$.—$B'C_6H_2(NO_2)_3OH$: needles.

Naphthylene-ethenyl-amidine

[1:2] $C_{10}H_6\!\!<\!\!\begin{array}{c}N\\NH\end{array}\!\!>\!CMe$. Formed from the acetyl derivative of nitro-(β)-naphthylamine by reduction with tin and HCl (Liebermann a. Jacobson, *A.* 211, 67). Formed also by the action of cold alcoholic HCl on (β)-naphthyl-ethyl-amino (Fischer a. Hepp, *B.* 20, 2472).—$B'HCl$ 2aq: needles, v. sol. water.

NAPHTHYLENE-ETHYL DIAMINE

$C_{10}H_6(NH_2)(NHEt)$ [1:4]. Formed by reducing nitroso-(α)-naphthyl-ethyl-amine with $SnCl_2$ (Kock, *A.* 243, 312). The free base is unstable. It yields (α)-naphthoquinone on oxidation.—$B''H_2Cl_2$. [152°]. Plates.—$B''2C_6H_2(NO_2)_3OH$. [180°]. Needles, sl. sol. water and alcohol.

DI - NAPHTHYLENE - GLYCOL, so called. $C_{22}H_{14}O_2$ *i.e.* $\begin{matrix}C_{10}H_6.C.OH\\ C_{10}H_6.C.OH\end{matrix}$ (?). Formed by the action of chloroform and aqueous NaOH on (β)-naphthol (Rousseau, *A. Ch.* [5] 28, 151). Small crystals, insol. water and alkalis, v. sl. sol. alcohol, HOAc, and chloroform, m. sol. ether.

Reactions.—1. *Chromic acid mixture* yields crystalline $C_{21}H_{12}O$ [188°].—2. Red-hot *soda-lime* forms dinaphthyl [187°].—3. Fuming *hydrochloric acid* (15 pts.) at 160° forms $C_{22}H_{14}Cl_2O$ 3aq crystallising in red needles.—4. With fuming *hydrobromic acid* it forms the corresponding $C_{22}H_{14}Br_2O$ 3aq crystallising in lustrous green plates; whence alcoholic ammonia produces $C_{22}H_{12}(OH)(NH_2)$ crystallising from benzene in needles and forming the crystalline salts $B'H_2Cl_2$, $B'_2H_2PtCl_6$, and $B'H_2Br_2$. The compound $C_{22}H_{14}Br_2O$ 3aq is converted by hot HOAc into $C_{22}H_{13}BrOHOAc$ crystallising in lustrous green tables and giving off HOAc at 100°.—5. *Bromine* in CS_2 forms orange plates of $C_{22}H_{13}Br_3O$.—6. HIAq (S.G. 1·7) forms, on boiling, crystals of $C_{22}H_{13}I_3O$.—7. Dilute *nitric acid* (S.G. 1·2) forms $C_{22}H_{12}(OH)(NO_3)$, which separates from HOAc as a red crystalline mass $C_{22}H_{12}(OH)(NO_3)HOAc$. Boiling dilute nitric acid forms red needles of $C_{22}H_{12}(NO_3)_2$ [190°].—8. H_2SO_4 (5 pts.) at 100° forms $C_{22}H_{12}(OH)(SO_4H)H_2SO_4aq$ crystallising in red needles with golden lustre, and separating from HOAc as $C_{22}H_{12}(OH)(SO_4H)HOAc$.

Di-acetyl derivative $C_{22}H_{12}(OAc)_2$. [192·5°]. Needles, sl. sol. alcohol, v. sol. C_6H_6.

Anhydride $C_{22}H_{12}O$. [198·5°]. Formed by heating 'dinaphthylene-glycol' with PCl_5. Formed also by the action of boiling alcohol on the compounds $C_{22}H_{13}Br_3O$ and $C_{22}H_{13}ClO$ (*v. supra*). Yellow needles (from benzene), almost insol. cold alcohol, v. sol. boiling benzene. Yields on reduction a compound $C_{22}H_{14}O$.

(α)-**DI-NAPHTHYLENE KETONE OXIDE** $C_{21}H_{12}O_2$ *i.e.* $C_{10}H_6<\begin{matrix}O\\ CO\end{matrix}>C_{10}H_6$. [240°]. Formed by boiling (α)-naphthyl ethyl carbonate (Bender, *B.* 13, 702). Yellow prisms, sl. sol. alcohol.

(β)-Dinaphthylene-ketone-oxide (?) $C_{21}H_{12}O_2$ *i.e.* $C_{10}H_6<\begin{matrix}O\\ CO\end{matrix}>C_{10}H_6$. [194°]. Formed, together with (β)-naphthol, alcohol, and CO_2, by long boiling of di-(β)-naphthyl-di-ethyl-ortho-carbonate $(C_{10}H_7O)_2:C:(OC_2H_5)_2$; its formation is explained by assuming the intermediate formation, by molecular change, of (β)-naphthol-carboxylic ether $C_{10}H_6(OH)CO_2Et$, which by elimination of H_2O and di-ethyl-carbonate would give dinaphthylene-ketone-oxide. Thin colourless prisms (from benzene). V. sl. sol. alcohol (Bender, *B.* 19, 2267).

NAPHTHYLENE MERCAPTAN $C_{10}H_8S_2$ *i.e.* $C_{10}H_6(SH)_2$. [181°] (G.); [174°] (E.). (210° at 15 mm.). Prepared by reducing the chloride of naphthalene 'α'-disulphonic acid with zinc-dust and H_2SO_4, and extracting the product with ether (Grosjean, *B.* 23, 2370; Ebert, *B.* 24, 145). Pearly leaflets (from alcohol), v. sl. sol. cold alcohol and ether. Its alcoholic solution gives a yellow pp. with lead acetate. Its alkaline solution is rapidly oxidised by air.

Acetyl derivative. [110°]. Crystals.

Benzoyl derivative. [153°].

NAPHTHYLENE - DI - METHYL - DIAMINE $C_{10}H_6(NH_2)(NMe_2)$ [1:4]. Formed by reducing nitroso-naphthyl-di-methyl-diamine or benzene-azo-dimethylnaphthylamine (Friedländer, *B.* 21, 3124). Liquid, m. sol. hot water.

Acetyl derivative $C_{10}H_6(NHAc)(NMe_2)$. [195°].

NAPHTHYLENE-(α)-NAPHTHYL-DIAMINE $C_{20}H_{16}N_2$ *i.e.* [1:4] $C_{10}H_6(NH_2)(NHC_{10}H_7)$. Formed by reducing nitroso-di-(α)-naphthylamine with $SnCl_2$ and HCl (Wacker, *A.* 243, 303). Minute crystals (from benzene), v. sol. alcohol.

NAPHTHYLENE - NAPHTHYL - BENZAMIDINE $C_{27}H_{18}N_2$ *i.e.* $C_6H_5.C\begin{matrix}\lessgtr NC_{10}H_7\\ \diagdown N.C_{10}H_6\end{matrix}$. [163°]. Formed by reducing benzoyl-nitro-di-(β)-naphthyl-amine with tin and HCl (Ris, *B.* 20, 2626). Slender needles (containing C_6H_6) [114°], m. sol. alcohol and ether.

NAPHTHYLENE - DI - NAPHTHYL - SULPHIDE OXIDE $C_{30}H_{20}SO$ *i.e.* $C_{10}H_7.O.C_{10}H_6.S.C_{10}H_7$. [111°]. Formed in small quantity as a by-product in the preparation of (α) and (β)-naphtho-nitrile by distilling a mixture of (α)- and (β)-potassium naphthalene-sulphonate with potassium ferrocyanide (Ekstrand, *B.* 17, 2601; *J. pr.* [2] 38, 140). Long needles. By $K_2Cr_2O_7$ and acetic acid it is oxidised to a compound [162°]. By heating with dilute HNO_3 at 130°–140° it yields a body $C_{20}H_{12}N_2SO_4$ which crystallises from hot acetic acid in small yellow prisms [231° uncor.], nearly insoluble in alcohol and CS_2. Br and I in CS_2 yield $C_{30}H_{17}Br_3SO$ [182°].

(α)-**DINAPHTHYLENE OXIDE** $C_{20}H_{12}O$ *i.e.* $\begin{matrix}C_{10}H_6\\ C_{10}H_6\end{matrix}>O$. [182°]. Formed by distilling (α)-naphthol (1 pt.) with lead oxide (3 pts.), the yield being 7 p.c. (Knecht a. Unzeitig, *B.* 13, 1724; *A.* 209, 134), and, together with naphthalene, by heating (α)-naphthol at 350°–400° (Merz a. Weith, *B.* 14, 195) or distilling it with an equivalent quantity of lime (Niederhäusern, *B.* 15, 1121). Colourless needles, insol. water, sl. sol. alcohol, v. sol. ether.

Picric acid compound $C_{20}H_{12}O\ 2C_6H_2(NO_2)_3OH$. [173°]. Red needles.

(β)-Dinaphthylene oxide $C_{20}H_{12}O$. [155°] (K. a. U.); [157°] (W.); [161°] (M. a. W.). V.D. 9·05 (obs.). Formed by distilling (β)-naphthol (1 pt.) with PbO (3 pts.) (K. a. U.). Formed also by passing a current of air into boiling (β)-naphthol (Merz a. Weith, *B.* 14, 200) and by heating di-oxy-(β)-dinaphthyl (1 pt.) with $ZnCl_2$ (4 pts.) for 6 hours at 270° (Walder, *B.* 15, 2171). Silvery plates, insol. water, sl. sol. alcohol, v. sol. ether.

Picric acid compound $C_{20}H_{12}O\ 2C_6H_2(NO_2)_3OH$. Red needles, v. sol. hot benzene.

References.—DI-BROMO- and DI-CHLORO- DI-NAPHTHYLENE OXIDE.

(α)-**DINAPHTHYLENE-OXIDE SULPHONIC ACID** $C_{20}H_8(SO_3H)_4O$. Prepared by sulphonating (α)-dinaphthylene-oxide.—$A^{iv}Ba_2$ 2aq: needles, sparingly soluble in water with a beautiful blue fluorescence (Knecht a. Unzeitig, *B.* 13, 1725).

(β) - **DINAPHTHYLENE - OXIDE - TETRA - SULPHONIC ACID** $C_{20}H_8(SO_3H)_4O$. Prepared by sulphonating (β)-dinaphthylene-oxide. — $A^{iv}Ba_2$ 2aq: tables (K. a. U.).

DINAPHTHYLENE-PHENYL-AMINE *v.* PHENYL-DINAPHTHYLENE-AMINE.

NAPHTHYLENE DISULPHOCYANIDE $C_{10}H_6(SCN)_2$. [78°]. Formed from $C_{10}H_6S_2Pb$, alcohol, and cyanogen chloride (Ebert a. Kleiner, *B.* 24, 146). Needles.

(αβ)-**NAPHTHYLENE-TOLAZINE** $C_{17}H_{12}N_2$ *i.e.* $C_6H_3(CH_3)<\begin{matrix}N\\|\\N\end{matrix}>C_{10}H_6$. [141°]. Formed by mixing acetic acid solutions, cooled to 0°, of (β)-naphthoquinone and tolylene-o-diamine (Hinsberg, *B.* 18, 1229). Distils without decomposition at a high temperature. Yellowish crystals. V. sol. alcohol, acetic acid, and benzene, insol. water. Dissolves in strong HCl with a brownish-red colour.

DI-NAPHTHYLENE-DI-THIO-DI-UREA *Octohydride* $CS<\begin{matrix}NH.C_{10}H_{10}.NH\\NH.C_{10}H_{10}.NH\end{matrix}>CS$. [175°]. Formed by boiling the tetrahydride of (1, 4')-naphthylene-diamine with CS_2 and alcohol (Bamberger a. Bammann, *B.* 22, 951). Crystalline powder, v. sol. alcohol.

NAPHTHYLENE-UREA $C_{11}H_8N_2O$ *i.e.* $C_{10}H_6<\begin{matrix}NH\\NH\end{matrix}>CO$. [c. 380°]. Formed from naphthylene-diamine and $COCl_2$ in toluene at 100° (Hartmann, *B.* 23, 1048).

(αα)-**DI-NAPHTHYL-ETHANE** $C_{22}H_{18}$ *i.e.* $(C_{10}H_7)_2C_2H_4$. [160°]. Formed, together with (α)-naphthyl-carbinylamine, by reducing the amide of thio-(α)-naphthoic acid in alcoholic solution with zinc-dust and HClAq (Bamberger, *B.* 21, 54). Hexagonal plates, v. sol. chloroform and benzene, m. sol. ether, sl. sol. alcohol. The alcoholic solution exhibits greenish-blue fluorescence.[1]

(ββ)-**Di-naphthyl-ethane** $C_{10}H_7.CH_2.CH_2.C_{10}H_7$ [253°]. Formed, in like manner, from thio-(β)-naphthoic amide (*B.*). Plates, v. sol. hot chloroform and benzene, sl. sol. ether and alcohol. Its solutions fluoresce bluish-violet.

References.—TRI-CHLORO- and TRI-CHLORO-TETRA-NITRO-DI-NAPHTHYL-ETHANE.

NAPHTHYL ETHER *v.* DI-NAPHTHYL OXIDE.

(α)-**NAPHTHYL-ETHYL-AMINE** $C_{12}H_{13}N$ *i.e.* $C_{10}H_7.NHEt$. *Ethyl-naphthylamine.* (303° i.V.) at 723 mm. (Bamberger a. Helwig, *B.* 22, 1312). Formed by cohobating naphthylamine with EtBr (Limpricht, *A.* 99, 117; Schiff, *A.* 101, 90). Obtained also by reducing $C_{10}H_7.NH.CS.CH_3$ with zinc-dust and HClAq (Bernthsen a. Trompetter, *B.* 11, 1756). Colourless crystals, becoming dichroic (steel-blue and brown-red) in light. Forms a nitrosamine, which, in contact with alcoholic HCl, changes to the isomeric nitroso-derivative $C_{10}H_6<\begin{matrix}NEt\\N\end{matrix}>O$ [133°] (Kock, *A.* 243, 310).—B'HCl. [193°].—$B'_2H_2PtCl_6$: yellow prisms.—B'HBr.—B'HI: four-sided prisms.

(β)-**Naphthyl-ethyl-amine** $C_{10}H_7.NHEt$. (305°) at 716 mm. Oil (Henriques, *B.* 17, 2668; Bamberger a. Müller, *B.* 22, 1297). Yields a red dye with diazotised sulphanilic acid. $FeCl_3$ gives no colour in the cold, a greenish-brown colour in warm solutions. $K_2Cr_2O_7$ and H_2SO_4 give a brown colour and pp.—B'HCl. [235°]. Plates, sl. sol. cold water.

Nitrosamine $C_{10}H_7.NEt(NO)$. [49°]. Crystals. Converted by alcoholic hydrogen chloride at 5° into nitroso-naphthyl-ethyl-amine $C_6H_4<\begin{matrix}C(NO):CNHEt\\CH=CH\end{matrix}$.—B'HCl. [108°]. Green prisms (from benzene) (Fischer a. Hepp, *B.* 20, 1248, 2471).

(α)-**Naphthyl-di-ethyl-amine** $C_{10}H_7NEt_2$. (291°). S.G. 1·005. Formed by heating (α)-naphthylamine (10 g.) with EtBr (15 g.) and alcohol or NaOHAq at 120° (B. E. Smith, *C. J.* 41, 180; Friedländer, *B.* 21, 3129). Formed also by heating (α)-naphthylamine hydrochloride with alcohol. Oil, v. sol. alcohol and ether. Forms a nitroso- derivative $C_{10}H_6(NO)NEt_2$ [165°].—B'HCl: silky plates, v. sol. hot water.—$B'_2H_2PtCl_6$: golden-yellow plates.—Sulphate: thick prisms.

Ethylo-iodide $C_{10}H_7NEt_3I$. [100°]. Cubes.

Ethylo-bromide $C_{10}H_7.NEt_3Br$. Tables (from water).

(β)-**Naphthyl-di-ethyl-amine** $C_{10}H_7.NEt_2$. (316° i.V.) at 717 mm. Oil (Bamberger a. Williamson, *B.* 22, 1760). Yields (β)-naphthylamine on heating with lime.—B'HCl. [175°]. Tables or needles, v. e. sol. water.—$B'_2H_2PtCl_6$. [95°].

Di-(β)-naphthyl-ethyl-amine $(C_{10}H_7)_2NEt$ [231°]. From di-(β)-naphthylamine and EtI at 150° (Ris, *B.* 20, 2619). Needles, m. sol. cold alcohol, insol. petroleum-ether.

(α)-**NAPHTHYL-ETHYL-AMINE TETRA-HYDRIDE** $C_{12}H_{17}N$ *i.e.* $\begin{matrix}CH_2.CH_2.C.C(NHEt):CH\\CH_2.CH_2.C-CH=CH\end{matrix}$. (287° i.V.) at 717 mm. Formed by adding sodium to a solution of naphthyl-ethyl-amine in isoamyl alcohol (Bamberger a. Helwig, *B.* 22, 1312). Colourless liquid, sl. sol. water, v. sl. sol. NaOHAq, v. sol. alcohol. Reduces warm alcoholic $AgNO_3$. Diazobenzene sulphonic acid yields an orange dye. $FeCl_3$ added to a solution of its hydrochloride gives a claret colour, changing to greenish-yellow. $K_2Cr_2O_7$ and H_2SO_4 give a dirty yellow pp. in the cold, but in warm solutions a red colour, becoming greenish-brown; further addition of $K_2Cr_2O_7$ ppts. blue-black flakes. $KMnO_4$ oxidises it to adipic and oxalic acids.—B'HCl. [118°]. Prisms or needles, v. sol. water.—$B'_2H_2PtCl_6$. Plates, sl. sol. cold water.

Nitrosamine $C_{10}H_{11}(NEt.NO)$. Formed by adding $NaNO_2$ to a solution of the base in HClAq. Yellow oil, exhibiting Liebermann's reaction. Tin and HClAq reconvert it into $C_{10}H_{11}(NEtH)$. When dissolved in alcoholic HCl it slowly changes to the isomeric $C_6H_8<\begin{matrix}C(NEtH):CH\\C(NO)=CH\end{matrix}$ crystallising in golden needles [119°].

ar-(β)-**Naphthyl-ethyl-amine tetrahydride** $\begin{matrix}CH_2.CH_2.C.CH:C(NHEt)\\CH_2.CH_2.C.CH:CH\end{matrix}$. (291·5°) at 724 mm. Formed, together with the alicyclic isomeride, by reducing (β)-naphthyl-ethyl-amine (15 g.) in isoamyl alcohol with sodium (24 g.) (Bamberger a. Müller, *B.* 22, 1304). Colourless oil, volatile with steam, v. sol. alcohol, v. sl. sol. water, insol. NaOHAq. Smells like piperidine. $FeCl_3$ colours a warm solution of its hydrochloride reddish-brown. $KMnO_4$ oxidises it to adipic acid.—B'HCl. [173·5°]. Needles, v. sol. water, ppd. as plates by addition of HCl.—$B'_2H_2PtCl_6$. Needles.

ac-(β)-**Naphthyl-ethyl-amine tetrahydride** $C_6H_4<\begin{matrix}CH_2.CH.NHEt\\CH_2.CH_2\end{matrix}$. (267°) at 724 mm. S.G.

$\frac{15}{}$ ·998. Formed as above (B. a. M.). Colourless oil, sl. sol. water, very volatile with steam. $FeCl_3$ colours a warm solution of its hydrochloride reddish-brown. Reacts with diazobenzene nitrate, forming $C_{10}H_{11}.NEt.N_2C_6H_5$ [58°]. — B'HCl. [223·5°]. Prisms (from water) or needles (from $CHCl_3$). Ppd. in plates by adding HCl to its aqueous solution.—$B'HNO_3$. [184°]. Needles or plates, v. sol. hot water.—$B'HNO_2$. [180°]. Needles.—$B'_2H_2PtCl_6$. [204°]. Orange-yellow stellate crystals.—$B'C_6H_2(NO_2)_3OH$. [183·5°]. Needles, v. sol. water and alcohol.

Acetyl derivative $C_{10}H_{11}.NEtAc$. (328° uncor.) at 718 mm. Oil.

Nitrosamine $C_{10}H_{11}.NEt(NO)$. Yellow oil, v. sl. sol. cold water.

Ar-(β)-**Naphthyl-di-ethyl-amine tetrahydride** $\begin{matrix} CH_2.CH_2.C.CH:CNEt_2 \\ CH_2.CH_2.C.CH:CH \end{matrix}$. (298°) at 709 mm. The chief product of the reduction of $C_{10}H_7NEt_2$ by sodium (Bamberger a. Williamson, *B.* 22, 1763). Liquid, sl. sol. water. Yields a red dye with *p*-diazobenzene sulphonic acid. $KMnO_4$ oxidises it to adipic acid.—B'HCl: granules, v. e. sol. water.

Ac-(β)-**Naphthyl-di-ethyl-amine tetrahydride** $C_6H_4<\begin{matrix} CH_2.CH.NEt_2 \\ CH_2.CH_2 \end{matrix}$. Liquid, sl. sol. water, insol. NaOHAq.—$B'H_2CO_3$: white needles.— B'HCl: prisms, v. sol. water.

(α)-NAPHTHYL ETHYL CARBONATE $C_{13}H_{12}O_3$ *i.e.* $C_{10}H_7.OCO.OEt$. [31°]. Obtained from (α)-naphthol and chloroformic ether (Bender, *B.* 13, 702; 19, 2266). Tables, sol. alcohol. By heating to boiling for some time it splits up into (α)-naphthol, a body $C_{21}H_{12}O_2$ [240°], which is probably a dinaphthylene-ketone-oxide $C_{10}H_6<\begin{matrix} O \\ CO \end{matrix}>C_{10}H_6$, alcohol, and CO_2.

Di-(β)-Naphthyl-di-ethyl-orthocarbonate $(C_{10}H_7O)_2:C:(OC_2H_5)_2$. (298°–300°). Obtained by the action of chloroformic ether upon (β)-naphthol (Bender). White amorphous mass, melting with the heat of the hand. HCl at 250° decomposes it into (β)-naphthol, EtCl, and CO_2. By long boiling it is decomposed into (β)-naphthol, a body $C_{21}H_{12}O_2$, which is probably a dinaphthylene-ketone-oxide, alcohol, and CO_2.

(α)-NAPHTHYL-ETHYLENE $C_{12}H_{10}$ *i.e.* $C_{10}H_7.CH:CH_2$. Formed by the action of Na_2CO_3 on β-bromo-α-naphthyl-propionic acid (Brandis, *B.* 22, 2158). Oil, smelling like styrene. Bromine in chloroform forms $C_{10}H_7.CHBr.CH_2Br$ [168°].

References. — Di-chloro- and Di-chloro-tetra-nitro-di-naphthyl-ethylene.

DI-(α)-NAPHTHYL-ETHYLENE-DIAMINE $C_{22}H_{20}N_2$ *i.e.* $C_2H_4(NHC_{10}H_7)_2$. [127°]. Formed from naphthylamine and $C_2H_4Br_2$ (Reuter, *B.* 8, 23).—$B''H_2SO_4$.

Di-(β)-Naphthyl-ethylene-diamine $C_2H_4(NHC_{10}H_7)_2$. [153°] (M.); [150°] (B.). Formed, together with di-(β)-naphthyl-pyrazine tetrahydride $C_2H_4<\begin{matrix} N(C_{10}H_7) \\ N(C_{10}H_7) \end{matrix}>C_2H_4$ [228°] by the action of ethylene bromide on (β)-naphthylamine in presence of sodium carbonate (Maschke, *C. C.* 1886, 824; Bischoff, *B.* 23, 1985). Plates and needles; sl. sol. ether, m. sol. absolute alcohol.

DI-(α)-NAPHTHYL-ETHYLENE-DI-CARBAMIC ETHER $C_{28}H_{28}N_2O_4$ *i.e.* $C_2H_4(N(C_{10}H_7).CO_2Et)_2$. [156°]. Formed from $C_2H_4(NHC_{10}H_7)_2$ and $ClCO_2Et$ (Reuter, *B.* 8, 25). V. sol. alcohol.

DI-(α)-NAPHTHYL-ETHYLENE DIOXIDE $C_{22}H_{18}O_2$ *i.e.* $C_2H_4(OC_{10}H_7)_2$. [126°]. Formed from (α)-naphthol, KOH, and $C_2H_4Br_2$ (Koelle, *B.* 13, 1956). Plates.

Di-(β)-Naphthyl-ethylene dioxide $C_2H_4(OC_{10}H_7)_2$. [217°]. Formed in like manner (K.). Plates; sl. sol. benzene and HOAc, insol. water, alcohol, and ether.

(β)-NAPHTHYL-ETHYL-HYDRAZINE $C_{12}H_{14}N_2$ *i.e.* $C_{10}H_7NEt.NH_2$. Formed from (β)-naphthyl-hydrazine and EtI in EtOH (Hauff, *A.* 253, 33). Yellow oil; v. sol. alcohol. Reduces Fehling's solution and HgO without forming a tetrazone.—B'HCl: plates.

NAPHTHYL ETHYL OXIDE *v. Ethyl ether* of Naphthol.

NAPHTHYL-ETHYL-NITROSAMINE *v. Nitrosamine* of Naphthyl-ethyl-amine.

NAPHTHYL-DI-ETHYL-PHOSPHINE $C_{14}H_{17}P$ *i.e.* $C_{10}H_7PEt_2$. (above 360°). Formed from $C_{10}H_7PCl_2$ and $ZnEt_2$ (Kelbe, *B.* 11, 1501). Yellow oil.

Ethylo-iodide $C_{10}H_7PEt_3I$. [209°]. Colourless leaflets.

NAPHTHYL-GLYCOCOLL *v.* Naphthyl-amido-acetic acid.

DI-NAPHTHYL-GLYCOL *v.* Di-naphthylene-glycol.

NAPHTHYL-GLYCOLLIC ACID *v.* Oxy-naphthyl-acetic acid.

(α)-NAPHTHYL-GLYOXYLIC ACID $C_{12}H_8O_3$ *i.e.* $C_{10}H_7.CO.CO_2H$. *Naphthoyl-formic acid.* [114°]. Obtained by saponification of its nitrile (Boessneck, *B.* 15, 3066; 16, 640), and by oxidation of (α)-naphthyl methyl ketone by $KMnO_4$ (Claus a. Feist, *B.* 19, 3181). Needles or plates; m. sol. water, v. sol. alcohol and ether. Gives a red colour on shaking with H_2SO_4 and benzene containing thiophene. Yields (α)-naphthoic acid [160°] on oxidation.—$CaA'_2 4\frac{1}{2}aq$: v. sol. water.— AgA': white pp., v. sl. sol. water.

Amide $C_{10}H_7.CO.CONH_2$. [151°]. Long white needles (from alcohol).

Nitrile $C_{10}H_7.CO.CN$. *Naphthoyl cyanide.* [101°]. Formed by heating (α)-naphthoyl chloride with $HgCl_2$ at 100°. Needles.

(β)-Naphthyl-glyoxylic acid $C_{10}H_7.CO.CO_2H$. [c. 75°]. Formed by gentle oxidation of (β)-naphthyl methyl ketone by dilute $KMnO_4$ (Claus a. Tersteegen, *J. pr.* [2] 42, 518). Reduced by sodium-amalgam to α-oxy-naphthyl-acetic acid $C_{10}H_7.CH(OH).CO_2H$.

NAPHTHYL-GUANIDINE $C_{11}H_{11}N_3$ *i.e.* $NH:C(NH_2).NHC_{10}H_7$. — $B'_2H_2CO_3$. Trimetric crystals; $a:b:c$ = ·666:1:1·270. — B'HCl. Trimetric crystals (Haushofer, *J.* 1882, 365).

Di-(α)-naphthyl-guanidine $C_{21}H_{17}N_3$ *i.e.* $NH:C(NHC_{10}H_7)_2$. *Menaphthylamine.* [c. 200°]. Formed by the action of gaseous cyanogen chloride on (α)-naphthylamine (Perkin, *C. J.* 9, 8; *A.* 98, 238). Small white needles with bitter taste; nearly insol. water, sl. sol. alcohol and ether. Cyanogen passed into its ethereal solution forms $C_{23}H_{17}N_5$, a pale-yellow crystalline mass; insol. water, m. sol. alcohol and ether; decomposed by cold HClAq in $C_{23}H_{15}N_3O_2$,

crystallising in yellow scales [245°], and decomposed by acids into oxalic acid and di-naphthyl-guanidine.—B'HCl: amorphous; v. sol. alcohol and ether, sl. sol. water.—$B'_2H_2PtCl_6$.

Tri-(α)-naphthyl-guanidine $C_{31}H_{23}N_3$ *i.e.* $C_{10}H_7N{:}C(NHC_{10}H_7)_2$. [178°]. Formed from (α)-naphthylamine and $MeS.C(NC_{10}H_7)(NHC_{10}H_7)$ [174°] (Evers, *B.* 21, 962). Flat needles; insol. water, v. sol. alcohol.

(β)-**NAPHTHYL-GUANIDO-BENZOIC ACID** $C_{18}H_{15}N_3O_2$ *i.e.* $C_{10}H_7.NH.C(NH).NH.C_6H_4CO_2H$. Formed by heating cyancarbimidamido-benzoic acid with excess of (β)-naphthylamine (Griess, *B.* 16, 338). Small crystalline spherules; insol. ether, v. sl. sol. hot water and hot alcohol.—HA'HCl: sparingly soluble six-sided plates.

(α)-**NAPHTHYL-HYDRAZINE** $C_{10}H_{10}N_2$ *i.e.* $C_{10}H_7NH.NH_2$. [116°]. (203° at 20 mm.). Formed by making a paste of (α)-naphthylamine and HClAq, adding $NaNO_2$ in the cold, filtering, and reducing with $SnCl_2$, the yield being 66 p.c. (Fischer, *A.* 232, 236). Plates; sl. sol. water, v. sol. other solvents. — B'HCl: plates. — $B'_2H_2SO_4$: plates.

Reactions.—1. *Acetone* forms $C_{10}H_7N_2H{:}CMe_2$ [74°].—2. *Pyruvic acid* produces the acid $C_{10}H_7N_2H{:}CMe.CO_2H$ [159°], which forms the ether EtA' [100°] (Schlieper, *A.* 239, 231).—3. *Di-bromo-pyruvic acid* forms the acid $C_{10}H_7N_2H{:}CH.C(N_2HC_{10}H_7)CO_2H$ [196°] (Nastvogel, *A.* 248, 89).—4. *Aceto-acetic ether* forms oxy-naphthyl-methyl-pyrazole $C_{14}H_{12}N_2O$ [c. 190°] (Knorr, *B.* 17, 551).

Tetrahydride $C_6H_8\!<\!\genfrac{}{}{0pt}{}{CH{:}CH}{C(N_2H_3)}\!>\!CH$. Obtained by treating a solution of the tetrahydride of (α)-naphthylamine hydrochloride (18 g.) with an equivalent quantity of $NaNO_2$ and dropping the mixture into a solution of $SnCl_2$ (45 g.) dissolved in HClAq at 0° (Bamberger a. Bordt, *B.* 22, 630). Prisms (from boiling ligroïn); sl. sol. water. Reduces Fehling's solution at 30°–40°. $K_2Cr_2O_7$ sets free nitrogen in the cold.—*B'HCl: silvery plates; v. sol. water.

(β)-Naphthyl-hydrazine $C_{10}H_{10}N_2$ *i.e.* $C_{10}H_7NH.NH_2$. [124°]. Formed in the same way as its (α)-isomeride (Fischer, *A.* 232, 242). Plates, m. sol. water, v. sol. hot alcohol. Turns red in air. Its solution in conc. HOAc is ppd. by water.

Reactions.—1. *Acetone* forms $C_{10}H_7N_2H{:}CMe_2$ [65°] (Schlieper, *A.* 236, 174).—2. *Aldehyde* yields $C_{10}H_7N_2H{:}CH.CH_3$ [128°].—3. *Phenyl-acetic aldehyde* forms a crystalline hydrazide decomposing at 100° (Ince, *A.* 253, 40).—4. *Acetophenone* forms a hydrazide crystallising in needles [c. 150°].—5. *Acetyl-propionic ether* forms $C_{17}H_{20}N_2O_2$ [130°], the acid corresponding to which at 175° forms the anhydride $C_{10}H_7N\!<\!\genfrac{}{}{0pt}{}{N{:}CMe}{CO.CH_2}\!>\!CH_2$ [119°] (Steche, *A.* 242, 368).—6. *Pyruvic acid* in alcoholic solution yields $C_{10}H_7N_2H{:}CMe.CO_2H$ [166°], which yields the ether EtA' [131°] (Schlieper, *A.* 236, 176).—7. *Di-bromo-pyruvic acid* yields yellow needles of $C_{10}H_7N_2H{:}CH.CO.C(OH).N_2HC_{10}H_7$? insoluble in alkalis (Nastvogel, *A.* 248, 85).—8. *Aceto-acetic ether* forms $C_{14}H_{12}N_2O$ [190°].

Salts.—*B'HCl: needles or plates.—*$B'_2H_2SO_4$: plates, sl. sol. hot water.—Nitrate: very soluble needles.

(β)-*Naphthyl-thiocarbazate* $C_{10}H_7N_2H_3HS.CS.N_2H_2C_{10}H_7$. [145°]. Plates.

Acetyl derivative $C_{10}H_7NH.NHAc$. [165°] (Hauff, *A.* 253, 25); [167°] (Hillringhaus, *B.* 22, 2657). Formed from (β)-naphthyl-hydrazine and HOAc or Ac_2O. Needles (from alcohol), m. sol. hot water. Reduces Fehling's solution.

Benzoyl derivative $C_{10}H_7NH.NHBz$. [155°]. Needles, insol. water, v. sol. hot alcohol.

Di-benzoyl derivative $C_{10}H_7N_2HBz_2$. [163°].

Di-(α)-naphthyl-hydrazine $C_{10}H_7.N_2H_2.C_{10}H_7$. *Hydrazo-naphthalene.* [275°].

Preparation.—1 pt. of azonaphthalene is finely suspended in a solution of 1½ pts. of NaOH in 160–170 pts. of alcohol, and the boiling mixture is treated with zinc-dust till decolourised; it is then poured into water containing NH_4HS and the pp. is dried and extracted with benzene, from which it crystallises on cooling.

Properties.—Colourless plates. Sublimable. V. sol. alcohol, ether, and benzene, insol. water. By warming with HCl it is converted into a mixture of two isomeric di-amido-dinaphthyls (Nietzki a. Goll, *B.* 18, 3253).

(1, 4) - **NAPHTHYL - HYDRAZINE SULPHONIC ACID** [1:4] $C_{10}H_6(N_2H_3).SO_3H$. Formed by reducing the diazo- compound of naphthionic acid with stannous chloride (Erdmann, *A.* 247, 333). Tufts of white needles, sl. sol. hot water, m. sol. hot HClAq.—A'Na 4aq: plates, sl. sol. cold water.

(1,4')-Naphthyl-hydrazine sulphonic acid [1:4'] $C_{10}H_6(N_2H_3)SO_3H$. Formed by reducing the diazo- compound of the (1,4')-naphthylamine sulphonic acid with $SnCl_2$. Plates, m. sol. water, v. sol. HCl.—A'Na 3½aq: needles, sl. sol. water.

Peri-Naphthyl-hydrazine sulphonic acid [1:1'] $C_{10}H_6(N_2H_3).SO_3H$. Formed, in like manner, from (1,1')-naphthylamine sulphonic acid. Small plates, sl. sol. hot water.—A'K: needles, v. sol. hot water.—A'Na: plates, v. sl. sol. water.

(α)-**NAPHTHYL-IMIDO-DIACETIC ACID** $C_{10}H_7N(CH_2.CO_2H)_2$. [133°]. Formed by the action of chloro-acetic acid and Na_2CO_3 on (α)-naphthyl-amido-acetic acid (Bischoff, *B.* 23, 2004). Colourless crystals, v. sol. alcohol.

(α)-*Naphthylamide* $C_{10}H_7N(CH_2.CO_2H)(CH_2.CONHC_{10}H_7)$. [199°]. Crystals (from benzene-alcohol).

Di-(α)-naphthylamide $C_{10}H_7N(CH_2.CONHC_{10}H_7)_2$. [202°]. Crystals, sl. sol. ligroïn.

(β)-Naphthyl-imido-diacetic acid $C_{14}H_{13}NO_4$. [182°]. Formed by heating chloro-acetic acid with (β)-naphthyl-amido-acetic acid and Na_2CO_3Aq at 160° (B.). Crystals, sol. alcohol, sl. sol. ether, insol. benzene. The solutions have a bluish-violet fluorescence.

(α) - **NAPHTHYL - β - IMIDO - BENZYL - MALONIC ETHER** $C_{24}H_{23}NO_4$ *i.e.* $C_6H_5.C(NC_{10}H_7).CH(CO_2Et)_2$. [145°]. Formed by the action of ω-chloro-benzylidene-(α)-naphthylamine upon sodio-malonic ether. Crystalline solid. Sl. sol. ether. By dilute HCl at 120° it is split up into acetophenone and (α)-naphthylamine (Just, *B.* 19, 987).

(β)-Naphthyl-β-imido-benzyl-malonic ether $C_{24}H_{23}NO_4$ *i.e.* $C_6H_5.C(NC_{10}H_7).CH(CO_2Et)_2$.

[140°]. Formed by the action of ω-chloro-benzylidene-(β)-naphthylamine$C_{10}H_7.N:CCl.C_6H_5$ upon sodio-malonic ether. Crystalline solid. Sl. sol. ether. By dilute HCl at 120° it is split up into acetophenone and (β)-naphthylamine (Just).

(β)-**NAPHTHYL-β-IMIDO-BUTYRIC ACID** $CH_3.C(NC_{10}H_7).CH_2.CO_2H$. [92°]. Needles, sol. water. Formed, together with its naphthalide, by heating a mixture of acetoacetic ether and (β)-naphthylamine at 150°–180°. By boiling with HCl it is converted into (*Py.* 1:3)-oxy-methyl-(β)-naphthoquinoline.

Naphthalide $C_{24}H_{20}NO$. [200°]. Needles, nearly insoluble in most solvents (Knorr, *B.* 17, 543).

DI-NAPHTHYL-IMIDO-THIOCARBAMIC ETHERS $C_{10}H_7NH.C(NC_{10}H_7).SR$. *Di-naphthyl-alkyl-ψ-thioureas.* Formed by heating di-naphthyl-thio-ureas with alkyl iodides (Evers, *B.* 21, 964).

Di-(α)-naphthyl-imido-thiocarbamic acid. *Methyl ether* $C_{10}H_7NH.C(NC_{10}H_7).SMe$. [136°]. Plates, sol. hot, v. sl. sol. cold, alcohol. Gives off HSMe on heating, leaving di-(α)-naphthyl-cyanamide, which on boiling with dilute HClAq yields di-(α)-naphthyl-urea. Boiling alcoholic potash also converts it into di-(α)-naphthyl-urea and HSMe. Dilute H_2SO_4 at 160° forms (α)-naphthylamine and $C_{10}H_7NH.CO.SMe$.—B'HI. [174°].—$B'_2H_2PtCl_6$. [202°]. Yellow powder.

Ethyl ether EtA'. [98°]. Prisms, sl. sol. hot alcohol.—B'HI. [157°].—$B'_2H_2PtCl_6$.

Propyl ether PrA'. [95°]. Plates.—B'HI. [97°].—$B'_2H_2PtCl_6$.

Ethylene derivative $C_{23}H_{18}N_2S$ *i.e.* $C_{10}H_7N:C\langle{}^{N(C_{10}H_7)}_{S.CH_2.CH_2}\rangle$. [139°]. Formed by boiling di-(α)-naphthyl-thio-urea with ethylene bromide. Needles, v. sol. alcohol.—$B'_2H_2PtCl_6$.

Di-(β)-naphthyl-imido-thiocarbamic acid. *Methyl ether* $C_{10}H_7NH.C(NC_{10}H_7).SMe$. [110°]. Needles, v. e. sol. warm alcohol and ether.—$B'_2H_2PtCl_6$.

Ethyl ether EtA'. [106°].—$B'_2H_2PtCl_6$. [155°].

Propyl ether PrA'. [66°].—$B'_2H_2PtCl_6$. [120°].

Ethylene derivative $C_{10}H_7N:C\langle{}^{N(C_{10}H_7)}_{S.CH_2.CH_2}\rangle$. [172°]. Plates (from alcohol).—$B'_2H_2PtCl_6$. [146°].

DINAPHTHYLINE *v.* DI-AMIDO-DINAPHTHYL.

(αβ)-**DI-NAPHTHYL-KETONE** $C_{21}H_{14}O$ *i.e.* $(C_{10}H_7)_2CO$. Mol. w. 268. [135°]. S. (alcohol) 1·3 at 14°. Formed by heating (α)-naphthoic acid with naphthalene and P_2O_5 at 210° (Kollarits a. Merz, *B.* 6, 544); by the action of a strip of zinc on a mixture of (α)-naphthoyl chloride and naphthalene (Grucarevic a. Merz, *B.* 6, 1241), and by heating (β)-naphthoyl chloride with mercuric dinaphthyl at 175° (G. a. M.). Pointed needles (from boiling alcohol). On distillation with soda lime it yields naphthalene and a mixture of (α) and (β)-naphthoic acids.

(ββ)-**Di-naphthyl ketone** $(C_{10}H_7)_2CO$. Obtained in two isomeric forms [125·5°] and [164°] by heating (β)-naphthoic acid with naphthalene and P_2O_5 (K. a. M.), or (β)-naphthoyl chloride with naphthalene and zinc (G. a. M.). The two varieties may be separated by crystallisation from ether-chloroform. Both varieties yield naphthalene and (β)-naphthoic acid on distillation with soda-lime. The solubility of the variety melting at 164° in alcohol at 19° is less (·08) than that of the variety melting at 125·5° (·38). The latter variety may also be prepared by distilling calcium (β)-naphthoate (Hausamann, *B.* 9, 1515).

Di-naphthyl ketone $(C_{10}H_7)_2CO$. [140°]. Formed by distilling potassium naphthalene (β)-sulphonate with KHC_2O_4 (Giuseppe, *B.* 6, 546).

NAPHTHYL-MELAMINE *v.* CYANIC ACIDS.

(α)-**NAPHTHYL MERCAPTAN** $C_{10}H_8S$ *i.e.* $C_{10}H_7.SH$. *Thionaphthol.* Mol. w. 160. (285°). S.G. $\frac{0}{4}$ 1·1729; $\frac{23}{4}$ 1·1549. Formed by reducing naphthalene (α)-sulphonic chloride with zinc-dust and dilute H_2SO_4 (Schertel, *A.* 132, 91; Krafft a. Schönherr, *B.* 22, 822). Formed also by saponifying its ethyl ether which may be formed by the action of potassium xanthate on (α)-diazonaphthalene chloride (Leuckart, *J. pr.* [2] 41, 216). Colourless oil, with unpleasant smell, sl. sol. aqueous alkalis, v. sol. alcohol and ether. Oxidised in alcoholic solution by the air to di-(α)-naphthyl disulphide [91°]. Yields di-naphthyl sulphide [107°] on heating.—$Hg(SC_{10}H_7)_2$.—$Pb(SC_{10}H_7)_2$: yellow pp.

Ethyl ether $C_{10}H_7SEt$. (167·5°) at 15 mm. S.G. $\frac{0}{}$ 1·1198; $\frac{50}{}$ 1·0797. Formed from $C_{10}H_7SH$ by heating with EtI, alcohol, and KOH at 120°–150°.

Acetyl derivative $C_{10}H_7SAc$. (188° at 15 mm.). S.G. $\frac{50}{}$ 1·1519.

Benzoyl derivative $C_{10}H_7SBz$. [117°]. (262° at 15 mm.).

(β)-**Naphthyl mercaptan** $C_{10}H_7SH$. [75°]. (Billeter, *B.* 8, 463; L.); [81°] (K. a. S.). (286°). Formed by reducing naphthalene (β)-sulphonic chloride, and also by heating (β)-diazo-naphthalene chloride with a solution of EtO.CS.SK, saponifying the oily product, and boiling with zinc-dust and HClAq (Maikopar, *Z.* 1869, 711; Leuckart, *J. pr.* [2] 41, 220). Small plates (from ether), sl. sol. water. Not volatile with steam. Yields the corresponding disulphide on oxidation.—$Pb(SC_{10}H_7)_2$: orange powder.

Ethyl ether $C_{10}H_7SEt$. [16°]. (170·5° at 15 mm.).

Acetyl derivative $C_{10}H_7SAc$. [53·5°]. (191° at 15 mm.). Formed by heating the mercaptan with AcCl at 75°.

Benzoyl derivative $C_{10}H_7SBz$. [108°]. (267° at 15 mm.).

DI-(α)-NAPHTHYL-METHANE $C_{21}H_{16}$ *i.e.* $(C_{10}H_7)_2CH_2$. [109°] (above 360°). S. (alcohol) ·8 in the cold; 6·6 at 78°. Formed by the action of H_2SO_4 on a cooled mixture of naphthalene (5 pts.), methylal (1 pt.) and chloroform (20 pts.) (Grabowski, *B.* 7, 1605). Short prisms (from alcohol), v. sol. ether and chloroform. Not affected by chromic acid mixture. *Picric acid compound* $C_{21}H_{16}2C_6H_2(NO_2)_3OH$. [143°]. Reddish-yellow prisms (from chloroform).

Di-(β)-naphthyl-methane [92°]. Prepared by reducing di-(β)-naphthyl-ketone with P and HIAq (Richter, *B.* 13, 1728). Slender white needles, v. sol. alcohol and benzene. Yields $C_{21}H_{14}Br_2$ [164°] and $C_{21}H_{14}Br_4$ [150°–160°].

NAPHTHYL-METHYL-ALCOHOL *v.* NAPHTHYL-CARBINOL.

(α)-**NAPHTHYL-METHYL-AMINE** $C_{10}H_7NHMe$. *Methyl-(α)-naphthylamine.* (293° uncor.). Formed, together with dinaphthylamine, by passing MeCl into melted (α)-naphthylamine (Landshoff, *B.* 11, 638). Dark-red oil. Its alcoholic solution gives a violet pp. with $FeCl_3$.—$B'_2H_2PtCl_6$ 2aq.

Acetyl derivative $C_{10}H_7NMeAc$. [91°] (L.); [95°] (Norton a. Livermore, *B.* 20, 2272). Small white prisms, sl. sol. water, v. sol. alcohol and ether. Dilute nitric acid (10 p.c.) forms $C_{10}H_6(NO_2).NMeNO_2$ [157·5°].

Benzoyl derivative $C_{10}H_7.NMeBz$. [121°]. Formed by heating (α)-naphthyl-di-methylamine with BzCl at 180° (Hess, *B.* 18, 687). Crystals.

(α)-Naphthyl-di-methyl-amine $C_{12}H_{13}N$ *i.e.* $C_{10}H_7NMe_2$. (267°) (L.); (274·5° i. V. at 711 mm.) (Bamberger a. Helwig, *B.* 22, 1315). S.G. $\frac{20}{}$ 1·0423. Formed by heating (α)-naphthylamine (1 mol.) with MeI (2 mols.) and MeOH (Landshoff, *B.* 11, 643; *J. pr.* [2] 17, 286; Monnet, Reverdin, a. Nölting, *B.* 12, 2305). Prepared by heating (α)-naphthylamine hydrochloride with MeOH for 8 hours at 170° (Hantzsch, *B.* 13, 1348; Friedländer, *B.* 21, 3124). Oil.

Reactions.—1. Forms a nitroso-compound which decomposes in an acid aqueous solution into (1, 4)-nitroso-naphthol and dimethylamine. 2. *Nitric acid* forms two nitro-derivatives [88°] and [128°]. — 3. By condensation with *benzoic aldehyde* in presence of $ZnCl_2$ at 110° it yields $C_6H_5.CH(C_{10}H_6NMe_2)_2$ [188°].—4. $C_6H_4NMe_2.CHO$[1:4] yields, in like manner, $NMe_2.C_6H_4.CH(C_{10}H_6NMe_2)_2$ [179°].—5. $COCl_2$, followed by Aq, yields $NMe_2.C_{10}H_6.CO_2H$ [164°].

Platinochloride $B'_2H_2PtCl_6$: yellow needles.

Methylo-iodide B'MeI. Yellowish-green flat needles, decomposed at 164° uncor. Not affected by NaOH, but Ag_2O yields a strongly alkaline hydroxide.—$(B'MeCl)_2PtCl_4$.

ar-Tetrahydride $C_6H_8\left<\begin{matrix}NMe_2:CH\\CH:CH\end{matrix}\right>$. (262°) at 721 mm. Formed by reducing the base, dissolved in isoamyl alcohol, with sodium (B. a. H.). Colourless oil. Yields a colouring matter with *p*-diazobenzene sulphonic acid. Reduces $AgNO_3$. Oxidised to adipic acid by $KMnO_4$. Yields $B'_2H_2PtCl_6$ and B'MeI [164·5°].

(β)-Naphthyl-methyl-amine.

Benzoyl derivative $C_{10}H_7.NMeBz$: [169°]; glistening plates. Formed by heating di-methyl-(β)-naphthylamine with benzoyl chloride at 180° (Hess, *B.* 18, 688).

(β)-Naphthyl-di-methyl-amine $C_{10}H_7NMe_2$ [46°]. (305° cor.). Formed by heating commercial trimethylamine with (β)-naphthol at 200° (Hantzsch, *B.* 13, 2055), and by heating (β)-naphthylamine with MeI and NaOHAq at 120° (Bamberger a. Müller, *B.* 22, 1306). Forms very soluble salts.—$B'_2H_2PtCl_6$.

Methylo-iodide $C_{10}H_7.NMe_3I$. Tables, sl. sol. cold water. With Ag_2O it yields a strongly alkaline hydroxide.

ar-Tetrahydride $C_6H_8\left<\begin{matrix}CH:CNMe_2\\CH:CH\end{matrix}\right.$. (287°) at 715 mm. Formed by reducing $C_{10}H_7NMe_3I$ dissolved in isoamyl alcohol with sodium (Bamberger a. Müller, *B.* 22, 1306). Colourless oil. Reduces auric chloride and $AgNO_3$. $FeCl_3$ gives a turbidity and a yellow colour. $K_2Cr_2O_7$ and H_2SO_4 give a yellow pp. and, on heating, a dirty-green colour. $KMnO_4$ oxidises it to adipic acid.—B'HCl.—$B'_2H_2PtCl_6$.—$B'HClHgCl_2$. [127·5°]. Needles, v. sl. sol. cold, v. sol. hot water. Picrate: needles.

ac-Tetrahydride $C_6H_4\left<\begin{matrix}CH_2.CHNMe_2\\CH_2.CH_2\end{matrix}\right.$. (166·5° at 22 mm.). Formed at the same time as the aromatic isomeride.—B'HCl: needles, v. sol. water.—$B'_2H_2PtCl_6$: orange needles, v. sol. water.

Di-(β)-naphthyl-methyl-amine $(C_{10}H_7)_2NMe$. [140°]. Formed from $(C_{10}H_7)_2NH$ and MeI at 100° (Ris, *B.* 20, 2619). Needles, m. sol. cold alcohol, insol. ligroïn.

Isomeride of naphthyl-methyl-amine *v.* NAPHTHYL-CARBINYL-AMINE.

(α)-**NAPHTHYL METHYL KETONE** $C_{12}H_{10}O$ *i.e.* $C_{10}H_7.CO.CH_3$. [34°]. (297°). Formed by the action of AcCl in presence of $AlCl_3$ on naphthalene dissolved in ligroïn (Pampel a. Schmidt, *B.* 19, 2898; Claus a. Feist, *B.* 19, 3180; *J. pr.* [2] 42, 517). Crystals, insol. water, v. sol. alcohol and ether. Oxidised by $KMnO_4$ to (α)-naphthyl-glyoxylic acid. Yellow ammonium sulphide at 220° forms $C_{10}H_7CMe\left<\begin{matrix}O\\NH\end{matrix}\right.$ [154°] (Willgerodt, *B.* 20, 2468).

Oxim $C_{10}H_7.CMe(NOH)$. [101°] (P. a. S.); [145°] (C. a. F.).

Phenyl-hydrazide $C_{10}H_7.CMe(N_2HPh)$. [146°] (P. a. S.); [173°] (C. a. F.). Needles.

Anilide $C_{10}H_7.CMe(NPh)$. [130°]. It will be seen that the melting-points of the oxim and phenyl-hydrazide of the ketone prepared by Claus are the same as those of the like derivatives of the (β)-ketone.

(β)-Naphthyl methyl ketone $C_{10}H_7.CO.CH_3$. [52°]. (301°). Formed, together with the (α)-isomeride by the action of Ac_2O on naphthalene in presence of $AlCl_3$ (Roux, *A. Ch.* [6] 12, 289; Müller a. Von Pechmann, *B.* 22, 2561). Leaflets, nearly insol. cold water. Oxidised by dilute $KMnO_4$ to (β)-naphthyl-glyoxylic acid [c. 75°], further oxidation forms (β)-naphthoic acid. Sodium-amalgam reduces it to $C_{10}H_7.CH(OH).CO_2H$ [176°].

Oxim $C_{10}H_7.C(NOH).CH_3$ [145°].

Acetyl derivative of the oxim [134°].

Phenyl-hydrazide [171°].

NAPHTHYL METHYL OXIDE *v. Methyl ether* of NAPHTHOL.

(α)-**NAPHTHYL-DI-METHYL-PYRROLE** $C_{16}H_{15}N$ *i.e.* $C_{10}H_7N\left<\begin{matrix}CMe:CH\\CMe:CH\end{matrix}\right.$. [123°]. (312°). Formed by heating its dicarboxylic acid at 250° (Knorr, *A.* 236, 309). Insol. water, v. sol. alcohol, ether, and chloroform.

(β)-Naphthyl-di-methyl-pyrrole $C_{16}H_{15}N$. [71°]. (341°). Formed in like manner.

(α)-**NAPHTHYL-DI-METHYL-PYRROLE DICARBOXYLIC ACID** $C_{18}H_{15}NO_4$ *i.e.* $C_{10}H_7N\left<\begin{matrix}CMe:C.CO_2H\\CMe:C.CO_2H\end{matrix}\right.$ [244°]. Formed by saponifying its ether, which is obtained by the action of (α)-naphthylamine on diacetyl-succinic ether (Knorr, *A.* 236, 308). Needles.—K_2A''.—BaA''.—AgHA''.

Ethyl ether Et_2A''. [91°].

(β)-Naphthyl-di-methyl-pyrrole-di-carboxylic acid $C_{10}H_7N\langle\begin{matrix}CMe:C.CO_2H\\ |\\ CMe:C.CO_2H\end{matrix}$. Its di-ethyl ether is obtained by mixing acetic acid solutions of di-aceto-succinic ether and (β)-naphthylamine (Knorr, *B.* 18, 304). Sparingly soluble in most solvents. Begins to decompose at 260° with evolution of CO_2.—BaA''.—$BaH_2A''_2$.

Di-ethyl ether $A''Et_2$: [124°]; needles.

DI-NAPHTHYL-METHYL-ψ-THIOUREA *v.* *Methyl ether* of DI-NAPHTHYL-IMIDO-THIOCARBAMIC ACID.

DI-(α)-NAPHTHYL OXIDE $(C_{10}H_7)_2O$. *Naphthyl ether.* [110°]. Formed by heating (α)-naphthol with $ZnCl_2$ or HCl (Merz a. Weith, *B.* 14, 195). Plates or tables, sol. hot alcohol and ether. May be distilled unchanged.—Picrate $C_{20}H_{14}O2C_6H_2(NO_2)_3(OH)$. [115°]. Red crystals.

Di-(β)-naphthyl oxide $(C_{10}H_7)_2O$. [105°]. Obtained by boiling (β)-naphthol with dilute (50 p.c.) H_2SO_4 (Graebe, *B.* 13, 1849), or by heating it with $ZnCl_2$ (2 pts.) at 190°, or with gaseous HCl (M. a. W.) Formed also by distilling aluminium (β)-naphthol (Gladstone a. Tribe, *C. J.* 41, 15). Pearly plates (from alcohol), sol. ether. Gives an orange colour with conc. H_2SO_4.

Picrate $C_{20}H_{14}O2C_6H_2(NO_2)_3OH$. [122°]. Small orange prisms.

DI-(α)-NAPHTHYL-PARABANIC ACID $C_{23}H_{14}N_2O_3$ *i.e.* $CO\langle\begin{matrix}N(C_{10}H_7).CO\\ N(C_{10}H_7).CO\end{matrix}\rangle$. [246°]. Formed by passing cyanogen gas into an alcoholic solution of methyl-di-(α)-naphthyl-imido-thio-carbamate and heating the crystals that separate with alcoholic HCl (Evers, *B.* 21, 973). Needles, v. sol. hot alcohol, sl. sol. ether, insol. water and dilute acids. Decomposed by boiling alcoholic potash into CO_2, oxalic acid, and (α)-naphthylamine.

(α)-NAPHTHYL PHENYL-AMIDO-METHYL KETONE $C_{18}H_{15}NO$ *i.e.* $C_{10}H_7.CO.CH_2.NHC_6H_5$. [130°]. Formed by the action of aniline on $C_{10}H_7.CO.CH_2Br$ in alcoholic solution (Pampel a. Schmidt, *B.* 19, 2899). Red crystals.

NAPHTHYL-PHENYL- compounds *v.* PHENYL-NAPHTHYL COMPOUNDS.

(α)-NAPHTHYL-DI-PHENYL METHYLENE-AMINE $C_{23}H_{17}N$ *i.e.* $C_{10}H_7.N:CPh_2$. Formed from (α)-naphthylamine and benzophenone-chloride Ph_2CCl_2 (Pauly, *A.* 187, 215). Golden plates (from ether), split up by acids into benzophenone and (α)-naphthylamine.

TRI-(α)-NAPHTHYL-PHOSPHATE $(C_{10}H_7O)_3PO$. [145°]. Prepared by heating (α)-naphthol with $POCl_3$; the yield being 65 p.c. of the theoretical (Schäffer, *A.* 152, 289; Heim, *B.* 16, 1769). Small glistening needles.

Tri-(β)-naphthyl-phosphate $(C_{10}H_7O)_3PO$. [111°]. Prepared by heating a mixture of (β)-naphthol and phosphorus-oxy-chloride; the yield being 65 p.c. of the theoretical (Heim, *B.* 16, 1768; *cf.* Schäffer). Fine white needles. Insol. water, sl. sol. cold alcohol.

NAPHTHYL-PHOSPHOROUS ACID *v.* NAPHTHALENE PHOSPHINIC ACID.

β-(α)-NAPHTHYL-PROPIONIC ACID $C_{13}H_{12}O_2$ *i.e.* $C_{10}H_7.CH_2.CH_2.CO_2H$. [148°]. Formed by reducing naphthyl-acrylic acid with sodium-amalgam (Brandis, *B.* 22, 2156). Needles (from alcohol), sol. boiling water.

(α)-NAPHTHYL-PROPYLENE-ψ-THIO-UREA $\begin{matrix}CH_3.CH.S\\ CH_2.N\end{matrix}\!\!>C.NH.C_{10}H_7$. [134°]. Formed by heating *s*-naphthyl-allyl-thio-urea [145°] with HClAq at 100° (Prager, *B.* 22, 3001). Tables, v. sol. chloroform, m. sol. ether, insol. water.—$B'_2H_2PtCl_6$. [206°].—$B'C_6H_2(NO_2)_3OH$. [192°].

NAPHTHYL-PURPURIC ACID $C_{11}H_7N_3O_4$. The K salt is formed by the action of aqueous KCy on di-nitro-naphthol (Sommaruga, *B.* 4, 94; *A.* 157, 328). The free acid is unstable. The K salt is golden-brown with metallic lustre. Potash-fusion yields benzoic, phthalic, and hemimellitic acids. The following salts were dried at 100°: NH_4A'.—KA'.—CaA'_2.—BaA'_2.

DI-(α)-NAPHTHYL-PYRAZINE TETRAHYDRIDE $C_{10}H_7N\langle\begin{matrix}CH_2.CH_2\\ CH_2.CH_2\end{matrix}\rangle NC_{10}H_7$. *Di-naphthyl-di-ethylene-diamine.* [265°]. Formed from ethylene bromide, (α)-naphthylamine, and NaOAc (Bischoff, *B.* 22, 1782). Prisms, v. sl. sol. alcohol.

Di-(β)-naphthyl-pyrazine tetrahydride. [228°]. Formed by the action of $C_2H_4Br_2$ on (β)-naphthylamine in presence of Na_2CO_3 (Bischoff, *B.* 23, 1984). Colourless crystals, insol. water, alcohol, ether, and HClAq, sol. hot HOAc.

(α)-NAPHTHYL-PYRIDINE HEXAHYDRIDE $C_{10}H_7NC_5H_{10}$. (185°–190° at 5–10 mm.). Formed by heating piperidine (2 mols.) with (α)-bromo-naphthalene (3 mols.) for 10 hours at 255° (Lellmann a. Büttner, *B.* 23, 1383). Thick yellow oil, with faint fæcal odour, rapidly becoming brown. V. sol. alcohol and ether. A solution of its hydrochloride is ppd. by $HgCl_2$, by $ZnCl_2$, and by chloride of gold.—B'HCl: groups of needles, v. sol. water.—$B'_2H_2PtCl_6$ 2aq.

(β)-Naphthyl-pyridine hexahydride. [58°]. Resembles the preceding in mode of preparation and properties. Colourless prisms, becoming grey on keeping.—B'HCl.—$B'_2H_2PtCl_6$ 6aq.

DINAPHTHYL-DIQUINONE, so-called, $C_{20}H_{10}O_4$ *i.e.* $C_6H_4\langle\begin{matrix}CO.CO.CH \quad CH.CO.CO\\ \text{———}C\text{——}C\text{————}\end{matrix}\rangle C_6H_4$. Obtained by oxidation of dinaphthyl-diquinhydrone $C_{20}H_{12}O_4$, a black powder formed by the action of dilute H_2SO_4 on (β)-naphthoquinone (Stenhouse a. Groves, *C. J.* 33, 415). Formed also by the oxidation of (β)-amido-(α)-naphthol by $FeCl_3$ or CrO_3 (Zincke a. Rathgen, *B.* 19, 2483). Small orange prisms, insol. water, v. sl. sol. other solvents. Not affected by boiling HNO_3 or by H_2SO_4.

Reactions.—1. Yields on reduction 'dinaphthyl-dihydroquinone.'—2. Distillation with *zinc-dust* converts it into dinaphthyl.—3. *Alkalis* form a green solution which, on exposure to air, changes to red from formation of $C_{20}H_{10}(OH)_2O_4$ [245°–250°] (Korn, *B.* 17, 3020).—4. $KMnO_4$ oxidises it to diphthalylic acid $C_{16}H_{10}O_6$.—5. *Aniline* forms $C_{14}H_{30}N_4O_2$ crystallising in red plates [250°] and forming a hydrochloride $C_{44}H_{30}N_4O_2H_2Cl_2$ crystallising in needles.

Iso-dinaphthyl-diquinone $C_{20}H_{10}O_4$. [250°–260°]. Formed by oxidising di-(β)-naphthyl with CrO_3 in HOAc (Staub a. Watson Smith, *C. J.* 47, 104). Amorphous yellow powder, sol. HOAc, sl. sol. most liquids. Turns brown at 215°.

NAPHTHYL - ROSINDULINE $C_{32}H_{21}N_3$ *i.e.* $C_6H_4\!<\!\genfrac{}{}{0pt}{}{C:N}{C(NC_{10}H_7).CH:C.NPh}\!>\!C_6H_4$. [247°]. Formed by heating benzene-azo-di-(α)-naphthylamine with aniline and alcohol at 165° (Fischer a. Hepp, *A.* 256, 246). Black needles, forming a blue solution in conc. H_2SO_4. Conc. HClAq at 210° splits it up into (α)-naphthylamine and rosindone $C_{22}H_{14}N_2O$.

(α)-**NAPHTHYL SILICATE** $C_{40}H_{28}SiO_4$ *i.e.* $(C_{10}H_7)_4SiO_4$. (425°–430° at 130 mm.). Needles (Hertkorn, *B.* 18, 1696).

(β)-**Naphthyl silicate.** (430° at 133 mm.). Crystalline (H.).

NAPHTHYL-SULPHAMIC ACID *v.* NAPHTHYLAMINE ν-SULPHONIC ACID.

NAPHTHYL SULPHATE.

Naphthyl-sulphuric acid $C_{10}H_8SO_4$ *i.e.* $C_{10}H_7O.SO_2.OH$. Formed by the action of $Cl.SO_2.OH$ on a cold solution of (β)-naphthol in CS_2 (Armstrong, *B.* 15, 204). It is also formed by dissolving (β)-naphthol (1 pt.) in cold H_2SO_4 (2 pts.) (Nietzki, *B.* 15, 305).—×NaA′. Slender leaflets, v. e. sol. water. Ppd. from aqueous solution by NaCl. Split up by boiling HClAq into (β)-naphthol and $NaHSO_4$. Does not react with diazo- salts.—×KA′: scales (from hot water). With PCl_5 it yields chloro-naphthalene. Bromine forms bromo-naphthol [84°].

DI-(α)-NAPHTHYL SULPHIDE $C_{20}H_{14}S$ *i.e.* $(C_{10}H_7)_2S$. [110°]. (290° at 15 mm.).

Formation.—1. By distilling a dry mixture of potassium naphthalene (α)-sulphonate and potassium sulphocyanide (Armstrong, *B.* 7, 407). 2. By distilling the lead salt of (α)-naphthyl mercaptan under diminished pressure (Krafft a. Schönherr, *B.* 22, 823).—3. By heating (α)-naphthyl mercaptan as long as H_2S is evolved (Leuckart, *J. pr.* [2] 41, 217).—4. By heating $(C_{10}H_7S)_2Pb$ with (α)-bromo-naphthalene at 235° for 4 hours (Krafft a. Bougois, *B.* 23, 3045).

Properties.—Needles, v. sol. benzene and HOAc, sl. sol. alcohol. Chromic acid in HOAc oxidises it to the sulphoxide [165°], and finally to the sulphone [187°] (Krafft, *B.* 23, 2368).

($\alpha\beta$)-**Di-naphthyl sulphide** $(C_{10}H_7)_2S$. [61°]. (290° at 15 mm.). Formed by heating the lead salt of (β)-naphthyl mercaptan with (α)-bromo-naphthalene at 230° (Krafft, *B.* 23, 2368). Lustrous leaflets (from alcohol). Oxidised by CrO_3 in HOAc to $(C_{10}H_7)_2SO_2$ [123°].

Di-(β)-naphthyl sulphide $(C_{10}H_7)_2S$. [151°]. (296° at 15 mm.). Formed by distilling the lead salt of (β)-naphthyl mercaptan under 10 mm. pressure (K. a. S.). Plates, v. sl. sol. hot alcohol, v. sol. CS_2. Oxidised by CrO_3 in HOAc to $(C_{10}H_7)_2SO_2$ [177°] (Krafft, *B.* 23, 2366).

($\alpha\alpha$)-**Di-naphthyl disulphide** $(C_{10}H_7)_2S_2$. [91°]. Formed by oxidising (α)-naphthyl mercaptan by exposing its alkaline solution to the air (Schertel, *A.* 132, 91; Leuckart, *J. pr.* [2] 41, 217). Monoclinic crystals, sl. sol. alcohol.

Di-(β)-naphthyl disulphide $(C_{10}H_7)_2S_2$. [137°] (L.); [139°] (C.). The chief product obtained by saponification of the oil which is formed by the action of potassium xanthate on (β)-diazo-naphthalene chloride (Leuckart, *J. pr.* [2] 41, 221). Formed also by reducing naphthalene (β)-sulphonic chloride with HIAq (Cleve, *B.* 21, 1100). Colourless plates, insol. water, v. sol. alcohol and ether. Reduced by zinc and H_2SO_4 to (β)-naphthyl mercaptan.

(β)-**NAPHTHYL SULPHOCYANIDE** $C_{11}H_7NS$ *i.e.* $C_{10}H_7SCN$. [35°]. Formed by the action of cyanogen chloride on $Pb(SC_{10}H_7)_2$ (Billeter, *B.* 8, 463). Decomposes on distillation. KHS forms KSCN and $HSC_{10}H_7$. Conc. HClAq forms $C_{10}H_7SH$, NH_3, and CO_2. Sodium-amalgam reduces it to sodium cyanide and $(C_{10}H_7)_2S_2$.

($\alpha\alpha$)-**DI-NAPHTHYL SULPHONE** $(C_{10}H_7)_2SO_2$. [187°]. Formed by oxidising ($\alpha\alpha$)-di-naphthyl sulphide by CrO_3 in HOAc (Krafft, *B.* 23, 2368; *cf.* Leuckart, *J. pr.* [2] 41, 218).

($\alpha\beta$)-**Di-naphthyl sulphone** $(C_{10}H_7)_2SO_2$. [123°]. Formed, together with the ($\beta\beta$)-isomeride by heating naphthalene (8 pts.) with H_2SO_4 (3 pts.) at 180° (Stenhouse a. Groves, *B.* 9, 682; Cleve, *B.* 10, 1723; *Bl.* [2] 25, 256; *cf.* Berzelius, *A. Ch.* [2] 65, 290). Formed also by oxidising the corresponding di-naphthyl sulphide (Krafft, *B.* 23, 2369). Prisms (from CS_2), m. sol. boiling alcohol and ether.

($\beta\beta$)-**Di-naphthyl-sulphone** $(C_{10}H_7)_2SO_2$. [177°]. Formed as above, and also by dissolving ($\beta\beta$)-di-naphthyl sulphide (1 pt.) in HOAc (200 pts.), warming, slowly adding a mixture of $K_2Cr_2O_7$ (3 pts.) dilute (1:3) H_2SO_4 (20 pts.) and HOAc (50 pts.), filtering, evaporating, and crystallising from alcohol (Krafft, *B.* 23, 2366). Long white needles. When heated with PCl_5 it yields (β)-chloro-naphthalene and naphthalene (β)-sulphonic chloride (Cleve, *Bl.* [2] 25, 25).

DINAPHTHYL SULPHONIC ACID *v.* DI-NAPHTHYL.

($\alpha\alpha$)-**DI-NAPHTHYL SULPHOXIDE** $(C_{10}H_7)_2SO$. [164·5°]. Formed by oxidation of ($\alpha\alpha$)-di-naphthyl sulphide with chromic acid mixture and HOAc (Krafft, *B.* 23, 2367). Formed also by oxidation of naphthylene di-naphthyl sulphoxide $C_{30}H_{20}SO$ [111°] (Ekstrand, *B.* 17, 2603). White crystals (from alcohol).

NAPHTHYL-SULPHURIC ACID *v.* NAPHTHYL SULPHATE.

NAPHTHYL SULPHYDRATE *v.* NAPHTHYL MERCAPTAN.

(α)-**NAPHTHYL-THIOCARBAMIC ACID** $C_{10}H_7NH.CO.SH$. *Methyl ether* MeA′. [122°]. Formed by the action of dilute H_2SO_4 on methyl di-naphthyl-imido-thiocarbamate [136°] (Evers, *B.* 21, 970). Needles, v. sol. dilute alcohol, insol. water, alkalis, and dilute acids. Alcoholic ammonia forms, on heating, (α)-naphthyl-urea.

Ethylene derivative

$CO\!<\!\genfrac{}{}{0pt}{}{N(C_{10}H_7)}{S.CH_2.CH_2}\!>$. [102°]. Formed by the action of dilute HClAq at 200° upon the substance $C_{10}H_7N:C\!<\!\genfrac{}{}{0pt}{}{N(C_{10}H_7)}{S.CH_2.CH_2}\!>$ (Evers, *B.* 21, 970). Needles.

(β)-**Naphthyl-thiocarbamic acid.** *Ethyl ether* $C_{10}H_7NH.CS.OEt$. [97°]. Formed by heating (β)-naphthyl thiocarbimide with alcohol at 130° (Cosiner, *B.* 14, 58). Needles or plates, v. e. sol. chloroform, m. sol. alcohol and ether.—$C_{10}H_7NAg.CS.OEt$. Ppd. by adding ammoniacal $AgNO_3$ to the alcoholic solution.

(α)-**Naphthyl-dithiocarbamic acid**

Methyl ether $C_{10}H_7NH.CS.SMe$. [185°]. Formed by heating $C_{10}H_7NH.CO.SMe$ with CS_2 (E.). Small needles; m. sol. hot dilute alcohol.

Ethylene derivative $CS<\frac{N(C_{10}H_7)}{S.CH_2.CH_2}>$ [199°]. Formed by the action of CS_2 on $CO<\frac{N(C_{10}H_7)}{S.CH_2.CH_2}>$ at 160° (Evers, *B.* 21, 972). Pearly plates (from hot alcohol).

(β)-Naphthyl-dithiocarbamic acid. *Tetrahydride.* Tetrahydronaphthylamine salt $C_{10}H_{11}NH_3S.CS.NHC_{10}H_{11}$. [142°]. Formed from the tetrahydride of (β)-naphthylamine and an ethereal solution of CS_2 (Bamberger a. Müller, *B.* 21, 857). Needles.

(β)-NAPHTHYL-THIO-SEMI-CARBAZIDE $C_{10}H_7NH.NH.CS.NH_2$. [204°]. Formed by heating (β)-naphthyl-hydrazine hydrochloride with ammonium sulphocyanide in alcoholic solution (Hauff, *A.* 253, 30; Hillringhaus, *B.* 22, 2657). Crystals; insol. water, sl. sol. cold alcohol.

(α)-NAPHTHYL-THIOCARBIMIDE $C_{10}H_7N:CS$. *Naphthyl mustard oil.* [58°]. Formed from di-naphthyl-thio-urea by distilling with P_2O_5 (Hall, *P. M.* [4] 17, 304) or by heating it with HClAq (34 p.c.) at 150° (Mainger, *B.* 15, 1414). Formed also by heating di-naphthyl-cyanamide with CS_2 at 200° (Huhn, *B.* 19, 2406). Long white needles; sol. alcohol, ether, and benzene. With naphthylamine in alcoholic solution it combines, forming di-naphthyl-thio-urea. Aniline forms phenyl-naphthyl-thio-urea.

(β)-Naphthyl thiocarbimide $C_{10}H_7NCS$. [62°]. Obtained in the same manner as its (α)-isomeride (Cosiner, *B.* 14, 61; Huhn, *B.* 19, 2407). Needles.

(β)-NAPHTHYL-THIOCARBIZINE $C_{11}H_8NS$ *i.e.* $C_{10}H_7.N<\frac{NH}{CS}$. [254°]. Formed by heating (β)-naphthyl-thio-semi-carbazide with dilute (20 p.c.) H_2SO_4 at 135° (Hauff, *A.* 253, 31). Pearly plates; insol. water, sl. sol. ether, v. sol. warm alcohol. May be sublimed.—B'HCl: needles; v. sol. hot water.—$B'H_2PtCl_6$.—$B'HNO_3$.

DI-(α)-NAPHTHYL-THIOHYDANTOÏN $C_{23}H_{16}N_2SO$ *i.e.* $C_{10}H_7N:C<\frac{N(C_{10}H_7)}{S.CH_2}>CO$. [176°]. Formed by the action of chloro-acetic acid on di-(α)-naphthyl-thio-urea (Evers, *B.* 21, 974). Plates; insol. water, v. sol. alcohol.

Di-(β)-naphthyl-thiohydantoïn. [174°]. Resembles the (α)-isomeride in mode of preparation and properties.

NAPHTHYL-THIOSINAMINE is NAPHTHYL-ALLYL-THIO-UREA (*q. v.*).

(α)-NAPHTHYL-THIO-UREA $C_{11}H_{10}N_2S$ *i.e.* $C_{10}H_7NH.CS.NH_2$. [198°]. Formed by heating naphthylamine hydrochloride with ammonium sulphocyanide (De Clermont a. Wehrlin, *C. R.* 82, 512). Small trimetric prisms (from alcohol); sl. sol. water, ether, and cold alcohol.

Acetyl derivative $C_{10}H_7NH.CS.NHAc$. [198°]. S. (alcohol) 2·5 at 78°. Formed from (α)-naphthylamine and acetyl sulphocyanide (Miquel, *Bl.* [2] 28, 103). Slender needles.

Benzoyl derivative $C_{10}H_7NH.CS.NHBz$. [173°]. S. (alcohol) 2 at 78°. Formed from (α)-naphthylamine and benzoyl sulphocyanide (Miquel, *A. Ch.* [5] 11, 326). Lustrous yellow prisms (from alcohol); insol. ether.

(β)-Naphthyl-thio-urea $C_{10}H_7NH.CS.NH_2$. [180°]. Formed by heating (β)-naphthylamine hydrochloride with potassium sulphocyanide (Cosiner, *B.* 14, 61). White trimetric plates.

Di-(α)-naphthyl-thio-urea $C_{21}H_{16}N_2S$ *i.e.* $CS(NHC_{10}H_7)_2$. [207° cor.] (E.); [197°] Brieger, *B.* 12, 1860; Huhn, *B.* 19, 2405). Formed by heating (α)-naphthylamine (100 g.) with CS_2 (50 g.) and alcohol (500 g.) for 14 hours at 75° (Delbos, *A.* 64, 371; Evers, *B.* 21, 963). Formed also by passing H_2S into a boiling solution of di-naphthyl-cyanamide $(C_{10}H_7N)_2C$ in dry benzene. Needles; almost insol. alcohol, ether, and benzene, sol. nitrobenzene. By adding HgO to its boiling solution in dry benzene it is re-converted into $C(NC_{10}H_7)_2$. MeI at 100° forms methyl di-naphthyl-imido-thio-carbamate $C_{10}H_7N:C(NHC_{10}H_7)SMe$ [136°] (*v.* DI-NAPHTHYL-IMIDO-THIO-CARBAMIC ETHERS.

Octohydride $CS(NHC_{10}H_{11})_2$. [170°]. Formed by heating (α)-naphthylamine tetrahydride with CS_2 and alcohol as long as H_2S is given off (Bamberger, *B.* 21, 1795). Needles, v. sol. alcohol, m. sol. ether.

Di-(β)-naphthyl-thio-urea $CS(NHC_{10}H_7)_2$. [193°] (C.; H.); [203° cor.] (E.). Prepared by heating (β)-naphthylamine in alcoholic solution with CS_2 for 14 hours at 75° (Cosiner, *B.* 14, 61; Evers, *B.* 21, 963). Formed also by passing H_2S into a boiling solution of *s*-di-(β)-naphthyl-cyanamide (carbo-di-(β)-naphthyl-imide) in dry cumene (Huhn, *B.* 19, 2407). White plates (from hot nitrobenzene), v. sl. sol. alcohol and ether. With MeI it forms the compound $C_{10}H_7NH.C(NC_{10}H_7).CSMe$ [110°], *v.* DI-NAPHTHYL-IMIDO-THIO-CARBAMIC ACID. By adding HgO to its boiling solution in benzene it is converted into $C(NC_{10}H_7)_2$. When heated with alcoholic NH_3 at 100° it yields (β)-naphthylamine and (β)-naphthyl-thio-urea (Gebhardt, *B.* 17, 3045). With mercuric cyanide and ammonia it yields $CN.C(NC_{10}H_7).NHC_{10}H_7$ [166°], which forms an acetyl derivative [141°] and a benzoyl derivative [188°] (Hefelmann, *C. C.* 1885, 884).

Octohydride $CS(NHC_{10}H_{11})_2$. [166°]. Formed by boiling with alcohol the product obtained by the action of CS_2 on the tetrahydride of (β)-naphthylamine (Bamberger a. Müller, *B.* 21, 858). White needles, v. sol. alcohol, v. e. sol. ether and benzene.

NAPHTHYL-TOLYL-AMINE *v.* TOLYL-NAPHTHYL-AMINE.

(α)-NAPHTHYL-UREA $C_{11}H_{10}N_2O$ *i.e.* $C_{10}H_7NH.CO.NH_2$. Obtained by saturating a solution of (α)-naphthylamine in dry ether with cyanic acid gas, and crystallising from hot alcohol (Schiff, *A.* 101, 90). Formed also, together with di-naphthyl-urea, by heating naphthylamine hydrochloride (3 pts.) with urea (1 pt.) at 150°–170° (Pagliani, *G.* 9, 30). Flat needles, nearly insol. water, m. sol. alcohol, v. sol. ether. Decomposes at 250° without previous fusion.

(β)-Naphthyl-urea $C_{10}H_7NH.CO.NH_2$. [c. 287°]. Prepared by heating urea with (β)-naphthylamine hydrochloride (Cosiner, *B.* 14, 62). White needles, sol. hot alcohol and hot water.

Di-(α)-naphthyl-urea $CO(NHC_{10}H_7)_2$. [270°].

Formation.—1. By heating the acid oxalate of (α)-naphthylamine (Delbos, *A. Ch.* [4] 21, 68), di-naphthyl-oxamide being first formed (Zinin, *A.* 108, 228).—2. By gradually heating (α)-naphthylamine (2 pts.) with urea (1 pt.) to 120° (Pagliani, *G.* 9, 28).—3. By boiling di-(α)-naphthyl-cyanamide with dilute alcohol (Huhn, *B.* 19,

2405).—4. By heating (α)-naphthylamine with carbamic ether at 185° (Smolka, *M.* 11, 200).

Properties.—Plates or needles, insol. water, sl. sol. boiling alcohol. Yields naphthylamine and no NH_3 on decomposition by KOH.

s-Di-(β)-naphthyl-urea $CO(NHC_{10}H_7)_2$. [293°] (H.); [286°] (E.).

Formation.—1. By the action of HgO on di-(β)-naphthyl-thio-urea suspended in spirit (Huhn, *B.* 19, 2406).—2. By boiling di-(β)-naphthyl-cyanamide $C(NC_{10}H_7)_2$ with dilute alcohol (H.).—3. By boiling potassium di-(β)-naphthoyl-hydroxylamine with water (Ekstrand, *B.* 20, 1360).

Properties.—Slender needles, sl. sol. alcohol, ether, benzene, and nitrobenzene.

u-Di-(β)-naphthyl-urea $(C_{10}H_7)_2N.CO.NH_2$. [193°]. Formed by heating the chloro-formyl derivative of di-(β)-naphthylamine with ammonia for an hour at 140° (Kym, *B.* 23, 428). Groups of long needles (from alcohol), sl. sol. cold alcohol).

Tetra-(β)-naphthyl-urea $(N(C_{10}H_7)_2)_2CO$. [288°] (K. a. L.); [295°] (K.). Formed by heating di-(β)-naphthylamine with $(C_{10}H_7)_2N.COCl$ at 200°–260° (Kühn a. Landau, *B.* 23, 811, 2161; Kym, *B.* 23, 1542). Prismatic needles, sl. sol. alcohol and ether, v. sol. hot benzene.

NAPHTHYL-URETHANE *v.* Naphthyl-carbamic ether.

NARCEÏNE $C_{23}H_{29}NO_9$. [134°] (Blyth); [145° cor.] (Hesse, *A.* 129, 251); [162°] (Claus a. Meixner, *J. pr.* [2] 37, 1; *cf.* Dott, *Ph.* [3] 20, 335). S. ·08 at 13°. S. (80 p.c. alcohol) ·1. Occurs in opium (Pelletier, *A. Ch.* [2] 50, 262; Couerbe, *A. Ch.* [2] 59, 151).

Preparation.—1. The aqueous extract of opium, from which morphine has been separated by Gregory's process, is mixed with ammonia, filtered, and ppd. by lead acetate. The filtrate is freed from lead by H_2SO_4, neutralised by ammonia, and evaporated. The narceïne is recrystallised from water (Anderson, *Tr. E.* 20, iii. 347).—2. A solution of the opium bases in HClAq is mixed with excess of NaOAc and allowed to stand for 24 hours. The filtrate evaporated to a small bulk on the water-bath deposits, after 24 hours, pure narceïne (Plugge, *Ar. Ph.* [3] 25, 343).

Properties.—Silky needles (containing 2aq), v. sol. hot water and alcohol, sl. sold cold water and chloroform, insol. ether. Cannot be sublimed. It loses its water of crystallisation at 100°, and at 140° gives off another H_2O (Hesse, *B.* 7, 105). It is insol. conc. KOHAq, sl. sol. dilute caustic potash and ammonia. Ppd. by $NaHCO_3$ from solutions of its salts. Inactive to light (Hesse, *A.* 176, 198). Can be extracted both from acid and alkaline solutions by shaking with benzene or chloroform (Plugge, *Ph.* [3] 20, 401). Narceïne is a somniferous poison; ·5 g. being probably a fatal dose.

Reactions.—1. *Zinc* and HClAq form a small quantity of an amorphous base $C_{23}H_{29}NO_6$ or $C_{23}H_{27}NO_6$ (Beckett a. Wright, *C. J.* 28, 701).—2. *Water* at 150° carbonises it.—3. *Chromic acid mixture* yields hemipic acid (10 p.c.) and methylamine (Beckett a. Wright, *C. J.* 29, 467).—4. *Ferric chloride* forms hemipic, but no opianic acid. Hemipic acid is also formed, though in smaller quantity, by oxidation by $KMnO_4$ or by MnO_2 and H_2SO_4. Alkaline $KMnO_4$ forms narceïc acid (*v. infra*).—5. Conc. HNO_3 yields oxalic acid.—6. Boiling *caustic potash* gives off ammonia and NMe_2, and forms a sparingly soluble acid $C_{23}H_{23}NO_8$ [210°].—7. *Potash-fusion* yields protocatechuic acid.

Tests.—1. Weak *iodine* solution colours solid narceïne dark blue, the colour not being removed by ammonia. The blue colour is destroyed by boiling water.—2. Conc. H_2SO_4 turns it brown, and then dissolves it, forming a yellow solution. Narceïne is not coloured by diluted sulphuric acid, but on heating over a water-bath a violet-red colour appears, which ultimately becomes cherry-red. If the red liquid be cooled and a trace of HNO_3 or KNO_2 be added, bluish-violet stripes appear (Plugge, *Ar. Ph.* [3] 25, 425).—3. *Erdmann's solution* gives a brown colour, turning reddish-brown on heating.—4. *Chloride of iodine* forms a greenish-yellow pp., which dissolves on heating (Dittmar, *B.* 18, 1612).—5. *Potassium chromate* gives no pp. in cold saturated solutions of salts of narceïne, but in hot solutions there is formed a pp. of narceïne chromate and free narceïne (Plugge, *Ar. Ph.* [3] 25, 793).—6. Narceïne is a feeble base, so that its salts may be titrated by standard alkali as if they contained no base (Plugge, *Ar. Ph.* [3] 25, 45).—7. When strongly heated it gives off vapours smelling like herring brine (Hesse).—8. *Chlorine-water* followed by ammonia gives a red colour.

Salts.—B'HCl (dried at 100°): concentric needles, sol. water and alcohol. S. ·36.—B'HCl 2½aq (Petit, *Bl.* [2] 18, 534). S. ·7.—B'HCl 3aq (Wright, *C. J.* 27, 109).—B'_5HCl (Petit).—$B'_{10}HCl$ (P.).—$B'_2H_2PtCl_6$ (dried at 100°): crystalline powder. [195°]. Golden needles (Claus).—$B'_2H_2PtCl_6$ 2aq: amorphous pp., changing to prisms (Hesse, *A.* 129, 250).—$B'_7(H_2SO_4)_4$ 10aq: crystals (Beckett a. Wright, *C. J.* 27, 69).—$B'_3H_2SO_4$.—$B'_4H_2SO_4$.—$B'_5H_2SO_4$.—Mercurico-chloride; oily at first, ultimately crystallising in concentric prisms (Hesse). [118°–122°] (Roser, *A.* 247, 175).—$B'_2H_2I_3$: slender needles (Jörgensen, *B.* 2, 460).—$B'HI_3$: needles (from alcohol).

Methylo-iodide B'MeI: [173° uncor.]; colourless needles (Claus a. Ritzefeld, *B.* 18, 1569).

Methylo-chloride B'MeCl: [210° uncor.]; easily soluble small white needles.—$(B'MeCl)_2PtCl_4$: nearly insoluble yellow powder.

Methylo-nitrate $B'MeNO_3$: [186° uncor.]; small white soluble needles (C. a. R.).

Ethylo-iodide B'EtI: granular crystals (Beckett a. Wright, *C. J.* 28, 703).—B'EtI 2aq. Yields alkaline B'EtOH which is readily split up into narceïne and alcohol.

Ethylo-bromide B'EtBr: [165° uncor.]; fine white soluble needles.—$(B'EtBr)CdBr_2$: small colourless needles (C. a. R.).

Ethylo-chloride B'EtCl: [170° uncor.]; small colourless needles.—$(B'EtCl)_2PtCl_4$: glistening yellow crystals [170° uncor.] (C. a. R.).—$(B'EtCl)HgCl_2aq$: [127°]; white crystalline pp.

Ethylo-nitrate $B'EtNO_3$: [155° uncor.]; long colourless silky needles, sol. water (C. a. R.).

Ethylo-oxalate $B'_2Et_2C_2O_4$: [c. 174° uncor.]; glistening needles (containing 6aq).

Benzylo-chloride $B'C_7H_7Cl$: [162° uncor.]; fine white needles, v. sol. hot water and

alcohol, insol. ether.—$(B'C_7H_7Cl)_2PtCl_4$: [165° uncor.]; yellow crystalline powder.

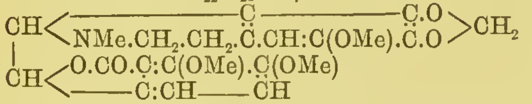
Methyl - narceïne $C_{23}H_{28}(CH_3)O_9N$. [175° uncor.]. Formed by adding KOH (2 pts.) to a boiling solution of narceïne-methylo-iodide (1 pt.) in 10 pts. of water (Claus a. Ritzefeld, *B.* 18, 1573). Fine colourless needles. V. sol. alcohol, sl. sol. water, nearly insol. ether.

Benzyl - narceïne $C_{23}H_{28}(C_7H_7)O_9N$. [169° uncor.]. Formed by the action of aqueous KOH upon narceïne-benzylo-chloride (Claus a. Ritzefeld, *B.* 18, 1574). Long white needles. V. sol. alcohol, nearly insol. water and ether. Alkaline reaction.—$(B'HCl)_2PtCl_4$ 2aq: [128° uncor.]; dark-yellow crystalline pp.

Narceïc acid $C_{15}H_{15}NO_8$. [184°]. Formed by oxidising narceïne with $KMnO_4$ (Claus a. Meixner, *J. pr.* [2] 37, 3). Prisms (containing 3aq), v. sol. alcohol, ether, chloroform, and hot water. Decomposes at 180°–200° into CO_2, di-methylamine, and di-oxy-naphthalene dicarb-oxylic acid $C_{12}H_8O_6$. Not acted upon by $FeCl_3$. —Na_3A'''.—Na_2HA''' 5aq [85°].—NaH_2A''' $4\frac{1}{2}$aq.—$Ba_3A'''_2$ 5aq.—Ag_3A'''.

ψ-Narceïne *v.* NARCOTINE.

NARCOTINE $C_{22}H_{23}NO_7$ *i.e.*



(Roser, *A.* 254, 357). Mol. w. 413. [155°] (Wynter Blyth, *C. J.* 33, 317); [176°] (Hesse). S. ·014 at 100°. S. (85 p.c. alcohol) 1 in the cold; 5 at 78° (Duflos, *B. J.* 12, 214). S. (ether) ·77 in the cold; 2·1 on boiling (Duflos); ·6 at 16° (Hesse). S. (isoamyl alcohol) ·325 in the cold. S. (benzene) 4·61 in the cold (Kubly, *J.* 1866, 823). S. (chloroform) 38 (Pettenkofer). S. (EtOAc) 1·7 (Henry). $[\alpha] = -130°$ in ethereal solution (Bouchardat, *A. Ch.* [3] 9, 213); $-185°$ in alcoholic solution; $-207°$ in chloroform at 22·5° (Hesse, *A.* 176, 192). Contained in opium to the amount of 5 to 8 p.c., and was the first alkaloid extracted therefrom (Derosne, *A. Ch.* 45, 257; Robiquet, *A. Ch.* [2] 5, 275; Dumas a. Pelletier, *A. Ch.* [2] 24, 188; 50, 269; Liebig, *A.* 6, 35; Brandes, *A.* 2, 274; Couerbe, *A. Ch.* [2] 59, 159; *A.* 17, 174; Regnault, *A. Ch.* [2] 68, 137; Wöhler, *A.* 50, 1; Blyth, *A.* 50, 29; Wertheim, *A.* 70, 71; 73, 208; Flückiger, *J.* 1869, 797).

Preparation.—1. The mother-liquor obtained in the preparation of morphine (*q. v.*) by Gregory's process is ppd. by ammonia, and the pp. recrystallised from boiling spirit (Anderson, *A.* 86, 179).—2. Opium is extracted with dilute HCl and the bases ppd. by KOH. The bases are treated with oxalic acid to ppt. papaverine, and the filtrate from acid papaverine oxalate ppd. by ammonia. The pp. is recrystallised from alcohol (Hesse, *A. Suppl.* 8, 284).—3. Conc. aqueous NaOAc added to a solution of the hydrochlorides of the opium bases throws down narcotine and papaverine. The pp. is redissolved in dilute HClAq and mixed with K_3FeCy_6 which ppts. papaverine ferricyanide. From the filtrate the narcotine is ppd. by ammonia (Plugge, *Ar. Ph.* [3] 25, 343).

Properties.—Trimetric prisms, or groups of needles. Cannot be sublimed. If cooled slowly after melting it forms slender radiating needles. Insol. cold water, m. sol. alcohol and ether. Lævogyrate in neutral solutions, dextrogyrate in acid solutions. Insoluble in aqueous potash, nearly insol. NH_3Aq. Dissolves in boiling baryta-water, but ppd. therefrom by NH_3Aq. Its solutions do not give a blue colour with $FeCl_3$. Narcotic poison, 3 g. killing a cat. Not acted upon by Ac_2O.

Reactions.—1. Distillation with conc. HIAq yields MeI (3 mols.) (Matthiessen a. Foster, *Tr.* 1863, 345; *C. J.* 16, 342; *A. Suppl.* 6, 60).—2. Conc. HClAq at 110° yields MeCl and, successively, di-methyl-nornarcotine, methyl-nornarcotine, and nornarcotine (Matthiessen a. Foster, *C. J.* 21, 257; Matthiessen, *Pr.* 17, 337; Matthiessen a. Wright, *Pr.* 17, 340). Distillation with equal volumes of H_2SO_4 and water gives $MeHSO_4$ and the three bodies last mentioned (Armstrong, *C. J.* 24, 56).—3. Boiling dilute KOHAq has no action, but potash-fusion at 200°–220° yields trimethylamine and other volatile amines (Hofmann, *A.* 75, 367).—4. Dilute *nitric acid* at 50° forms meconin, opianic acid, hemipic acid and cotarnine.—5. Distillation with HCl and platinic chloride also yields opianic acid and cotarnine. The same products are formed by oxidation with H_2SO_4 and MnO_2 (Wöhler).—6. *Water* at 140° splits it up into meconin and hydrocotarnine (Beckett a. Wright, *C. J.* 28, 583). *Sodium-amalgam* gives the same products.—7. *Iodine* acting on an alcoholic solution of narcotine forms tarconine methylo-periodide and iodo-tarconine methylo-periodide (Jörgensen, *J. pr.* [2] 2, 446; Roser, *A.* 245, 317).

Tests.—1. Conc. H_2SO_4 forms a yellow liquid which, when heated becomes orange-red and finally violet-red (Husemann, *A.* 128, 305).—2. H_2SO_4 containing a little HNO_3 gives a reddish-yellow colour.—3. Does not liberate iodine from iodic acid.—4. Does not reduce alkaline K_3FeCy_6 (Kieffer, *A.* 103, 277).—5. *Bromine* gradually added to a boiling solution of narcotine in dilute HClAq forms a rose-coloured liquid, the colour being destroyed by excess of bromine.—6. *Potassio-mercuric iodide* forms a yellowish-white pp. (Groves, *C. J.* 11, 97). Phosphomolybdic acid, picric acid, potassium sulphocyanide, and auric chloride also give pps. in solutions of salts of narcotine.—7. A solution of *potassium chromate* added to one of a salt of narcotine, ppts. free narcotine (Plugge, *Ar. Ph.* [3] 25, 793). $K_2Cr_2O_7$ ppts. narcotine bichromate.—8. Salts of narcotine require, on titration, the same amount of alkali for neutralisation as if the base were absent (Plugge, *Ar. Ph.* [3] 25, 45).—9. *Chloride of iodine* gives a curdy yellowish pp. (Dittmar, *B.* 18, 1612).

Salts.—B'HCl. Needles, v. sol. water. $[\alpha]_D = -47°$ to $-50°$ in a 2 p.c. solution containing excess of HCl. $[\alpha]_D = -104·5°$ in a 2 p.c. solution in 80 p.c. alcohol containing excess (1 mol.) of HCl (Hesse, *A.* 176, 192).—B'HCl aq (Dott, *J.* 1884, 1389).—B'_5HCl (Beckett a. Wright, *C. J.* 29, 164).—B'_7HCl.—B'_8HCl (B. a. W.).—Mercurico-chloride: white pp. (Hinterberger, *A.* 82, 311).—$B'_2H_2PtCl_6$ yellow crystalline pp. (Blyth). Decomposed by boiling water (De Coninck, *Bl.* [2] 45, 131).—$B'_2H_2PtCl_6$ 2aq (Hesse).—$B'_2H_2SO_4$ 4aq (Dott).—$B'_2H_2Cr_2O_7$.—$B'HI_3$: shining laminæ, converted by boiling alcohol into tarconine periodide $C_{12}H_{11}NO_3HI_2$

Jörgensen, *B.* 2, 460).—B'_3HOAc aq: needles (Dott). — Binoxalate: v. e. sol. water. — Cyanurate $B'H_3O_3C_3N_3$ $1\frac{1}{2}$aq; needles [c. 175°], v. sl. sol. water (Claus, *J. pr.* [2] 38, 229).

Methylo-chloride $B'MeCl$. Formed by heating narcotine with MeI and decomposing the viscid $B'MeI$ with AgCl (Roser, *A.* 247, 168). Groups of needles, v. sol. water and alcohol. Yields ψ-narceïne (*v. infra*) on distillation with aqueous NaOH.—$B'_2Me_2PtCl_6$.

Ethylo-iodide $B'EtI$ (How, *A.* 92, 327). Oil.

Ethylo-chloride ×$B'EtCl$. Yields ψ-methyl-narceïne [173°] on treatment with NaOHAq.—$B'_2Et_2PtCl_6$.

Nornarcotine $C_{19}H_{17}NO_7$. Obtained by heating narcotine with fuming HIAq (Matthiessen a. Wright, *Pr.* 17, 340). White amorphous mass, turning brown in air. Almost insol. water, insol. alcohol and ether. A concentrated solution of its hydrochloride is ppd. by HCl and also by water. The hydrochloride is tasteless, and its solution gives with KOH, Na_2CO_3, and NH_3 pps. soluble in excess, and with platinic chloride a yellow pp., quickly turning brown.

Methyl derivative $C_{20}H_{19}NO_7$. Formed by heating narcotine with HClAq for some days. White amorphous mass, almost insol. water, insol. alcohol and ether. Its solution in conc. HClAq is ppd. by water. Astringent taste. The platinochloride is a yellow pp., slowly turning brown. The ppd. base is soluble in excess of NH_3Aq and Na_2CO_3Aq but sl. sol. KOHAq.

Di-methyl-derivative $C_{21}H_{21}NO_7$. Formed by heating narcotine with HClAq for 2 hours or with diluted H_2SO_4 at 100°. White amorphous mass, almost insol. water, v. sol. alcohol, sl. sol. ether. Its solution in HClAq is ppd. by water. Its hydrochloride tastes bitter. The platinochloride is a yellow pp. The ppd. base is insol. Na_2CO_3Aq, sl. sol. NH_3Aq, sol. KOHAq.

ψ-Narceïne $C_{23}H_{27}NO_8$. [c. 175°]. Formed by boiling narcotine with MeI, decomposing the resulting methylo-iodide by AgCl, adding an equivalent amount of NaOH, and distilling with steam (Roser, *A.* 247, 169). Slender white needles (containing 3aq), v. sol. alcohol and hot water, sl. sol. cold water, insol. ether. Dissolves in aqueous KOH and NH_3, but is reppd. by CO_2. Inactive to light. Coloured blue by iodine. Conc. H_2SO_4 forms a brownish-yellow solution, turned dirty-violet on heating. Chlorine-water followed by ammonia gives a red colour. According to Roser, this body is probably identical with narceïne. $B'_2H_2SO_4$ 2aq: tufts of needles. —$B'HCl$ 3aq.—$B'_2H_2PtCl_6$. [198°]. Thin needles, insol. water.—Aurochloride: [130°]; yellowish-red needles.—Mercury double salt [123°].

ψ-Methyl-narceïne $C_{24}H_{29}NO_8$. *ψ-Homo-narceïne.* [173°]. Formed by passing steam through a mixture of narcotine ethylo-chloride and aqueous NaOH (Roser, *A.* 247, 173). White needles (containing 3aq), v. sol. water and alcohol, insol. ether. Gives a blue colour with iodine. The hydrochloride and sulphate are v. sol. water.—$B'_2H_2PtCl_6$ 2aq: small yellow needles.

Teropiammon $C_{30}H_{29}NO_{13}$. A crystalline compound, insol. water, found among the products of the action of dilute HNO_3 on narcotine (Anderson). It forms a crimson solution in H_2SO_4 and yields NH_3 and opianic acid on boiling with potash.

Cotarnine $C_{12}H_{15}NO_4$ *i.e.*

$\left[{}^2_3{:}1{:}4:5\right]CH_2{<}{}^{O}_{O}{>}C_6H(OMe)(CHO).CH_2.CH_2.NHMe$ (Roser, *A.* 254, 354). [133°].

Formation.—1. By the oxidation of narcotine by MnO_2 and H_2SO_4 (Wöhler, *A.* 50, 19; Matthiessen a. Foster, *Pr.* 11, 55; Beckett a. Wright, *C. J.* 28, 575); by platinic chloride (Blyth, *Mem. C. J.* 2, 168), by dilute nitric acid (Anderson, *C. J.* 5, 266; *A.* 86, 196) or by $K_2Cr_2O_7$ (M. a. F.).—2. By the oxidation of hydrocotarnine (Beckett a. Wright, *C. J.* 28, 580).

Properties.—Colourless needles, sl. sol. water, v. sol. alcohol and ether. Decomposed on fusion. A solution of its hydrochloride is neither ppd. by HCl nor by water. Its salts taste bitter. The freshly ppd. base dissolves in excess of aqueous NH_3 and Na_2CO_3, but is v. sl. sol. KOHAq. Decomposes on fusion. Cotarnine is not poisonous.

Reactions.—1. *Nitric acid* forms a red solution and, on heating, oxidises it to apophyllenic and oxalic acids.—2. Aqueous HCl, HI, or H_2SO_4 at 140° yields MeCl, MeI, or $MeHSO_4$ and cotarnamic acid.—3. *Zinc* and dilute HClAq yield hydrocotarnine.—4. *Bromine-water* forms $C_{12}H_{12}Br_3NO_3$ (Wright, *C. J.* 32, 533). Bromine water added to a solution of cotarnine hydrochloride forms $C_{12}H_{12}Br_3NO_3HBr$, a crystalline pp. [190°–200°] (Von Gerichten, *B.* 14, 311).

Salts. — $B'HCl$ $2\frac{1}{2}$aq: long silky crystals (Blyth).—$B'_2H_2PtCl_6$: lemon-yellow crystalline pp., or dark-red six-sided prisms.—$B'HClHgCl_2$: pale-yellow pp.—$B'HBr$ 2aq.—$B'HI$: yellow needles, sl. sol. cold water and alcohol (Roser, *A.* 249, 156).—$B'HI_3$. [142°] (Jörgensen, *J. pr.* [2] 2, 455).

Benzoyl derivative $C_{12}H_{14}BzNO_4\frac{1}{2}$aq. [123°]. Formed by shaking cotarnine with BzCl and dilute NaOHAq (Roser, *A.* 254, 335). Long needles, insol. water, v. e. sol. hot alcohol.

Oxim $C_{12}H_5NO_3(NOH)$. [168°]. Prisms, insol. water, m. sol. alcohol, sol. alkalis.—$B'HCl$: small yellow needles, v. sol. water, m. sol. alcohol.—$B'_2H_2PtCl_6$: yellow crystalline pp. decomposed by boiling water.

Oxim of the benzoyl derivative $C_8H_6O_3(CH{:}NOH).C_2H_4.NMeBz$. [166°]. Formed by warming benzoyl-cotarnine with alcoholic hydroxylamine hydrochloride. Small pointed crystals, insol. water and ether, v. sol. alcohol, sol. NaOHAq.

Methyl-cotarnine

Methylo-iodide $C_{11}H_{11}O_4NMe_3I$. Formed by warming cotarnine with MeI (Roser). Yellow needles, sl. sol. cold water and alcohol. Decomposed by boiling NaOHAq into cotarnone and NMe_3.

Methylo-chloride $C_{11}H_{11}O_4NMe_3Cl$ 3aq. Formed from the iodide and AgCl. Crystals (from water). On warming with alcoholic hydroxylamine hydrochloride at 100° it yields $C_{14}H_{19}ClN_2O_3$ 2aq or $C_8H_6O_3(CN).C_2H_4NMe_3Cl$ a crystalline body, v. sol. water, converted by hot NaOHAq into NMe_3 and $C_8H_6O_3(CN).CH{:}CH_2$

[16 The last body forms a dibromide [140°]. $(C_{1?}H_{11}O_4NMe_3Cl)_2PtCl_4$.

Bromo-cotarnine $C_{12}H_{14}BrNO_4$. [100°]. Formed by treating hydrocotarniue hydrobromide with bromine-water (Wright, *C. J.* 32, 525). Crystals (from ether); decomposing at 100°. Reduced by zinc and HClAq to bromo-hydrocotarnine [78°]. — B'HBr. — Crystals, v. sol. water. Above 200° it melts, gives off gases, and forms a small quantity of tarconine hydrobromide, together with a blue substance $C_{20}H_{14}N_2O_6HBr$ iusoluble in alcohol.

Cotarnone $C_{11}H_{10}O_4$ *i.e.* $CHO.C_8H_6O_3.CH{:}CH_2$. [78°]. Formed by warming methyl-cotarnine methylo-chloride with aqueous NaOH (Roser, *A.* 249, 163). Plates (from alcohol), slightly volatile with steam. Insol. cold water, m. sol. alcohol, ether, and HOAc.

Oxim $C_8H_6O_3(CH{:}NOH).CH{:}CH_2$. [132°]. Slender needles (from dilute alcohol).

Cotarn-lactone $C_{11}H_{10}O_6$ *i.e.*

$$CH_2{<}\substack{O\\O}{>}C_6H(OMe){<}\substack{CO.O\\CH(CH_2OH)}{>}. \quad [154°].$$

Formed by oxidising cotarnone with $KMnO_4$ (Roser, *A.* 254, 341). Prisms, sl. sol. cold alcohol or water. Forms with baryta the salt $Ba(C_{11}H_{11}O_7)_2$ 5aq.

Acetyl derivative $C_{11}H_9AcO_6$. [174°].

Benzoyl derivative $C_{11}H_9BzO_6$. [184°].

Cotarnic acid $C_{10}H_8O_7$ *i.e.*

$$CH_2{<}\substack{O\\O}{>}C_6H(OMe)(CO_2H)_2\left[\tfrac{1}{2}{:}3{:}5{:}6\right]. \quad [178°].$$

Formed by oxidising cotarnone or cotarn-lactone with aqueous $KMnO_4$ (Roser, *A.* 249, 165; 254, 345). Plates. Forms, on melting, the anhydride $C_{10}H_6O_6$ [162°]. On heatiug with P and HIAq it yields gallic acid. HClAq at 100° forms $CH_2{<}\substack{O\\O}{>}C_6H_2(OMe)CO_2H$ [210°]. Bromine in HOAc produces the compound $CH_2{<}\substack{O\\O}{>}C_6Br_3(OMe)$ [160°].

Salts.—KHA″$2\frac{1}{2}$aq: needles, v. sol. water. —BaA″: plates.—Ag_2A''.

Hydrocotarnine $C_{12}H_{15}NO_3$ *i.e.*

$$CH_2{<}\substack{O\\O}{>}C_6H(OMe){<}\substack{CH_2.NMe\\CH_2.CH_2}. \quad [50°] \text{ (H.)};$$

[55°] (B. a. W.). Occurs in opium (Hesse, *A. Suppl.* 8, 326). Formed by reducing cotarnine with zinc and HClAq, and, together with meconin, by the action of zinc and HClAq on narcotine (Beckett a. Wright, *C. J.* 28, 577). It is also formed in small quantity (2 to 5 p.c.) in the preparation of opianic acid by the oxidation of narcotino. Monoclinic prisms (from ether), v. sol. alcohol and benzene. Tho crystals contain water of crystallisation ($\frac{1}{2}$aq). Conc. H_2SO_4 forms a yellow solution, changing on heating to crimson and, finally, to a dirty violet colour. Easily oxidised to cotarnine. Not attacked by Ac_2O. Bromine added to a solution of its hydrobromide forms $C_{12}H_{14}BrNO_3$ [78° cor.], which yields the crystalline salts $C_{12}H_{14}BrNO_3HBr$ and $(C_{12}H_{14}BrNO_3)_2H_2PtCl_6$.

Salts.—B'HCl aq.—$B'_2H_2PtCl_6$.—B'HI. S. 2 at 18°.—B'HBr $1\frac{1}{2}$aq.

Ethylo-iodide B'EtI. White micaceous plates, sl. sol. water. Yields $(B'Et)_2CO_3$ 4aq, B'EtCl [100°], both crystallino, and $(B'EtCl)_2PtCl_4$.

Acetyl-hydrocotarnine-acetic acid $C_{16}H_{19}NO_6$ [201°]. Formed by boiling cotarnine (1 pt.) with acetic anhydride (10 pts.) for $1\frac{1}{2}$ hours. Small needles. Sol. alcohol and benzene, sl. sol. boiliug water, insol. cold water, and ether.—A'Ag: white pp.—A'_2Ca: very soluble small needles.

Ethyl ether A'Et: [113°]; white feathery needles (Bowman, *B.* 20, 2431).

Oxy-hydrocotarnine methylo-iodide

$$CH_2{<}\substack{O\\O}{>}C_6H(OMe){<}\substack{CH(OH).NMe_2I\\CH_2\text{——}CH_2}.$$

Methyl derivative $C_8H_6O_3{:}C_3H_5(OMe)NMe_2I$. [173°]. Formed by the action of MeI in the cold on a solution of cotarnine in MeOH (Roser, *A.* 254, 360). Yellow needles, v. sol. hot water and alcohol. Ppd. unchanged by adding NaOH to its warm aqueous solution. Boiling with water and Ag_2O expels $NHMe_2$.—$(C_{14}H_{20}NO_4Cl)_2PtCl_4$: orange pp.

Ethyl derivative $C_{11}H_{11}O_3(OEt)NMe_2I$. [168°]. Formed by the action of MeI on a cold solution of cotarnine in EtOH. Plates, v. e. sol. water and alcohol.

Isobutyl derivative $C_{13}H_{17}O_3N(OEt)I$. [120°]. Formed from cotarnine, MeI, and isobutyl alcohol. Plates (from water).

Cotarnamic acid $C_{11}H_{11}NO_3$. Formed by heating cotarnine with aqueous HCl at 140° (Matthiessen a. Foster, *A. Suppl.* 2, 379; Gerichten, *B.* 14, 310). Yields apophyllenic acid on oxidation by dilute HNO_3.—$C_{11}H_{11}NO_3HCl$ aq. White needles, sl. sol. cold water. On treatment with nitrous acid or on exposure to air its solution becomes green, with red fluorescence, and exhibits a spectrum resembling that of chlorophyll.

Tarconine $C_{11}H_9NO_3$. Formed by heating bromo-cotarnine hydrobromide at 200° (Wright, *C. J.* 32, 535) or tarconine methylo-chloride with conc. HClAq for 4 hours at 150° (Roser, *A.* 245, 321). Ppd. from solutions of its salts by KOH, but not by Na_2CO_3. Its hydrochloride heated at 200° forms a blue base $C_{20}H_{14}N_2O_6$, forming the blue salts $B'_4H_3Br_3$ and $B'_2H_2SO_4$.—*Salts*: B'HCl $1\frac{1}{2}$aq: needles, v. e. sol. water and alcohol.—$B'_2H_2PtCl_6$: insol. alcohol.

Methylo-iodide B'MeI. Formed by the action of H_2S on the periodide which is formed by boiling narcotine in alcoholic solution with iodine and some HCl. Tufts of yellow needles (from water or alcohol).—$B'MeI_3$. [160°]. Reddish-brown needles (from alcohol or HOAc).—$B'MeI_7$ (Jörgensen).—$B'MeBiI_4$.

Methylo-chloride B'MeCl: yellow needles.—$(B'MeCl)_2PtCl_4$: yellow crystalline pp., sl. sol. water.—$B'HAuCl_4$.

Bromo-tarconino $C_{11}H_8BrNO_3$ *i.e.*

$$C_1H_3BrO.C_5H_3N{<}\substack{CO\\CH_2}{>}O. \quad [235°\text{–}238°].$$

Formed by heating tho hydrobromide of the compound $C_{12}H_{12}Br_3NO_3$ (*v. Cotarnine*, Reaction 4) with water at 180° (Wright; Gerichten, *A.* 210, 84). Orango-red needles (containing 2aq), becoming crimson and anhydrous at 100°. Sl. sol. cold water, insol. ether. Water at 160° splits it up into cuprouino and tarnino. Conc. HClAq at 120° forms nartic acid, tarnine, CO_2, and CO. Chromic acid mixture yields bromoform and apophyllenic acid. Bromine-water added to a solution of its hydrochloride yields cuprine, bromo-apophyllenio acid, and dibromo-apophyl-

lin. Distillation over soda-lime yields pyridine.—B'HCl 2aq: crystals, sl. sol. cold water.—B'HBr 2aq.—$B'_2H_2PtCl_6$: needles (from hot conc. HClAq).

Methylo-chloride $C_{11}H_8BrNO_3MeCl$: slender needles, v. e. sol. water, m. sol. alcohol.—$(B'MeCl)_2PtCl_4$.—$B'MeAuCl_4$.

Methylo-bromide $C_{11}H_8BrNO_3MeBr$. Formed by the action of bromine-water on an aqueous solution of tarconine methylo-chloride, the perbromide first formed being decomposed by H_2S (Roser, *A.* 245, 324). Long needles (containing aq), changing on standing to flat prisms.—$B'MeBr_3$. [165°]. Yellow rectangular plates (from alcohol or HOAc).

Methylo-iodide $C_{11}H_8BrNO_3MeI$. [204°]. Formed from bromo-tarconine and MeI (Gerichten, *A.* 210, 170). Yellow needles, sol. water, insol. ether. Turns brown at 170°. Boiling baryta-water converts it into formic aldehyde and methyl-bromo-tarconic acid. Moist Ag_2O forms the hydroxide crystallising in small red needles.

Ethylo-iodide $C_{10}H_8BrNO_3EtI$. [206°]. Formed from ethyl iodide and bromo-tarconine. Yellow needles. Yields $(B'EtCl)_2PtCl_4$.

Iodo-tarconine $C_{11}H_8INO_3$. Formed by heating its methylo-chloride at 180° (Roser, *A.* 245, 319). Crystallises from water in yellowish-red needles (containing aq), becoming dark red on drying.—B'HCl 2aq: silky yellow needles, v. sol. water, sl. sol. HClAq.

Methylo-chloride $C_{11}H_8INO_3MeCl$ aq. Formed from the methylo-iodide and AgCl. Yellowish-white needles (from alcohol), m. sol. water.—$(B'MeCl)_2PtCl_4$: needles, sl. sol. hot water.—$B'MeAuCl_4$: needles (from hot water).

Methylo-iodide $C_{11}H_8INO_3MeI$. Formed by the action of iodine on narcotine in alcoholic solution, the resulting periodides being decomposed by H_2S (Roser, *A.* 245, 317). Yellow needles, changing on standing to prisms; almost insol. cold water, sl. sol. hot alcohol.—$B'MeI_3$. [171°]. Needles, sl. sol. alcohol.

Methyl-tarconic acid $C_{11}H_{11}NO_3$. [244°]. Formed from the aqueous solution obtained by the action of Ag_2O and water on tarconine methylo-chloride by boiling alone or with baryta (Roser, *A.* 245, 322; 254, 366). Not a true homologue of tarconic acid. Thin yellow needles (containing 2aq), v. sol. hot water, alcohol, mineral acids, and KOHAq, insol. ammonia.—$C_{11}H_{11}NO_3HCl$aq: white prisms or needles; turns yellow on drying at 100°.—$C_{11}H_{11}NO_3H_2SO_4$ 3aq: white prisms.—$(C_{11}H_{11}NO_3)_2H_2SO_4$ 6aq: yellowish crystals.

Bromo-methyltarconic acid $C_{11}H_{10}BrNO_3$. [233°]. Formed by boiling bromo-tarconine methylo-hydroxide with baryta-water (Gerichten, *A.* 210, 79; Roser, *A.* 245, 326). The ppd. Ba salt is decomposed by H_2SO_4 or HOAc. Yellow prisms (containing 2aq), insol. cold water and ether, sl. sol. hot alcohol. Darkens at 215°. Heated with conc. HClAq it yields MeCl, HBr, and tarconic acid.—CuA'_2.—BaA'_2: yellow pp.—$(HA'HCl)_2PtCl_4$: needles, m. sol. dilute HCl.

Ethyl-bromo-tarconic acid $C_{12}H_{12}BrNO_3$. [225°]. Formed by the action of baryta on bromo-tarconine ethylo-iodide (or ethylo-hydroxide) (Gerichten, *A.* 212, 182). Yellow needles (containing 2 aq), v. sl. sol. cold water, v. sol. alcohol, insol. ether. Its aqueous solution is neutral. Conc. H_2SO_4 forms a yellow solution. Conc. HClAq converts it, on heating, into EtCl, HBr, and tarconic acid.—HA'HCl: yellow needles.—$(HA'HCl)_2PtCl_4$.—$Cu'A_2$.

Tarconic acid $C_{10}H_7NO_3$. Formed by heating bromo-methyl-tarconic acid with conc. HClAq at 155° (Gerichten, *A.* 212, 184). Slender yellow needles, turning brown in air. Its alkaline solution is brown, becoming greenish-blue on standing. It reduces $AgNO_3$ in the cold.—HA'HCl: prisms, m. sol. hot water, insol. cold alcohol. $FeCl_3$ colours its solution red.

Nartic acid $C_{20}H_{16}N_2O_6$. *Nartine.* Formed by heating bromo-tarconine or tarnine with conc. HClAq at 130° (Gerichten, *A.* 212, 194; 212, 170). Yellow needles, decomposing at 200° without melting. Turns brown in air. NaOH does not ppt. it from acid solutions. Its solution in NaOHAq turns greenish-blue when exposed to air. Reduces $AgNO_3$. $KMnO_4$ oxidises it to a pyridine carboxylic acid. On distillation with soda-lime it yields pyridine.—$H_2A''H_2Cl_2$. [above 275°]. Yellow needles, m. sol. water.—$H_2A''HCl$: yellow needles, sl. sol. water.

Tarnine $C_{11}H_9NO_4$. [above 290°]. Formed by heating bromo-tarconine with water at 130° (Gerichten). Orange needles (containing $1\frac{1}{2}$aq) m. sol. hot water and dilute alcohol, insol. ether—×B'HCl: yellow needles, sol. water.—$B'_2H_2PtCl_6$. Decomposed by boiling water.

Cupronine $C_{20}H_{18}N_2O_6$. Formed, together with tarnine, by heating bromo-tarconine with water at 140° (Gerichten, *B.* 14, 315; *A.* 210, 190°). Black powder, insol. hot water, alcohol, and ether. Forms a brown solution in aqueous NaOH or Na_2CO_3. Conc. H_2SO_4 forms a magenta-red solution, changing to violet on dilution. Conc. HClAq does the same.—B'HCl: coppery needles.—B'HBr: bluish-green needles with coppery lustre, sl. sol. water, forming a blue solution.

Cuprine $C_{11}H_7NO_3$. Formed by the action of bromine on a solution of bromo-tarconine hydrobromide (Gerichten, *A.* 210, 89). Minute blue needles with coppery lustre, sol. water and alcohol, insol. ether. Weak base, the hydrochloride crystallising in concentric groups of needles, the platinochloride being a deep-blue flocculent pp.

Apophyllenic acid is the mono-methyl ether of PYRIDINE DICARBOXYLIC ACID.

Di-bromo-apophyllin *v.* vol. i. p. 553.

Oxy-narcotine $C_{22}H_{23}NO_8$. Crystals which remain undissolved in the process of purifying narceïne (Beckett a. Wright, *C. J.* 29, 461). Small crystals (from alcohol), v. sl. sol. water and alcohol, insol. ether, nearly insol. benzene and chloroform. Ppd. from solutions of its salts by NaOH and Na_2CO_3, but redissolved in excess. Oxidised by $FeCl_3$ to hemipic acid and cotarnine.—B'HCl 2aq: crystals.—$B'_2H_2PtCl_6$.

NARINGIN $C_{21}H_{26}O_{11}$. *Aurantiin. Hesperidine.* [171°]. S. ·33 in the cold. $[\alpha]_D = -84·5$ in aqueous solution; $-87·6$ in alcoholic solution (W.); $[\alpha]_j = -64·6$ (H.). Occurs in the flowers and other parts of *Citrus decumana.* The dry orange-blossoms contain about 2 p.c. It crystallises on cooling from the liquor left in the still after distilling over the oils with steam (Hoffmann, *Ar. Ph.* [3] 14, 139; Will, *B.* 18, 1311;

20, 295). White crystals (containing 4aq), nearly insol. cold water, sol. alcohol, insol. ether. Has a very bitter taste. Split up by dilute H_2SO_4 (3 p.c.) at 95° quantitatively into naringenin and isodulcite. It dissolves in alkalis with a yellowish-red colouration. Ferric salts produce a brownish-red colouration with dilute aqueous solutions. By sodium-amalgam it is converted into a colouring matter which dissolves in alcohol with a red colour and bluish fluorescence.

Naringenin $C_{15}H_{12}O_5$ probably [4:1] $C_6H_4(OH).CH:CH.CO.O.C_6H_3(OH)_2$ [1:3:5]. [248°]. Formed, together with isodulcite, by heating naringin with dilute (2–3 p.c.) H_2SO_4 on the water-bath. Glistening colourless, tasteless, and odourless crystals. V. sol. alcohol, ether, and benzene. Dissolves in alkaline hydrates forming yellow solutions, and is reprecipitated by CO_2. Ferric salts give a brown-red colouration. By sodium-amalgam it is converted into a colouring matter which dissolves in alcohol with a red colour and bluish fluorescence. By boiling with concentrated aqueous NaOH it is decomposed into phloroglucin and *p*-coumaric acid (Will, *B.* 18, 1322; 20, 297).

Naringenic acid is *p*-Coumaric acid.

NARTIC ACID *v.* Narcotine.

NATALOÏN *v.* Aloïn.

NEODYMIUM. The name given by Auer von Welsbach to that constituent of didymium which yields rose-coloured salts (*v.* Didymium, vol. ii. p. 383; *cf.* Metals, rare, this vol. p. 240).

NEOSSIDINE *v.* Proteïds, *Appendix C.*

NEOSSINE *v.* Proteïds, *Appendix C.*

NERIODOREÏN. A bitter yellow powder, extracted by alcohol from the bark and wood of *Nerium odorum*, an Indian plant prescribed for leprosy (Greenish, *Ph.* [3] 11, 873). It is sol. water, insol. chloroform. Its solution is ppd. by tannin and by ammoniacal lead acetate, and reduces Fehling's solution.

Neriodorin. A bitter resin, accompanying the preceding body, sl. sol. water and alcohol, v. sol. $CHCl_3$.

NEURIDINE $C_5H_{14}N_2$. A product of the putrefaction of flesh, appearing on the second day and disappearing about the fourth day (Brieger, *B.* 16, 1187, 1405; Bocklisch, *B.* 18, 86; Gautier, *Bl.* [2] 48, 12). It also occurs in fresh human brain (Brieger, *J. Th.* 1884, 92). Gelatinous mass with disgusting smell, v. e. sol. water, insol. alcohol and ether. Very poisonous (G.). Its solution is ppd. by $HgCl_2$ and by lead acetate. Yields di- and tri- methylamine on boiling with NaOHAq.—$B''H_2Cl_2$: needles, v. sol. water, insol. alcohol and ether.—$B''H_2PtCl_6$.

NEURINE $C_5H_{15}NO_2$ *i.e.* $CH_2(OH).CH_2.NMe_3OH$. *Choline. Di-methyl-oxy-ethyl-amine methylo-hydroxide. Tri-methyl-oxethyl-ammonium hydroxide. Sincaline.*

Occurrence.—In cotton seeds (Böhm, *J. pr.* [2] 30, 37); in putrefying flesh (Gautier, *Bl.* [2] 48, 13); in germinating pumpkin sprouts (E. Schulze, *H.* 11, 365); in the seeds of *Trigonella Fœnum-græcum* (Jahns, *B.* 18, 2518); in the seeds of vetch, *Vicia sativa* (Schulze, *B.* 22, 1827); in hops and beer (Griess a. Harrow, *C. J.* 47, 298; *B.* 18, 717); in areca nuts (Jahns, *B.* 23, 2972); in the fly agaric (Harnack, *J.* 1876, 803); in herring brine (Bocklisch, *B.* 18, 1923); in ergot of rye (Brieger, *H.* 11, 184); and in beet-root juice (Lippmann, *B.* 20, 3201).

Formation.—1. By boiling the bile of pigs or oxen with baryta (Strecker, *C. R.* 52, 1270; *A.* 123, 353; Dybkowsky, *J. pr.* 100, 163; Hüfner, *J. pr.* [2] 19, 302).—2. By boiling ox-brain with baryta (Liebreich, *A.* 134, 29; Baeyer, *A.* 140, 306).—3. By extracting yolk of egg with ether and alcohol, evaporating the extract, and boiling the residue with baryta (Diaconoff, *J.* 1867, 776; 1868, 730). In this preparation two similar bases occur, containing 34 and 32 p.c. Pt in their platinochlorides (Hundeshagen, *J. pr.* [2] 28, 247).—4. Together with glycero-phosphoric acid, oleïc, and palmitic acids by the action of alkalis on lecithin (Liebreich; Gobley, *C. R.* 70, 1297; Bokay, *H.* 1, 157; 12, 148).—5. Together with sinapic acid and barium sulphocyanide, by heating sinapine sulphocyanide with baryta-water (Claus a. Keesé, *Z.* [2] 4, 46).

Syntheses.—1. By heating trimethylamine (5 g.) with glycolic chlorhydrin (10 g.) at 100°; the resulting chloride $HO.CH_2.CH_2.NMe_3Cl$ being decomposed by moist Ag_2O (Wurtz, *C. R.* 65, 1015; 68, 1434; *A. Suppl.* 6, 116).—2. By the union of ethylene oxide with trimethylamine (Wurtz, *A. Suppl.* 6, 201).

Properties.—Strongly alkaline syrup, decomposed on boiling in concentrated aqueous solution into glycol and trimethylamine. Conc. HIAq and P at 140° forms $C_2H_4I.NMe_3I$. Weaker HIAq yields $C_2H_4I.NMe_3Cl$. Yields muscarine and betaïne on oxidation. Not poisonous.

Salts.—$C_2H_4(OH)NMe_3Cl$. Dimorphous: usually as long needles, sometimes in thin trimetric plates.—$(C_2H_4(OH)NMe_3Cl)_2PtCl_4$. Trimorphous: orange prisms (from warm saturated solution), reddish-brown trimetric tablets from a cold saturated solution, or regular octahedra from a solution containing 15 p.c. of alcohol. The first and third forms left in contact with their mother liquid change into the second form (Hundeshagen, *J. pr.* [2] 28, 245).—$(C_2H_4(OH)NMe_3Cl)AuCl_3$: yellow needles, sl. sol. cold water.—$C_2H_4(OH)NMe_3I$. Formed from $C_2H_4(OH)NMe_2$ and MeI (Knorr, *B.* 22, 1116).

Acetyl derivative of the chloride $C_2H_4(OAc).NMe_3Cl.—C_7H_{16}NO_2ClAuCl_3$: nodules.

NEURO-KERATIN *v.* Proteïds, *Appendix C.*

NICKEL. At. w. 58·6. Mol. w. unknown, as element has not been gasified. [c. 1400°–1420°] (Schertel, *N.* 22, 543); [c. 1450°] (Pictet, *C. R.* 88, 1317). S.G. 8·97 to 9·26 (Rammelsberg, *J.* 2, 282; for other values *v.* Clarke's *Table of Specific Gravities* [new ed.], 12). S.H. 14° to 97° ·10916 (Regnault, *A. Ch.* [3] 63, 1). $V_t = V_0 (1 + 3 \times \cdot 00001279t)$ $t = 40°$ (Fizeau, *C. R.* 68, 1125). E.C. at 0° (Hg at 0° = 1) 7·374 (Matthiessen a. Vogt, *P. M.* [4] 26, 242). S.V.S. c. 6·5. H.C. $[Ni^2, O^3, 3H^2O] = 120{,}380$ (*Th.* 3, 307). For spectrum of Ni (ultra-violet) *v.* Liveing a. Dewar, *Pr.* 43, 430.

Occurrence.—In some meteorites, from 3 to 8 p.c. associated with ·2 to 1 p.c. of Co. In the sun's atmosphere (Cornu, *C. R.* 86, 983). Ni has been found, to the extent of ·75 p.c., in a Pt ore from the Ural (Terreil, *C. R.* 82, 1116). Chiefly as *copper-nickel* Ni_2As_2, *white-nickel* $NiAs_2$, and Mg-Ni silicate, *garnierite*. Ni antimonide, arsenate, oxide, sulphide, carbonate, &c., also occur, chiefly in combination with com-

pounds of Co, Fe, Sb, and Bi. Ni compounds are always present in Co ores, and Co is almost invariably a constituent of Ni ores. Ni compounds have been known to the Chinese for centuries; Ni forms a constituent of Chinese armour. Copper-nickel was known to the German miners in the Middle Ages; having in vain attempted to extract Cu from this mineral, they gave it the name of *kupfer-nickel*, or false copper. In 1751 Cronstedt showed the mineral to contain a special metal, to which he gave the name of nickel. The metal was obtained in impure condition by Cronstedt, and examined by Bergmann, Richter, and others. Fleitmann prepared larger quantities of Ni, and applied it to coat iron and steel. Böttger, c. 1840, introduced the practice of electro-nickel-plating; this application of Ni has become an important trade since c. 1869.

Formation.—Copper nickel, or *speiss* (a by-product in the production of smalt), is powdered and roasted (to remove As and oxidise Ni), again roasted with charcoal, dissolved in HNO_3Aq, saturated with H_2S, and the filtrate is ppd. by Na_2CO_3; the Ni is separated from the Fe and Co in the pp. by different processes (*v. Preparation*); the Ni is ppd. by alkali as $NiO.xH_2O$, the pp. is dehydrated by heat, and reduced by C or in H. An ammoniacal solution of Ni-NH_4 sulphate is sometimes decomposed by electrolysis.

Preparation.—A salt of Ni, tolerably free from Co, is obtained by such a method as the following from arsenical Ni sulphide, or *speiss*; speiss is a deposit formed in the pots in which roasted Co arsenide, mixed with *copper-nickel*, is fused with K_2CO_3 and quartz, in the preparation of smalt. The roasted ore, or *speiss*, is fused with chalk and fluorspar; the slag being poured off, the metal is powdered and roasted for a long time in a reverberatory furnace till fumes of As_2O_3 cease to come off; the product is dissolved in HClAq, the solution is diluted, bleaching powder is added to oxidise the Fe salts, and milk of lime to ppt. Fe_2O_3 with As oxide; the filtrate is acidified and ppd. by H_2S, the filtrate from this pp. is heated with bleaching powder to ppt. Co oxide, and the Ni remaining in solution is ppd. as oxide by milk of lime (Louyet, *J. Ph.* [3] 15, 204; for other methods *v.* Wagner, *Berg und Hüttenm. Zeit.* 1870. 134; Gilchrist, *B.* 16, 264; Donath, *D. P. J.* 236, 327; Wöhler, *P.* 6, 227; Cloez, *J.* 1857. 619; *v.* also Dictionary of Applied Chemistry).

Impure Ni may be purified by dissolving in HClAq with addition of HNO_3, evaporating to dryness, dissolving in water, acidulating with HClAq, boiling with excess of $NaHSO_3$ (to reduce As_2O_5 to As_2O_3), saturating the warm liquid with H_2S (after SO_2 is all removed), filtering after 12 hours or so, evaporating the filtrate to dryness, dissolving the residue in water, filtering, treating the filtrate with Cl and then ppg. Fe and Co by $BaCO_3$, removing excess of Ba by dilute H_2SO_4Aq, filtering, and ppg. Ni as carbonate by Na_2CO_3 (Cloez, *J.* 1857. 619). After ppg. As, Cu, Sb, Pb, and Bi by H_2S, the filtrate may be much concentrated and Ni ppd. as oxalate, by addition of oxalic acid (Deville, *A. Ch.* [3] 46, 82). Winkler (*Fr.* 6, 18) boils a solution of commercial $NiCO_3$ with NaClO till all Co is ppd., this occurs only when a large quantity of Ni is also thrown down; he filters, ppts. by H_2S, boils the filtrate, and ppts. $NiCO_3$ by addition of Na_2CO_3. Co is the most difficult impurity to separate from Ni salts; the most effectual method is to dissolve in HNO_3Aq, concentrate, neutralise by KOHAq, mix with KNO_2Aq, strongly acidify with acetic acid, and allow to stand for a few days, when the Co is completely ppd. as Co-K nitrite, and the filtrate contains the Ni (*cf.* Zimmermann, *A.* 232, 324).

Ni is obtained from $NiCO_3$ (or $NiO.H_2O$ ppd. from solutions by KOHAq) by washing thoroughly, spreading out to dry, heating till CO_2 is all removed, and then reducing by H, at c. 270 (Müller, *P.* 136, 51), or by heating with C; the latter method is conducted by making the NiO into a paste with oil, placing this in a crucible lined with charcoal, and heating in a powerful air- or blast-furnace.

$NiCO_3$ may be dissolved in HClAq, the solution evaporated to dryness, the residue of $NiCl_2$ thoroughly dehydrated, then sublimed in a porcelain tube in a stream of Cl, and finally reduced by heating in H (Winkler, *Fr.* 6, 18).

NiC_2O_4 yields Ni when heated out of contact with air; this may be done by heating under a layer of pounded glass which does not contain any heavy metal.

Ni is also obtained by electrolysing solutions of its salts, using a weak current; the best solution to use seems to be an ammoniacal one of Ni-NH_4 sulphate (*v.* Becquerel, *C. R.* 55, 18; *cf.* Zimmermann, *A.* 232, 324).

Properties.—A very lustrous metal; white, with a slight greyish-yellow tinge. Hard; easily polished; ductile, malleable, and very tenacious. By heating in a porcelain oven, crystals of Ni, apparently regular, have been obtained. Slightly magnetic, but less so than Fe or Co. Ni obtained by reduction of NiO by charcoal usually contains a little C; such C-containing Ni is softer and less malleable than the purer metal (Boussingault, *Chem. Ind.* 1878. 130). As obtained by reducing NiO by H, or by heating NiC_2O_4, Ni forms a greyish-black, somewhat porous, pyrophoric powder. As obtained by reducing $NiCl_2$ in H, the metal forms a compact sponge, and also lustrous leaflets (Winkler, *Fr.* 6, 18; Gard, *J.* 1877. 266). By electrolysis of Ni solutions by a very weak current, Ni is obtained as coherent, lustrous, white plates (Becquerel, *C. R.* 55, 18). After fusion of large quantities of Ni, the metal becomes porous and crystalline, and loses its ductility; this is probably due to absorption of gases, and may be prevented by adding $\frac{1}{8}$ p.c. of Mg (Fleitmann, *B.* 12, 454).

Ni shows *passivity*, *i.e.* under certain conditions it is unacted on by HNO_3Aq. According to Saint-Edme (*C. R.* 106, 1079), commercial sheet Ni is passive in ordinary HNO_3Aq, and passive Ni remains passive when heated to bright redness in H, whereas Fe loses its passivity (*cf. Passivity of iron*, under Iron, this vol. p. 52).

Ni is a metallic element. The oxides are basic, or react as peroxides; NiO forms a series of corresponding salts; Ni_2O_3 probably forms salts by reacting with acids, but these salts are reduced very easily to salts of NiO. Ni is closely related in its chemical properties to Co; it is classed with Co and Fe, and also shows analogies with Mn; *v.* Iron group of elements, this vol. p. 65. No Ni salts are known correspond-

ing with the cobalto- and cobalti-cyanides, M_4CoCy_6 and M_3CoCy_6; nor are nickel-ammonio-bases known analogous with the cobaltamines, although some Ni compounds, *e.g.* the haloid compounds, combine with NH_3. The ultra-violet spectra of Ni and Co do not exhibit much analogy (*v.* Liveing a. Dewar, *Pr.* 43, 430).

The at. w. of Ni has been determined (1) by reducing NiO in H (Erdmann a. Marchand, *A.* 82, 76; Russell, *C. J.* [2] 1, 51); (2) by analysing Ni oxalate (Schneider, *P.* 101, 387; 107, 605; 130, 303); by determining Cl in $NiCl_2$ (Dumas, *A. Ch.* [3] 55, 149); (3) by ppg. $NiSO_4Aq$ by $BaCl_2Aq$ (Sommaruga, *W. A. B.* 54 [2] 57); (4) by the reaction of $AuCl_3Aq$ on Ni, and determining the Au ppd. (Winkler, *Fr.* 6, 22; *cf.* Krüss a. Schmidt, *B.* 22, 11; but *v.* also Winkler, *B.* 22, 890); (5) by decomposing by heat strychnine-Ni cyanide and brucine-Ni cyanide (Lee, *C. N.* 24, 237); (6) by dissolving Ni in HClAq, and measuring H evolved (Russell, *C. J.* [2] 7, 294); (7) by determining S.H. of Ni, the result obtained shows that 58·6, and not a multiple of this number, is the at. w.; this result has been confirmed recently; (8) by determining V.D. of gaseous $Ni(CO)_4$ (Mond, Langer, a. Quincke, *C. J.* 57, 749).

Alleged decomposition of nickel.—Krüss a. Schmidt (*B.* 22, 11) found that by repeatedly treating NiS, prepared from the ordinary sulphate, with NH_4 sulphide, until the latter was no longer coloured brown, a bright-yellow residue was obtained; from this residue they prepared various salts, which they regarded as compounds of a new metal, and finally they obtained the supposed new metal by electrolysing an aqueous solution of the chloride, and also by reducing the dichloride in H. Krüss a. Schmidt (*B.* 22, 2026) prepared what they considered to be pure Ni, and by fractionally ppg. this as basic Ni-NH_4 arsenite they obtained two different substances, one having an at. w. 56–58, and the other an at. w. 61-100; hence they concluded that their former results were confirmed, that is, that Ni is really a compound or a mixture of two elements. Considerable doubt was thrown on these results by the work of Winkler on the reaction between pure $AuCl_3$ and Ni (*B.* 22, 890); and Fleitmann's experiments on large quantities of Ni also tend to show that Ni has not been separated into unlike parts (*Chem. Zeitung*, 13, 757).

Reactions and Combinations.—1. Pieces of Ni do not oxidise in *ordinary air*; *heated in air* Ni is superficially oxidised to NiO; Ni obtained by reduction of NiO at low temperatures is pyrophoric.—2. Ni burns to NiO when heated in *oxygen.*—3. By heating in *chlorine*, *bromine*, or *iodine*, $NiCl_2$, $NiBr_2$, or NiI_2 is produced.—4. Heated with *sulphur*, NiS is formed.—5. Ni combines with *phosphorus* when the elements are heated together.—6. Combines with *arsenic* in several proportions (*v. Nickel, arsenides of*, p. 501).—7. Absorbs, and probably also combines with *carbon* (*v. Nickel, carbides of*, p. 501).—8. Combines with *carbon monoxide* (*v. Nickel carbon-oxide*, p. 501).—9. By reducing NiO in presence of SiO_2, Ni is obtained, containing *silicon* (*v. Nickel, silicides of*, p. 503).—10. *Steam* is slowly decomposed by Ni at red heat, NiO being formed (Regnault, *A. Ch.* [3] 62, 352).—11. *Nitric acid* forms $Ni(NO_3)_2$, but Ni is passive in conc. HNO_3Aq.—12. *Sulphuric and hydrochloric acids* react very slowly with Ni (*v.* Tissier, *C. R.* 50, 106).—13. Aqueous *sulphurous acid* is decomposed by Ni at c. 200°, with production of Ni_3S_4 (Geitner, *A.* 139, 354).—14. *Carbon dioxide* is reduced to CO by heating with Ni to redness (Bell, *C. N.* 23, 358).—15. Heated in *carbon monoxide* to 350°–450°, C is deposited and CO_2 produced (*v. supra*, No. 8; also *Nickel carbon-oxide*, p. 501).—16. Forms *alloys* with several metals (*v. Nickel, alloys of, infra*).—17. Occludes about 165 times its volume of *hydrogen* (Raoult, *C. R.* 69, 826).

Detection and Estimation.—Ni compounds give a bead with *borax* which is violet when hot and reddish-brown when cold in the oxidising flame, and in the reducing flame becomes opaque and grey from reduced Ni. Brown-black NiS is ppd. by alkali sulphides, insol. dilute cold HClAq, somewhat sol. yellow NH_4 sulphide; H_2S produces no pp. in acid solutions; moist NiS ppd. from cold solutions, oxidises rather easily in the air. Very small traces of Ni may be detected, in the absence of most other metals, by the rose-red colour produced by adding K_2CS_3Aq (Braun, *J.* 1868. 376). To detect small quantities of Ni in presence of Co, Papasogli places a piece of Zn in a solution of the double cyanides of the two metals: if Ni is present a red colour is produced (*J.* 1879. 1055); Donath a. Mayrhofer (*Fr.* 20, 379) add excess of NaOHAq, then I, boil, treat the pp. with NH_3Aq and NH_4ClAq, and test the solution by NH_4HS (*v.* also Jorisson, *Fr.* 21, 208).

Ni may be estimated as NiO after ppn. as $NiO.xH_2O$ by addition of KOHAq to a hot solution. For separation of Ni from Co *v.* COBALT, vol. ii. p. 218. Classen recommends the ppn. of Ni as oxalate, which on heating out of contact with air gives NiO (*Fr.* 16, 471; 18, 189, 386). Ni may also be estimated by electrolysing a solution of Ni-NH_4 oxalate in presence of excess of NH_4 oxalate (*v.* Classen; for description of apparatus *v.* Dittmar's *Exercises in Quantitative Chemical Analysis* [Glasgow, 1887]; *cf.* Merrick, *C. N.* 24, 100).

Technical Applications.—Alloys of Ni with Cu, and with Cu and Zn, are used for coinage in some countries, and for other purposes. These alloys are nearly white and hard. Many articles of iron and steel are now covered with a deposit of Ni. This covering is only very slightly acted on by ordinary air. *Nickel-plating* is usually accomplished by electrolysing an ammoniacal solution of Ni-NH_4 sulphate, using Ni as one of the electrodes, and the substance to be plated as the other (*v. D. P. J.* 201, 145; 206, 288; 211, 74; 212, 160; 219, 469; *v.* also Adams, *C. R.* 70, 123, 137; Becquerel, *ibid.* 70, 124, 137, 181; *v.* also DICTIONARY OF APPLIED CHEMISTRY).

Nickel, alloys of. An alloy of Ni with *aluminium*, approximately Al_6Ni, is obtained by melting together 8 parts Al with 3 parts dry $NiCl_2$ and 20 parts mixed KCl and NaCl, and treating with dilute HClAq (Michel, *A.* 115, 102). Alloys of Ni with *copper*, and with *copper and zinc*, are used for coinage and other purposes under the names of *German silver*, *packfong*, &c. Ramsay (*C. J.* 55, 532) found that an amalgam

of Ni with *mercury* could be obtained in small quantities by electrolysing dilute solutions of Ni salts in contact with Hg.

Nickel, ammonio-compounds of. Some Ni compounds, *eg.* $NiCl_2$ and $NiBr_2$, combine with NH_3; *v. Nickel bromide, Nickel chloride*, &c.

Nickel, antimonates of, $Ni(SbO_3)_2.6H_2O$ and $Ni(SbO_3)_2.12H_2O$; *v.* Heffter, *P.* 86, 446.

Nickel, antimonide of. NiSb occurs native as *breithauptite.*

Nickel, arsenates of, *v.* vol. i. p. 309. $Ni_3(AsO_4)_2.8H_2O$ occurs native as *nickel-bloom.*

Nickel, arsenides of. A brittle compound, Ni_2As, is formed by heating Ni with excess of As; also by very strongly heating Ni arsenates in a charcoal-lined crucible. (For other arsenides *v.* Descamps, *C. R.* 86, 1065.) Various Ni ores are essentially compounds of Ni and As; Ni_3As_2 = *speiss*; NiAs = *copper-nickel*; $NiAs_2$ = *white-nickel.*

Nickel, arsenite of, *v.* vol. i. p. 306.

Nickel, borate of, *v.* vol. i. p. 530.

Nickel, bromide of, $NiBr_2$. This, the only compound of Ni with Br, is obtained by passing Br vapour over finely-divided Ni heated to low redness. $NiBr_2$ forms a brownish-yellow solid; it sublimes in yellow, glittering scales (Berthemot, *A. Ch.* [3] 44, 389; Rammelsberg, *P.* 55, 243). Heated in air, or in steam, $NiBr_2$ forms NiO; it is completely decomposed by HNO_3Aq. Soluble alcohol and ether; deliquescent; soluble water to a green liquid.

The *hydrate* $NiBr_2.3H_2O$ is obtained, in green needles, by digesting Ni with BrAq; also by dissolving NiO or $NiCO_3$ in HBrAq, and evaporating (Rammelsberg, *P.* 55, 243). This hydrate is dehydrated at c. 200°. H.F. $[Ni, Br^2, Aq] = 71,820$ (*Th.* 3, 307).

A compound of nickel-bromide with ammonia, $NiBr_2.6NH_3$, is obtained as a violet powder, by passing NH_3 over powdered $NiBr_2$; also, as a blue powder, by warming conc. $NiBr_2Aq$ with excess of NH_3Aq, and cooling. NH_3 is given off when the compound is heated: $NiBr_2.6NH_3$ is soluble in a little water without decomposition; much water causes ppn. of $NiO.H_2O$ (Rammelsberg, *l.c.*).

Nickel, carbides of. Commercial Ni always contains a little C. For experiments on carbonisation of Ni *v.* Gard, *Am. S.* [3] 14, 274; Boussingault, *C. R.* 86, 509; Pebal, *A.* 233, 160; Gautier a. Hallopeau, *C. R.* 108, 1111; Mond, Langer, a. Quincke, *C. J.* 57, 749.

Nickel carbon-oxide $Ni(CO)_4$. Mond, Langer, a. Quincke (*C. J.* 57, 749) found that Ni decomposes CO at 350°–450°, with separation of C and formation of CO_2. When the product was allowed to cool in CO they noticed that the escaping gas caused a Bunsen flame to become very luminous, and when heated deposited Ni. Following up this observation they found that when finely-divided Ni, produced by reducing the oxide in H, is allowed to cool in a slow current of CO the gas is readily absorbed by the Ni when the temperature has fallen to c. 100°, and that by replacing the CO by CO_2, N, H, or air, a mixture of gases is obtained which deposits Ni when heated above 150°. By analysing the mixture of gases thus obtained, and determining the Ni by passing the gases through a capillary tube at 180°, M., L., a. Q. found that one volume of the Ni compound present in the gases gave four volumes of CO. The analyses led to the formula NiC_4O_4. By passing the mixed gases through a tube surrounded with salt and ice a colourless mobile liquid was obtained, which was proved, by estimations of Ni and C, to be NiC_4O_4. The V.D. determined at 50° was found to be 86·9; NiC_4O_4 requires 80·4. The new compound is called nickel-carbon-oxide by its discoverers; it boils at 43° at 751 mm., solidifies at −25° to needle-shaped crystals, and has S.G. 1·3185 at 17°. The vapour is very poisonous. The compound is sol. alcohol, benzene, and chloroform; it is not acted on by dilute acids or alkalis, nor by conc. HClAq; conc. HNO_3Aq and *aqua regia* dissolve it readily. The vapour ppts. Ag from AgCl in NH_3Aq; it is decomposed by Cl, giving $NiCl_2$ and $COCl_2$; Br acts similarly; electric sparks produce Ni and CO.

Nickel, chloride of, $NiCl_2$. H.F. $[Ni,Cl^2] = 74,530$ (*Th.* 3, 307); $[NiCl^2,Aq] = 19,170$. S.G. 2·56 (Schiff, *A.* 108, 21). Prepared by gently heating powdered Ni in a stream of dry Cl, and subliming in the Cl (H. Rose, *P.* 20, 156). Also by dissolving NiO or $NiCO_3$ in HClAq, or Ni in *aqua regia*, and evaporating to dryness. Golden yellow scales. Sublimes readily without melting. Prepared in the wet way, $NiCl_2$ is deliquescent and easily soluble in water; sublimed $NiCl_2$ dissolves slowly in boiling water. Heated in air Cl is evolved and NiO formed. Heated in a stream of O, is entirely changed to Ni_3O_4 (Schulze, *J. pr.* [2] 21, 407). KOHAq decomposes sublimed $NiCl_2$ only after prolonged boiling. PH_3 forms Ni_3P_2, and HCl; molten P forms Ni_3P_2 and PCl_3 (H. Rose, *P.* 27, 117). For S.G. of conc. $NiCl_2Aq$ *v.* Franz, *J. pr.* [2] 5, 274.

The *hexa-hydrate* $NiCl_2.6H_2O$ (Laurent, *A. Ch.* [3] 60, 354) is obtained by cooling conc. $NiCl_2Aq$. Soluble in $1\frac{1}{2}$–2 parts water; sol. in alcohol. Sabatier (*Bl.* [3] 1, 88) describes a *dihydrate* $NiCl_2.2H_2O$, obtained by placing the hexahydrate over H_2SO_4 *in vacuo* at 20° for three months. Thomsen gives $[Ni, Cl^2, 6H^2O] = 94,860$ (*Th.* 3, 307).

The *oxychloride* $NiCl_2.8NiO.13H_2O$ is obtained by adding a little NH_3Aq to $NiCl_2Aq$ (Raoult, *C. R.* 69, 826).

Compounds with ammonia. (1) $NiCl_2.6NH_3$ is obtained by passing NH_3 over dry $NiCl_2$ (H. Rose, *P.* 20, 155); also by adding alcohol to $NiCl_2$ in NH_3Aq (Erdmann, *Gm.-K.* (6th edit.) 3, 553; F. Rose, *Gm.-K.* (6th edit.) 3, 561). Soluble without change in cold water; decomposed slowly by much cold water, quickly by hot water. Slightly sol. conc. NH_3Aq; insol. alcohol. (2) $NiCl_2.2NH_3$; obtained by heating $NiCl_2.6NH_3$ to 120°. Gives $NiCl_2$ when heated in *vacuo*, and a little Ni when very strongly heated.

Compounds with ammonium chloride. (1) $NiCl_2.NH_4Cl.6H_2O$; green deliquescent crystals, obtained by evaporating a solution of the constituents in the ratio $NiCl_2:NH_4Cl$ (Hantz, *A.* 66, 283). Jörgensen (*Gm.-K.* (6th edit.) 3, 561) obtained crystals containing c. ·5 p.c. $NiCl_2$ by evaporating $NiCl_2Aq$ with a large excess of NH_4Cl. (2) $NiCl_2.4NH_4Cl.7H_2O$; yellow, star-shaped, crystals, obtained by decomposing Ni-NH_4 sulphate solution by an equivalent of $BaCl_2$, filtering and evaporating over H_2SO_4 (Adams a. Meyrick, *J.* 1871. 308; *cf.* Tupputi, *A. Ch.* [3] 78, 169).

$NiCl_2$ form *double salts* with CsCl, $CdCl_2$, and

$AuCl_3$ (*v.* Goddefroy, *B.* 8, 9; von Hauer, *W. A. B.* 20, 40; *ibid. W. A. B.* 17, 348).

Nickel, chromates of, *v.* vol. ii. p. 156.

Nickel, cyanide and double cyanides of, *v.* vol. ii. p. 343.

Nickel, ferricyanide of, *v.* vol. ii. p. 339.

Nickel, ferrocyanides of, *v.* vol. ii. p. 336.

Nickel, fluoride of, NiF_2. S.G. 2·855 at 14° (Clarke, *Am. S.* [3] 13, 291). The hydrate $NiF_2.3H_2O$ is obtained by dissolving $NiO.H_2O$ or $NiCO_3$ in HFAq, and evaporating (Berzelius; Clarke, *Am. S.* [3] 13, 291). Decomposed by much hot water to *oxyfluoride* $Ni_2OF_2.H_2O$ (Berzelius). Combines with AlF_3, fluorides of the alkali metals (Wagner, *B.* 19, 896), and with SiF_4 (*v. Nickel, silicofluoride of,* p. 503), TiF_4 (*v.* Titanium fluoride), and ZrF_4 (*v.* Zirconium fluoride). With $Mo_2O_2F_2$ forms the compound $NiF_2.MoO_2F_2.6H_2O$ (Delafontaine, *J.* 1867. 236).

Nickel, hydroxides or hydrated oxides of, *v. Nickel, oxides and hydrated oxides of, infra.*

Nickel, iodide of, NiI_2. $[Ni, I^2, Aq] = 41{,}400$ (*Th.* 3, 307). Prepared by heating Ni, reduced from NiO by H, with I, and subliming the NiI_2 from the residue of Ni and NiO (Erdmann, *J. pr.* 7, 249). Also by heating $NiI_2.6H_2O$, which is obtained by dissolving $NiO.H_2O$ in HIAq, or by treating finely divided Ni with excess of I and water. Iron-black, lustrous, metal-like, scales. Deliquescent; soluble in water, forming a brown liquid, which becomes green on dilution. Partly decomposed when strongly heated in air. By digesting NiI_2Aq with $NiO.H_2O$, or by evaporating NiI_2Aq, Erdmann (*l.c.*) obtained the *oxyiodide* $NiI_2.9NiO.15H_2O$.

Compounds with ammonia. (1) $NiI_2.4NH_3$; a yellow-white mass; by passing NH_3 over NiI_2 (Rammelsberg, *P.* 48, 119). (2) $NiI_2.6NH_3$; by adding excess of NH_3Aq to conc. NiI_2Aq, warming, and cooling or adding alcohol (Erdmann, *l.c.*; Rammelsberg, *l.c.*).

Nickel, nitride of. A compound of Ni with N is said to be formed by heating NiO to c. 200° in NH_3; it is decomposed at a higher temperature (Warren, *C. N.* 55, 155).

Nickel, oxides and hydrated oxides of. Nickel forms three oxides; NiO, Ni_3O_4, and Ni_2O_3; a fourth oxide, Ni_2O, probably exists; there are indications of the existence of oxides intermediate between Ni_3O_4 and Ni_2O_3, and also of an oxide containing more O than Ni_2O_3. Hydrates of NiO and Ni_2O_3, and perhaps of Ni_3O_4, have been isolated. The oxides of Ni are basic, but the only Ni salts which have been prepared with certainty correspond with NiO. NiO is oxidised by heating to c. 400°, but the product is reduced to NiO at c. 600°.

Nickel monoxide NiO (*Nickelous oxide. Protoxide of nickel*). Occurs native as *bunsenite*. Obtained by heating Ni or $NiCl_2$ in steam (Regnault, *A. Ch.* [3] 62, 352); by heating the hydrate or $NiCO_3$ in absence of air; by strongly heating $Ni(NO_3)_2$ (Russell, *C. J.* [2] 1, 58), $NiSO_4$ (Baubigny, *C. R.* 97, 951), or a mixture of $NiSO_4$ and K_2SO_4 (Debray, *C. R.* 52, 985); by reducing Ni_2O_3 by H at 190°–230° (Moissan, *A. Ch.* [5] 21, 238; *cf.* Wright a. Luff, *C. J.* 33, 1; also Müller, *P.* 136, 59), or by NH_3 at c. 180° (Vorster, *Dissertation*, Göttingen, 1861), at a moderate temperature. NiO is obtained in green regular octahedra by heating Ni borate with CaO in a porcelain oven, and treating the product with HClAq (Ebelmen, *C. R.* 33, 526).

NiO is a green powder, becoming deep-yellow when heated (Moissan, *A. Ch.* [5] 21, 238; Zimmermann, *A.* 232, 324). S.G. 5·6 (Playfair a. Joule, *C. S. Mem.* 3, 81); 6·66 (Rammelsberg, *J.* 2, 282); 6·8 crystallised (Ebelmen, *C. R.* 33, 526). Heated to 350°–440°, NiO is oxidised to Ni_2O_3, which is again deoxidised to NiO at c. 600° (Moissan, *A. Ch.* [5] 21, 199). NiO is readily reduced to Ni; reduction by CO begins at c. 120°, by H at c. 220°, by C at c. 450° (Wright a. Luff, *C. J.* 33, 1); reduction by NH_3 begins at c. 200° (Vorster, *Dissertation*, Göttingen, 1861). NiO is oxidised to Ni_2O_3 by ozonised O (Schönbein, *J. pr.* 93, 35). NiO, if not strongly heated, dissolves in NH_3Aq; it decomposes NH_4 salts with evolution of NH_3. NiO dissolves in acids forming salts NiX_2, $X = NO_3$, ClO_3, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c.

Hydrate of nickel monoxide $4NiO.5H_2O = 4Ni(OH)_2.H_2O$ (*Nickelous hydrate*; *nickelous hydroxide*). This hydrate is obtained as a pale greenish pp., by adding alkali solution to solution of a Ni salt. According to Teichmann (*A.* 156, 17) the hydrate can be obtained free from acid only from $Ni(NO_3)_2Aq$; T. recommends to add NaOHAq, free from carbonate, to cold $Ni(NO_3)_2Aq$, to wash the excess of pp. with cold water till the alkaline reaction disappears, then to wash with water containing a little NH_3, and finally with boiling water, and to dry at 100°. $4NiO.5H_2O$ is also obtained, as a green crystalline powder, by heating NiO or $NiCO_3$ in NH_3Aq (*Gm.-K.* (6th edit.) 3, 536).

Nickelous hydrate is a pale-green powder; slightly soluble in water (Fresenius). If not washed free from alkali it oxidises in presence of air and SO_2Aq, but the product is reduced to NiO by excess of SO_2Aq (Wicke, *Z.* 1865. 86). When strongly heated, H_2O is evolved and NiO remains. H_2O_2Aq forms a hydrate of Ni_3O_4 (Schönbein, *J. pr.* 93, 35); but, according to Bayley, H_2O_2Aq is without action (*P. M.* [5] 7, 126). Oxidised by Cl and hypochlorites to $Ni_2O_3.xH_2O$. Soluble in NH_3Aq and solutions of NH_4 salts. $4NiO.5H_2O$ reacts with acids as a strong base, forming salts NiX_2, $X = NO_3$, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c. Thomsen gives $[NiO^2H^2, H^2SO^4Aq] = 26{,}110$; and $[NiO^2H^2, 2HClAq] = 22{,}580$ (*Th.* 3, 307).

Nickel sesquioxide Ni_2O_3 (*Nickelic oxide. Sometimes called nickel peroxide*). A black powder; S.G. 4·84 at 16° (Herapath, *P. M.* 64, 321). Obtained by decomposing by heat at the lowest possible temperature $Ni(NO_3)_2$ (Berzelius; Vorster, *Dissertation*, Göttingen, 1861), or $Ni(ClO_3)_2$ (Wächter, *J. pr.* 30, 327); also by melting $NiCl_2$ with $KClO_3$ (Schulze, *J. pr.* [2] 21, 107); also by treating Ni salts in solution with KClOAq or KBrOAq (Schröder, *C. C.* 1890. 931). Heated in air to c. 600° Ni_2O_3 is reduced to NiO (Moissan, *A. Ch.* [5] 21, 199); reduction in H begins at c. 190° (M., *l.c.*). Dissolves in H_2SO_4Aq or HNO_3Aq with evolution of O, in HClAq with evolution of Cl; in each case salts of NiO are produced. Soluble in NH_3Aq with evolution of N (Müller, *P.* 136, 59).

Hydrates of nickel sesquioxide. (1) $Ni_2O_3.2H_2O$; brownish crust, S.G. 2·744, obtained by electrolysing an alkaline solution of

Ni-K tartrate (Wächter, *J. pr.* 30, 327). (2) $Ni_2O_3.3H_2O$; by oxidising NiO or $4NiO.5H_2O$, suspended in water, by Cl or BrAq; also by adding alkali and NaClO to solution of a Ni salt (Wächter, *l.c.*). A black solid, which reacts with acids and NH_3Aq as Ni_2O_3 does; reduced to $4NiO.5H_2O$ by SO_2Aq (Wicke, *Z.* 1865. 86), also by Na_2SO_3Aq (Schulze, *J.* 1864. 270). H.F. $[Ni^2,O^3,3H^2O] = 120,380$ (*Th.* 3, 307). Carnelley a. Walker (*C. J.* 53, 91) think that no definite stable hydrate of Ni_2O_3 exists.

Nickelo-nickelic oxide Ni_3O_4. A grey, metal-like, non-magnetic solid, obtained by passing O over $NiCl_2$ at 350°–440° (Baubigny, *C. R.* 87, 1082).

Nickelo-nickelic hydrate. A black powder, having the compositiou $Ni_8O_9.H_2O$ ($=Ni_2O_3.6NiO.H_2O$), is said to be formed by heating $NiCO_3$ to 300° (H. Rose, *P.* 84, 571).

Nickel suboxide. An oxide, Ni_2O, is said to be produced by reducing NiO in H at 210°–214° (Müller, *P.* 136, 59); also by reducing NiO in CO at a low temperature (Bell, *C. N.* 23, 258, 267).

Nickel peroxide. By the reaction of hypochlorites on $Ni_2O_3.3H_2O$ one or more oxides are produced containing more O than Ni_2O_3. Wicke gives the composition Ni_4O_7 (*Z.* 1865. 303); Bayley (*C. N.* 39, 81) gives the formula Ni_3O_5. Carnot (*C. R.* 108, 610) says that Ni salt solutions give Ni_2O_3 when treated with hypochlorites or with Br and KOHAq.

Nickel, oxychloride of, *v. Nickel chloride*, p. 501.

Nickel, oxyfluoride of, *v. Nickel fluoride*, p. 502.

Nickel, oxyiodide of, *v. Nickel iodide*, p. 502.

Nickel, phosphides of. Ni and P combine when heated together. Various compounds have been described: (1) Ni_5P_2; by heating Ni, bone ash, quartz-sand, and C (*Gm.-K.* (6th ed.) 3, 542). (2) Ni_2P; by reducing $5NiO.P_2O_5$ in H (Struve, *J.* 1860. 76). (3) Ni_3P_2; by reducing $3NiO.P_2O_5$ in H (H. Rose, *P.* 24, 332), also by heating $NiCl_2$ or NiS in PH_3, or by passing PH_3 over heated Ni (Davy; Schrötter, *W. A. B.* 2, 304).

Nickel, salts of. *Compounds obtained by replacing H of acids by Ni.* The Ni salts which have been studied all correspond with the oxide NiO, and belong to the form NiX_2 where $X = ClO_3$, NO_3, $\frac{1}{2}SO_4$, $\frac{1}{2}CO_3$, $\frac{1}{3}PO_4$, &c. The oxide Ni_2O_3 probably forms salts, but they are very easily reduced to salts of NiO. The Ni salts are obtained by dissolving Ni, NiO, or $NiCO_3$ in acids. The salts of Ni are generally yellowish when dehydrated, and green when combined with water. Some of the compounds of Ni combine with NH_3. The haloid compounds, the sulphate and nitrate of Ni, and some of the other salts, are soluble in water; the oxides, sulphides, phosphate, carbonate, and a few other salts, are insoluble in water. Solutions of Ni salts in water are green; they redden litmus slightly. Most Ni salts are decomposed by heating in air; $NiCl_2$, $NiBr_2$, and NiI_2 can be sublimed unchanged. The chief Ni salts of oxyacids are the *antimonate*, *arsenates* and *-ite*, *borate*, *bromate*, *carbonate*, *chlorate*, *chromate*, *iodate* and *periodate*, *molybdates*, *nitrates* and *-ite*, *phosphates* and *-ite* and *hypophosphite*, *selenate*, *silicates*, *sulphates* and *-ite*, *thiosulphate* (*v.* Carbonates, Nitrates, &c.).

Nickel, selenide of, NiSe. A silver-white, brittle, crystalline, solid; S.G. 8·46; obtained by action of Se vapour on finely powdered Ni. Melts at red heat, with loss of Se. Insoluble in HClAq; slowly dissolved by HNO_3Aq, quickly by *aqua regia* (Little, *A.* 112, 211).

Nickel, silicides of. Commercial Ni generally contains more or less Si. For experiments on the quantity of Si taken up by Ni *v.* Gard, *Am. S.* [3] 14, 274.

Nickel, silicofluoride of, $NiSiF_6.6H_2O$. Hexagonal rhombohedral, green crystals; S.G. 2·109; by dissolving $NiCO_3$ in H_2SiF_6Aq. Decomposed at red heat, giving NiF_2 and SiF_4 (Berzelius; Marignac, *Ann. M.* [5] 15, 262).

Nickel, sulphides of. Four sulphides of Ni are known: Ni_2S, NiS, Ni_3S_4, and NiS_2. NiS is somewhat soluble in NH_4 sulphide; it also forms a compound with K_2S. The only sulphide produced by the direct union of Ni and S is NiS.

Nickel monosulphide NiS. Occurs native as *capillary pyrites* or *millerite*. Formed by heating Ni with S; by heating NiO with S, or in a stream of H_2S (Tupputi, *A. Ch.* [3] 78, 133; 79, 153); also by heating $NiCl_2$ with K_2SAq in a sealed tube to c. 160° (Sénarmont, *A. Ch.* [3] 30, 142). As prepared by these methods, NiS is a yellow, brittle, solid; decomposed very slowly by steam at red heat (Regnault, *A. Ch.* [3] 62, 280); not decomposed by H; slowly acted on by Cl when hot (*v. P.* 42, 540); oxidised by heating in air; acted on by PH_3, when hot, with formation of Ni_3P_2 (Schrötter, *W. A. B.* 2, 304); insol. HClAq, sol. HNO_3Aq and *aqua regia*.

NiS, in combination with water, is ppd. from neutral Ni solutions by H_2S, or by NH_4HSAq; also by heating Ni salts with $Na_2S_2O_3Aq$ preferably in sealed tubes at c. 120° (Gibbs, *Am. S.* [2] 37, 346). Thomsen gives $[Ni,S,nH^2O] = 19,400$ (*Th.* 3, 307). The pp. thus obtained is browu-black; if ppd. from boiling solutions it may be washed and dried without change, but if ppd. from cold solutions it oxidises in the air (Clermont a. Guiot, *C. R.* 84, 714; 85, 73). Decomposed by boiling with water (Geitner, *A.* 139, 354). Somewhat soluble in NH_3Aq and alkali sulphide solutions; the brown solutions thus obtained deposit NiS by standing in air or on addition of a weak acid. Accordiug to Baubigny (*C. R.* 94, 1417) the pp. produced by H_2S iu neutral solutions of Ni salts is a hydrosulphide which is decomposed to NiS and H_2S by filtration. A very dilute aqueous solution of a *colloidal form* of NiS was obtained by Winssinger (*Bl.* [2] 49, 452) by ppg. from a very dilute solution aud dialysing.

Compound with potassium sulphide, $3NiS.K_2S$. A yellow, lustrous, crystalline solid; obtained by fusing $NiSO_4$ with K_2CO_3.

Nickel disulphide NiS_2. A dark iron-grey powder; obtained by strongly heating $NiCO_3$ with K_2CO_3 and S, and treating with water (Fellenberg, *P.* 50, 75).

Nickelo-nickelic sulphide Ni_3S_4. An amorphous greyish-black solid of this composition is obtained by heating $NiCl_2Aq$ with polysulphides of K to 160° (Sénarmont, *A. Ch.* [3] 30, 142); by heating Ni with SO_2Aq or Na_2SO_3Aq to 200°, Ni_3S_4 is obtained in rhombohedral crystals (Geitner, *A.* 139, 354).

NICKEL SUBSULPHIDE Ni_2S. A yellow, metal-like solid; obtained by heating $NiSO_4$ to redness, also by heating $NiSO_4$ or ppd. NiS with S in H (H. Rose, *P.* 110, 31). Ni_2S was obtained in small crystals by heating Ni in CS_2 vapour to bright redness (Gautier a. Hallopeau, *C. R.* 108, 1111). Prolonged heating in CS_2 produces NiS.

Nickel, sulphocyanide of, *v.* vol. ii. p. 350.

M. M. P. M.

NICOTIANIC ACID *v.* PYRIDINE CARBOXYLIC ACID.

NICOTINE $C_{10}H_{14}N_2$ *i.e.*

$$CH{\ll}\begin{array}{l}N{-}CH_2\\CH{:}CH\end{array}{>}CH.CH{<}\begin{array}{l}CH_2.CH\\CH_2.CH_2\end{array}{\gg}N\ (?)\quad\text{or}$$

$$\begin{array}{l}CH{:}CH.C.CHEt.CH_2\\CH{:}\ N\ .C.\ NH\ .CH_2\end{array}$$ (Pinner, *B.* 24, 61). *Dipyridyl hexahydride* (Liebrecht, *B.* 19, 2587). Mol. w. 162. (247° cor.) at 745 mm. S.G. $\frac{10}{4}$ 1·0183; $\frac{20}{4}$ 1·0110 (Landolt, *A.* 189, 318). V.D. 5·61 (calc. 5·58 (Barral, *J.* 1847, 614). S.H. ·420 (Colson, *Bl.* [3] 3, 8). *Heat of solution and of neutralisation* (Colson, *A. Ch.* [6] 19, 407). $[\alpha]_D = -161·6°$ (L.).

Occurrence.—In leaves of tobacco (*Nicotiana Tabacum*) (Vauquelin; Posselt a. Reimann, *B. J.* 10, 193), and in the leaves of *Macrophylla rustica* and *M. glutinosa.* Occurs also in Pituri (Gerard, *J.* 1878, 915; Petit, *J.* 1879, 791). According to Zeise and to Vohl and Eulenberg (*Ar. Ph.* [2] 147, 130) it is not present in tobacco smoke, but Heubel obtained evidence of its presence therein (*D. P. J.* 207, 343).

Preparation.—Tobacco leaves (10 pts.) are soaked in water for 24 hours, and the mixture heated to 100° by steam. The aqueous extract is mixed with lime (1 pt.) and distilled. The distillate is neutralised by oxalic acid and evaporated to a thin syrup. Addition of conc. KOHAq now separates the base, which is rectified in a current of H (Laiblin, *A.* 196, 130).

Properties.—Colourless liquid, not frozen at −10°. Smells like tobacco, unless it is quite pure. It is very hygroscopic. Mixes with water, developing heat. Lævorotatory. The optical activity of its aqueous solution varies greatly with concentration: in a 4 p.c. solution $[\alpha]_D = -77°$ at 20°; in a ·88 p.c. solution $[\alpha]_D = -79°$ (Pribram, *B.* 20, 1840). Solutions of salts of nicotine are dextrorotatory. Nicotine has a burning taste and is very poisonous. Nicotine turns brown on exposure to air and light. Its solutions are strongly alkaline. It is very soluble in water, alcohol, ether, terpenes, and fatty oils. At 100° it dissolves 10 p.c. of sulphur. Ether extracts it from the aqueous solution. KOH separates it from aqueous solution.

Estimation.—1. By distilling with potash, extracting the distillation with ether, evaporating the ether, converting the residue into sulphate and repeating the process.—2. Tobacco is mixed with aqueous NaOH and some alcohol and extracted with ether. The extract is evaporated and the nicotine distilled over with steam and estimated by titration with standard acid, or by the polarimeter (Kissling, *Fr.* 21, 75; 22, 199; *Chem. Zeit.* 13, 1030; Popovici, *H.* 13, 445; Biel, *Ar. Ph.* [3] 26, 322).

Reactions.—1. *Oxidised* by nitric acid, chromic acid mixture, or $KMnO_4$ to pyridine carboxylic (nicotinic) acid (Huber, *A.* 141, 271; Laiblin, *B.* 10, 2136).—2. Alkaline K_3FeCy_6 oxidises it to isodipyridyl (C. a. E.).—3. Nicotine (5 pts.) heated with sulphur (1 pt.) at 140° gives H_2S and 'thiotetrapyridine' $C_{20}H_{18}N_4S$, which separates from boiling alcohol in sulphur-yellow crystals [155°], and forms the salts $B''H_2Cl_2$, $B''H_2PtCl_6$, and $B''HHgCl_3$. On distillation with finely-divided copper, thiotetrapyridine is converted into isodipyridyl (Cahours a. Etard, *C. R.* 88, 999; 90, 275).—4. Vapour of nicotine passed through a red-hot tube is partly decomposed, yielding paraffins, olefines, pyridine, methyl-pyridine, and collidine (C. a. E.).—5. Nicotine (5 pts.) heated with selenium (1 pt.) at 240° forms isodipyridyl and collidine dihydride $C_8H_{13}N$ (203°) (Cahours a. Etard, *C. R.* 92, 1079).—6. *Bromine* added to a dilute aqueous solution of nicotine forms a yellow flocculent pp. If this be dissolved by heating to 70° red crystals of the tetrabromide $C_{10}H_{14}N_2Br_4$ separate on cooling. With conc. HBrAq they form the salt $C_{10}H_{14}N_2Br_4HBr$ (Cahours a. Etard, *C. R.* 90, 1315).—7. By distilling the double chloride of zinc and nicotine with lime there is formed pyrrole, methylamine, NH_3, and a liquid base $C_{10}H_{11}N$ (250°–270°) with disgusting odour. A solution of the hydrochloride of this base is coloured dark red on boiling with $PtCl_4$ (Laiblin, *A.* 196, 172).—8. *Sodium* reduces nicotine in alcoholic solution to dipiperidyl.—9. HI and P at 260° gives nicotine dihydride.—10. H_2O_2 in presence of platinum black forms orange granular crystals of oxy-nicotine $C_{10}H_{14}N_2O$, which is oxidised by $KMnO_4$ to nicotinic acid, and forms a picrate [154°–158°] (Pinner a. Wolffenstein, *B.* 24, 65).—11. HgO at 240° yields oxytrinicotine $C_{60}H_{54}N_{12}O_4$ (?) which separates in brown flakes on addition of KOH to its acid solution. Its platinochloride $C_{60}H_{54}N_{12}O_4 4H_2PtCl_6 12aq$ is brownish-yellow (Etard, *C. R.* 97, 1218).

Salts.—$B''H_2Cl_2$: long fibrous deliquescent crystals (Barral, *A.* 44, 281). $[\alpha]_D = +102°$.—$B''H_2PtCl_6$: yellow crystalline pp. or ruby-red prisms, very soluble in excess of nicotine, insol. alcohol and ether. Not decomposed by boiling water (O. De Coninck, *Bl.* [2] 45, 131).—$B''H_4PtCl_6$: orange prisms (from HClAq). Obtained by adding nicotine to a solution of platinous chloride in HClAq (Raewsky, *J.* 1847, 615). The mother-liquor from which this salt has separated deposits red crystals of $B''H_2PtCl_4$.—$B''_2H_2SO_4$: crystals, v. sol. water and alcohol.—$B''HgCl_2$: white pp., formed by adding mercuric chloride to a solution of nicotine. Insol. water and ether, almost insol. alcohol (Ortigosa, *A.* 41, 118).—$B''3HgCl_2$. Long crystals, deposited on standing by a dilute solution of nicotine hydrochloride to which $HgCl_2$ has been added until a permanent pp. begins to form (Boedeker, *A.* 73, 372).—$B''HCl4HgCl_2$: crystalline pp. obtained by adding a cold neutral solution of nicotine hydrochloride to a large excess of mercuric chloride.—$B''H_2ZnCl_4 4aq$: crystals (from 80 p.c. alcohol) (Vohl, *J. pr.* [2] 2, 331).—$B''H_2Cl_2Sn_2Cl_4 aq$. [162°]. Crystals, got by adding tin to the hydrochloride (Colson, *Bl.* [3] 3, 11).—$B''H_2CdCl_4 2aq$ (V.).—$B''H_2I_2$: needles (Wertheim, *J.* 1863, 441).—$B''HgI_2$: colourless crystals (from hot water).—$B''H_2HgI_4$: yellow prisms, sol. cold water and alcohol.—$B''ZnI_2$.—$B''HI_3$.—$B''HCl,HI_3$.—$B''AgNO_3$. Prisms.—Tartrate $B''(C_4H_6O_6)_2 2aq$: white crystalline

tufts, v. sol. water (Dreser, *Ar. Ph.* [3] 27, 266).—Nitroprusside: sol. water (Davy, *Ph.* [3] 11, 756).—Chloro-iodide, dark-yellow pp. (Dittmar, *B.* 18, 1612).—Picrate $B''2C_6H_2(NO_2)_3OH$. [218°]. Yellow needles (P. a. W.).

Methylo-iodide $B''Me_2I_2$ (Stahlschmidt, *A.* 90, 222). With moist Ag_2O it yields a caustic base. It yields the salts $B''Me_2PtCl_6$, $B''2MeAuCl_4$, and $B''Me_2Cl_24HgCl_2$. When the methylo-iodide is treated with alcoholic KOH at 45° it gives a ruby-red colouration; on addition of acids the colour remains red, and, on pouring into a large quantity of water, shows a green fluorescence (O. De Coninck, *C. R.* 104, 1374).

Ethylo-iodide $B''Et_2I_2$: prisms, v. sol. water, sl. sol. alcohol and ether (Von Planta a. Kekulé, *A.* 87, 2). Yields with Ag_2O a caustic base. It forms the crystalline salts $B''Et_2PtCl_6$ and $B''2EtAuCl_4$, and amorphous $B''Et_2Cl_23HgCl_2$. An alcoholic solution of the ethylo-iodide is coloured garnet-red, and finally crimson, by heating with addition of potash for 10 hours on a water-bath. After acidifying and pouring into water the colour is still red (De Coninck, *C. R.* 104, 513).

Isoamylo-iodide $B''2C_5H_{11}I$. Yields $B''(C_5H_{11})_2PtCl_6$ (Stahlschmidt).

Nicotine dihydride $C_{10}H_{16}N_2$. *Hydronicotine.* (264°). S.G. $\frac{17}{}$ ·993. $[\alpha]_D = -15° 40'$ in a 13·7 p.c. solution. Formed by heating nicotine with fuming HIAq and red phosphorus at 265° for 10 hours (Etard, *C. R.* 97, 1218). Liquid, with faint odour, miscible with water, alcohol, and ether. Lævorotatory. Its hydrochloride is not ppd. by $HgCl_2$.—$B''H_2PtCl_6aq$: pale-yellow crystals, v. sl. sol. water.

Isonicotine *v.* DIPYRIDYL TETRAHYDRIDE.

NICOTINIC ACID *v.* PYRIDINE CARBOXYLIC ACID.

Homo-nicotinic acid *v.* DI-METHYL-PYRIDINE CARBOXYLIC ACID.

NIGRANILINE *v.* ANILINE BLACK.

NIGROSINE. A name used by Wolff (*Chem. Ind.* 2, 290, 319) to denote a blue-black substance $C_{36}H_{27}N_3$, found among the products of the action of arsenic acid on aniline hydrochloride at 230°. Its hydrochloride $C_{36}H_{27}N_3HCl$ exhibits in solution blood-red fluorescence, and is decolourised by reducing agents. The name 'nigrosine' has also been applied to indulines, more especially when obtained by the action of nitro-benzene on a mixture of pure aniline and aniline hydrochloride.

NIOBATES *v.* p. 506.

NIOBIUM. Nb (*Columbium*). At. w. 94. Mol. w. unknown. S.G. 7·06 at 15·5° (Roscoe, *C. N.* 37, 26).

Occurrence.—Niobates occur in a few rare minerals, *e.g.* in *columbite*, *tantalite*, *samarskite*, *yttro-ilmenite*, *euxenite*, and some varieties of *pitch-blende.* Niobates are generally accompanied by tantalates, tungstates, titanates, zirconates, and compounds of Th, Ce, and Yt.

History.—In 1801, Hatchett found a new oxide in a mineral called *columbite* from Massachusetts; to the metal of the new oxide he gave the name columbium (*Crell's Ann.* 1, 197, 257, 352). In the following year, Ekeberg (*Scher. J.* 9, 597) examined two minerals—one from Finland, the other from Sweden—and announced the discovery of a new oxide; as the oxide was soluble only in caustic alkalis and was ppd. by acids, Ekeberg gave to the metal of this oxide the name tantalum. In 1809, Wollaston (*S.* 1, 520) pronounced the oxides discovered by Hatchett and Ekeberg, respectively, to be identical. Berzelius confirmed the decision of Wollaston (*P.* 4, 6); he proposed to apply the name tantalum to the characteristic metal of *columbite* and the minerals examined by Ekeberg. Oxide of tantalum was recognised as present in several rare minerals (*v.* Hermann, *J. pr.* 38, 91; H. Rose, *P.* 63, 321). In 1844, H. Rose began a series of researches on the minerals containing tantalum compounds (*P.* vols. 63, 69, 73, 74, 90, 99, 100, 101, 102). Rose concluded that oxides of three distinct metals exist in these minerals: oxide of tantalum in *tantalite* from Finland and Sweden; and oxides of two new metals, which he called niobium and pelopium, in *tantalite* from Massachusetts (formerly called *columbite*) and in a *tantalite* from Bavaria. In 1853, Rose came to the conclusion that the compounds described by him as oxides of niobium and pelopium were really two different oxides of the same metal which was different from tantalum; this metal Rose called niobium (from Niobe, the daughter of Tantalus) (Rose, *P.* 63, 317). As different specimens of niobium oxide showed considerable differences of S.G., Marignac re-examined the ground, and showed that some of Rose's oxides of niobium contained tantalum (*C. R.* 60, 234, 1355). Marignac also showed that the most probable formulæ for the oxide and chloride of Nb are Nb_2O_5 and $NbCl_5$, respectively. Blomstrand (*J. pr.* 97, 57) confirmed Marignac's results. Determinations of S.G. of gaseous Nb chloride and oxychloride by Deville a. Troost (*C. R.* 56, 891) have shown the formulæ $NbCl_5$ and $NbOCl_3$ to be molecular. H. Rose supposed he had obtained Nb by reducing a compound of Nb, K, and F by Na; Delafontaine showed that Rose's supposed Nb was really NbO, and that the compound from which it was obtained contained O (*Ar. Sc.* 27, 167). Blomstrand obtained Nb, containing some H, in 1864 by reducing the chloride in H; in 1878 Roscoe prepared approximately pure Nb by the same method (*C. N.* 37, 25).

The existence of three other metals in niobium-containing minerals has been asserted by von Kobell (*J. pr.* 79, 291; 83, 193, 449), and Hermann (*J. pr.* 38, 91, 119; *J. pr.* [2] 3, 373; 4, 178; 15, 105); but the researches of Blomstrand and Marignac (*l.c.*) make the existence of these metals—*diomium*, *ilmenium*, and *neptunium*—very doubtful.

Preparation.—Very finely-powdered *columbite* is fused with 3 times its weight of $KHSO_4$, in an iron or Pt crucible, until completely dissolved; after cooling, the residue is powdered and treated with boiling water, whereby sulphates of K, Fe, and Mn are removed; the insoluble portion is washed, and digested with yellow NH_4 sulphide, sulphides of Sn and W thus go into solution and FeS remains mixed with Nb_2O_5 and Ta_2O_5; the residue is washed and digested with HClAq, to remove FeS; the insoluble in acid is thoroughly washed with boiling water until white. To separate Nb from this mixture of Nb_2O_5 and Ta_2O_5, the whole is dissolved in HFAq, the solution is heated to boiling, and

$\frac{1}{4}$ part KHF_2 is added for each part of mixed Nb_2O_5 and Ta_2O_5 used; the liquid is evaporated until 1 g. of the mixed oxides is present in about 7 c.c., and allowed to cool; crystals of K_2TaF_7 separate, these are washed with cold water till the washings give no red, but a pure yellow, pp. with tincture of galls; the filtrate is concentrated with addition of KHF_2, and the second crop of K_2TaF_7 crystals is removed and washed. After one or two repetitions of this process, fine tablets of $NbOF_3.2KF$ separate on evaporating the filtrate from the K_2TaF_7 crystals; the tablets are collected, pressed, and heated in a Pt dish with H_2SO_4 until HF is completely removed; the residue is boiled with a large quantity of water for some time, when a white pp. of $Nb_2O_5.xH_2O$ separates out (Berzelius; *v.* also Marignac, *Ar. Sc.* 23, 167, 249; 25, 5). The pp. of $Nb_2O_5.xH_2O$ is washed, dried, and heated to redness; it is then mixed with a large excess of charcoal, the mixture is heated, then placed in a large hard glass tube (a small quantity being used, as $NbCl_5$ is very voluminous), heated in dry CO_2 until perfectly dry, and allowed to cool in dry CO_2; the CO_2 is then completely expelled by dry Cl, and the tube is then heated to redness while dry Cl passes through it; $NbCl_5$ collects in the tube, and is distilled in a stream of dry Cl. The $NbCl_5$ is then vapourised in a current of perfectly dry H, with precautions to prevent the entrance of air and moisture, and the mixed vapour is passed through a red-hot tube of hard glass. The grey, lustrous crust of Nb which forms in the tube is finally strongly heated in a stream of perfectly dry H (Roscoe, *C. N.* 37, 25). Nb thus prepared contains about ·27 p.c. H.

Properties and Reactions. — A steel-grey lustrous metal. S.G. 7·06 at 15·5° (Roscoe, *l.c.*). Insol. HClAq, HNO_3Aq, or *aqua regia*; sol. conc. H_2SO_4. Heated in air, burns to Nb_2O_5. Heated in Cl forms $NbCl_5$.

The at. w. of Nb has been determined (1) by determinations of V.D. of $NbCl_5$ and $NbOCl_3$ (Deville a. Troost, *C. R.* 56, 891; 60, 1221); and by analyses of $NbCl_5$ (H. Rose, *P.* 104, 432; Blomstrand, *Acta Univ. Lund.* 1864; Marignac, *Bibl. Univ. Genève*, 1865 and 1866); (2) by analyses of $NbOF_3.2KF$. aq (Marignac, *l.c.*).

Nb is metallic in its physical properties. NbO and Nb_2O_5 dissolve in conc. H_2SO_4, but no definite sulphates or other salts of the oxides have been isolated. $Nb_2O_5.xH_2O$ forms several niobates, in which Nb forms part of the negative radicle. Nb forms the third member of the oven-series family of Group V.; it is closely related to Ta, and less closely to N, P, V, As, Sb, Di, Er, and Bi (*v.* Nitrogen group of elements, this vol.).

Detection and Estimation.—Niobates dissolve in hot HClAq; on adding water and boiling, $Nb_2O_5.xH_2O$ ppts. Solutions in HClAq are coloured blue, then dark brown, by Zn. K_4FeCy_6Aq gives a red pp., and K_3FeCy_6Aq a bright-yellow pp., with aqueous solutions of alkali niobates; gall tincture gives an orange-red pp. Nb is estimated as Nb_2O_5; the process is sufficiently described under *Preparation* (*cf.* Rammelsberg, *P.* 136, 177, 362; 144, 56, 191).

Niobium, acids of, and their salts. Niobic oxide, Nb_2O_5, reacts with alkali oxides to form salts; these niobates may be regarded as derived from various hydrates of Nb_2O_5. Hydrated niobic oxide, $Nb_2O_5.xH_2O$, is obtained by fusing Nb_2O_5 with $KHSO_4$, washing with water, dissolving in HClAq, and ppg. by NH_3Aq; the pp. thus obtained by Santesson (*Bl.* [2] 24, 52) contained c. 8·4 p.c. water, which corresponds with the composition $3Nb_2O_5.4H_2O$ $(=Nb_6O_{11}(OH)_8)$. The hydrate $Nb_2O_5.7H_2O$ is obtained, according to Santesson (*l.c.*), by reacting on $NaNbO_3$ with H_2SO_4Aq and drying at 100° (*v. Hydrates of niobic oxide*, p. 509). Niobates have not been obtained by neutralising hydrates of Nb_2O_5, but either by fusing Nb_2O_5 with basic oxides or carbonates, or by double decomposition from solutions of alkali niobates.

Niobates. The niobates belong to the form $xNb_2O_5.yMO$, where $M=K_2$, Ca, Mg, Mn, &c. Niobates are known corresponding with the meta- and pyrophosphates; and, besides these, salts have been isolated in which the ratio of the basic to acidic oxide varies from 1:2 to 4:1. The niobates are prepared by fusing Nb_2O_5 with basic oxides, carbonates, and a few other salts; some niobates are obtained by ppg. solutions of alkali niobates by solutions of metallic salts. The alkali niobates are soluble in water; the others are insoluble. Solutions of the alkali niobates are decomposed by H_2SO_4Aq with ppn. of $Nb_2O_5.xH_2O$; CO_2 ppts. acid salts. Solutions of niobates in HClAq are reduced by Zn to Nb_3O_5 (blue), and then to Nb_2O_4 (brown-black) (*v. Niobium oxides*, p. 508). *Fluoniobates* and *fluoxyniobates* are also known (*v.* next page).

Potassium niobates. (1) *Metaniobate*, $KNbO_3$. Small rectangular tablets; sol. water; obtained by dissolving Nb_2O_5 in molten CaF_2, fusing the product with K_2CO_3, in ratio $K_2CO_3:Nb_2O_5$, and repeatedly treating the mass (after cooling) with boiling dilute H_2SO_4Aq (Joly, *Fremy's Encyclop. Chimique*). (2) *Pyroniobate*, $K_4Nb_2O_7.11H_2O$. Insol. water; obtained by melting Nb_2O_5 with a large excess of K_2CO_3, and washing with water (Santesson, *Bl.* [2] 24, 52). (3) $3Nb_2O_5.4K_2O.16H_2O$, and (4) $7Nb_2O_5.8K_2O.32H_2O$. The former salt is obtained by fusing Nb_2O_5 with 2 to 3 times its weight of K_2CO_3, dissolving in water, and evaporating *in vacuo*; large monoclinic crystals, efflorescent in air, loses $12H_2O$ at 100°, and is dehydrated at red heat. The second salt is obtained in quadratic octahedra by slowly evaporating a solution of the first salt (Marignac, *A. Ch.* [4] 8, 5; 13, 5). (5) $2Nb_2O_5.3K_2O.13H_2O$; rhombic pyramids, by adding KOHAq to solution of salt (3) or (4), and evaporating slowly (Marignac, *l.c.*). (6) $2Nb_2O_5.2K_2O.11H_2O$; the crystalline residue obtained by fusing Nb_2O_5 and K_2CO_3, in the ratio $Nb_2O_5:K_2CO_3$, and treating with water, has this composition (Santesson, *Bl.* [2] 24, 52). (7) $4Nb_2O_5.3K_2O$; obtained by strongly heating Nb_2O_5 with twice its weight of $KHSO_4$ for some hours, and washing with water (Joly, *Fremy's Encyclop. Chimique*). (8) $3Nb_2O_5.K_2O.5H_2O$; prepared by boiling $KNbOF_3.2KFAq$ with $KHCO_3$, washing the powder which separates, and drying at 100° (Marignac, *l.c.*).

Sodium niobates. (1) *Metaniobate*, $2NaNbO_3.5H_2O$. Rhombic prisms; obtained by fusing Nb_2O_5 with 3 pts. Na_2CO_3, allowing to stand in contact with cold water (which dissolves Na_2CO_3), dissolving in hot water, and crystallising

(Joly, *Fremy's Encyclop. Chimique*). Santesson (*Bl.* [2] 24, 52) obtained this salt by boiling $Nb_2O_5.xH_2O$ with NaOHAq; the salt remained insoluble in NaOHAq, slightly soluble in cold water. (2) $4Nb_2O_5.Na_2O.H_2O$; a salt, probably with this composition, was obtained by Santesson (*l.c.*) as a gelatinous pp. by passing CO_2 into solution of $NaNbO_3$. (3) $3Nb_2O_5.2Na_2O.9H_2O$. An insoluble amorphous salt, obtained by fusing Nb_2O_5 with NaOH and treating with water (Santesson, *l.c.*).

Niobates of Ca, Mg, and Mn—viz. $Ca_2Nb_2O_7$, $Ca(NbO_3)_2$; $Mg_2Nb_2O_7.2MgO$, $Mg_2Nb_2O_7.MgO$, $Mg_2Nb_2O_7$; $Mn(NbO_3)_2$—have been obtained by Joly (*l.c.*) by fusing $CaCl_2$, $MgCl_2$, and $MnCl_2$, with Nb_2O_5. Joly also obtained a niobate of Fe, and a niobate of Fe and Mn. H. Rose (*P.* 90, 456) obtained niobates of Cu, Hg, and Ag by adding salts of these metals to solutions of $NaNbO_3$.

FLUONIOBATES. These salts, which may also be regarded as compounds of NbF_5 with metallic fluorides, and sometimes also with HF, are obtained by dissolving $Nb_2O_5.xH_2O$ in large excess of HFAq, adding metallic carbonates, and evaporating; the fluoniobates are also formed by dissolving fluoxyniobates (*v. infra*) in HFAq and evaporating (Marignac, *A. Ch.* [4] 13, 5; Santesson, *Bl.* [2] 24, 52). The following are the principal fluoniobates:—

$(NH_4)_2NbF_7.2NbOF_3.NH_4F$;
$Co_5Nb_3F_{25}.5HF.28H_2O$
$(=3NbF_5.5CoF_2.5HF.28H_2O)$;
$Cu_4Nb_2F_{18}.HF.18H_2O$
$(=2NbF_5.4CuF_2.HF.18H_2O)$;
$Fe_3Nb_2F_{16}.19H_2O$ $(=2NbF_5.3FeF_2.19H_2O)$;
$Mn_5Nb_3F_{25}.5HF.13H_2O$
$(=3NbF_5.5MnF_2.5HF.13H_2O)$;
$Ni_5Nb_3F_{25}.5HF.28H_2O$
$(=3NbF_5.5NiF_2.5HF.28H_2O)$;
$K_2NbF_7(NbF_5.2KF)$.

FLUOXYNIOBATES. These salts are obtained by dissolving Nb_2O_5 with alkali fluorides in HFAq, and evaporating. They may be regarded as derived from the hypothetical acids H_2NbOF_5, H_3NbOF_6, and H_4NbOF_7; they may also be looked on as compounds of $NbOF_3$ with alkali fluorides. The fluoxyniobiates have been examined chiefly by Marignac (*A. Ch.* [4] 8, 5; 13, 5).

Ammonium fluoxyniobates. 1. $(NH_4)_2NbOF_5$ $(=NbOF_3.2NH_4F)$. Obtained by dissolving Nb_2O_5 and NH_4F in HFAq, and evaporating; easily soluble rhombic prisms, isomorphous with $WO_2F_2.2NH_4F$.—2. $(NH_4)_3NbOF_6$ $(=NbOF_3.3NH_4F)$. Obtained similarly to the foregoing salt; forms octahedral crystals, isomorphous with $ZrF_4.3NH_4F$ (Baker, *C. J.* 35, 762).—3. $(NH_4)_4NbOF_7$ $(=NbOF_3.4NH_4F)$. Obtained by dissolving $Nb_2O_5.xH_2O$ in conc. NH_4FAq; cubic and octahedral crystals of the regular system (Joly, *P.* 108, 467). — 4. $(NH_4)_5Nb_3O_3F_{14}.H_2O$ $(=3NbOF_3.5NH_4F.H_2O)$. Obtained by adding less than an equivalent of NH_4F to Nb_2O_5 in HFAq, and evaporating.

Potassium fluoxyniobates. — 1. $K_2NbOF_5.H_2O$ $(=NbOF_3.2KF.H_2O)$. Obtained by evaporating a solution of Nb_2O_5 in HFAq after addition of KF. By crystallising from water, the salt separates in such fine tablets that the liquid appears to gelatinise; monoclinic tables are obtained by crystallising from water containing a little HF. Loses H_2O at 100°; melts at red heat; sol. in 12–13 pts. water at 17°–21°; easily soluble in hot water. — 2. K_3NbOF_6 $(=NbOF_3.3KF)$. Obtained by adding excess of KF to solution of the foregoing salt. Cubical crystals belonging to the regular system (Baker, *C. J.* 35, 761).—3. $K_5Nb_3O_3F_{14}.H_2O$ $(=3NbOF_3.5KF.H_2O)$. Obtained by adding less than an equivalent of KF to Nb_2O_5 in HFAq, evaporating a little, separating from $K_2NbOF_5.H_2O$ which separates, and evaporating the mother-liquor.—4. $K_3NbOF_6.HF$ $(=NbOF_3.3KF.HF)$. Obtained by dissolving Nb_2O_5 in considerable excess of HFAq, and adding excess of KF; isomorphous with $SnF_4.3KF.HF$.

Fluoxyniobates of Cu and Zn have also been obtained; $CuNbOF_5.4H_2O$, and $ZnNbOF_5.6H_2O$.

Niobium, alloys of. An alloy of Nb with Al, approximately of the composition Nb_2Al_3, was obtained by Marignac (*Ar. Sc.* 31, 89) by heating $NbF_5.2KF$ with Al in a carbon crucible, and treating with cold HClAq. A grey, crystalline, metal-like powder; S.G. 4·45 to 4·52. Soluble in hot HClAq with evolution of H. Insoluble in HNO_3Aq or dilute H_2SO_4Aq; boiling conc. H_2SO_4 forms SO_2 and S; soluble in HFAq.

Niobium, bromide of. $NiBr_5$. Formula probably molecular, because of similarity with $NbCl_5$, which has been gasified. A purple-red solid, obtained by passing CO_2 laden with Br vapour over a heated mixture of Nb_2O_5 and C (H. Rose, *P.* 104, 442).

Niobium, carbide of. By heating to c. 1500° a mixture of 4 pts. Nb_2O_5, 1 pt. sugar carbon, and 1 pt. Na_2CO_3, Joly obtained large violet needles of the composition NbC (*Bl.* [2] 25, 206).

Niobium, carbonitride of. By heating Nb_2O_5 with a mixture of Na_2CO_3 and C to c. 1200°, Deville (*C. R.* 66, 180) obtained a crystalline mass, which evolved NH_3 when heated with molten KOH; according to Joly (*Bl.* [2] 25, 206), this substance is either a carbonitride of Nb, or a mixture of carbide, NbC, with nitride NbN.

Niobium, chlorides of. Two chlorides of Nb are known, $NbCl_5$ and $NbCl_3$.

NIOBIUM PENTACHLORIDE $NbCl_5$. Mol. w. 270·85. V.D. 138·9 (Deville a. Troost, *C. R.* 60, 1221). Melts at 194° and boils at 240° (D. a. T., *l.c.*).

Preparation.—Perfectly dry Nb_2O_5 is mixed with a large excess of dry sugar or starch, the mixture is completely charred by heating in a closed crucible, and a small quantity is then placed in a rather wide tube of hard glass, narrowed here and there, connected with a CO_2 and a Cl apparatus; the tube is gently heated for some time while a stream of perfectly dry CO_2 is passed through it, and is then allowed to cool in the CO_2; when cold, perfectly dry Cl is passed through the tube; when every trace of CO_2 is expelled, the tube is gradually heated to bright redness in the stream of Cl; $NbCl_5$, mixed with a little $NbOCl_3$, collects in the wider parts of the tube. The $NbCl_5$ is separated from the less volatile $NbOCl_3$ by distillation in dry Cl.

As $NbCl_5$ is very voluminous the operation must be conducted in wide tubes and with small quantities of the mixed Nb_2O_5 and C (H. Rose).

Properties and Reactions.—Yellow needles; melts at 194°, beginning to sublime at 125°, boils at 240° (Deville a. Troost, *C. R.* 60, 1221). Vapour

is yellow. Soluble in alcohol. Fumes in air, giving off HCl. Decomposed by water to HCl and $Nb_2O_5.xH_2O$. Soluble in cold conc. HClAq; Zn produces a blue colour in this solution; on dilution and heating, $Nb_2O_5.xH_2O$ separates. Soluble in conc. H_2SO_4 with evolution of HCl. Vapour of $NbCl_5$ is reduced to Nb by heating with H (Blomstrand; Roscoe, *C. N.* 37, 25). $NbOCl_3$ is produced by heating with Nb_2O_5. $Nb_2O_2S_3$ is formed by heating in CS_2 vapour (Delafontaine, *Ar. Sc.* 27, 167).

Niobium trichloride $NbCl_3$. When vapour of $NbCl_5$ is slowly passed through a red-hot tube, a dark-grey metal-like crust forms on the sides of the tube; this crust is $NbCl_3$ (Roscoe, *C. N.* 37, 25). Not volatile; non-deliquescent; unchanged by H_2O or NH_3Aq; by HNO_3Aq gives HCl and $Nb_2O_5.xH_2O$. Heated in air, gives off white fumes. When heated in CO_2, produces CO and $NbOCl_3$.

Niobium, fluoride of. No fluoride of Nb has been isolated with certainty. $Nb_2O_5.xH_2O$ dissolves easily in HFAq; on evaporation a non-crystallisable mass is obtained, which evolves white fumes when heated and leaves Nb_2O_5. Solution of $Nb_2O_5.xH_2O$ in HFAq yields *fluoniobates* when mixed with metallic carbonates and evaporated; these fluoniobates may be regarded as compounds of NbF_5 with metallic fluorides (*v. Fluoniobates*, p. 507).

Niobium, haloid compounds of. The only haloid compound of Nb which has been gasified is $NbCl_5$; the trichloride is also known, and the formula $NbCl_3$ is probably molecular. No fluoride or iodide has been isolated, but several compounds are known, which may be regarded as formed by the union of NbF_5 with more positive fluorides (*v. Fluoniobates*, p. 507). $NbCl_3$ reduces CO_2 to CO at a high temperature. Oxyhaloid compounds are known, of the form $NbOX_3$, where X = Br, Cl, or F.

Niobium, hydride of, ?NbH. Marignac (*Ar. Sc.* 1868) obtained a heavy grey powder, having approximately the composition NbH, mixed with a little Nb_2O_5, by heating K_2NbF_7, mixed with a little KHF_2, and covered with NaCl, with excess of Na in an iron crucible. The reaction was energetic; the fused mass was broken up, treated with water, then with water containing a little HF, then washed with water, and finally filtered and dried. The powder obtained by Marignac had S.G. 6 to 6·6; it dissolved in conc. HFAq with rapid evolution of H; it was insoluble in HClAq, HNO_3Aq, and dilute H_2SO_4Aq, sol. warm conc. H_2SO_4, also in molten $KHSO_4$; heated in air or O to above 100° it burned to Nb_2O_5 and H_2O; it was unchanged when heated in H. Krüss a. Nilson (*B.* 20, 1691) repeated Marignac's experiments, using a quantity of Na equivalent to the K_2NbF_7; they obtained a mixture of c. 77 p.c. NbH, c. 21·5 p.c. Nb_2O_5, and c. 1 p.c. Fe_2O_3. K. a. N. give S.H. of NbH as ·097 at 0° to 100°, ·092 at 0° to 210·5°, ·087 at 0° to 301·5°, and ·083 at 0° to 449°.

Niobium, nitride of, ?NbN. $NbCl_5$ absorbs NH_3; on heating, NH_4Cl is evolved, and a black mass remains which contains N. Heated with KOHAq, NH_3 is evolved; it is not attacked by HNO_3Aq; soluble in HFAq; heated in air, it oxidises with incandescence. The composition of this body is approximately NbN (H. Rose; Deville, *C. R.* 66, 180; Joly, *Bl.* [2] 25, 206). By reducing Nb_2O_5 with a mixture of soda and C, Deville obtained a crystalline mass, probably a mixture of nitride and carbide of Nb.

Niobium, nitro-carbide of, *v. Niobium, carbonitride of*, p. 507.

Niobium, oxides of. Three oxides of Nb have been isolated, NbO, NbO_2, and Nb_2O_5; a fourth, Nb_3O_5, probably exists. Nb_2O_5 is formed by heating Nb in air or O, also by decomposing $NbOCl_3$ by water, and in other ways; NbO_2 is produced by the partial reduction of Nb_2O_5 in H; NbO is obtained by the incomplete reduction of $NbOF_3$ or $NbOCl_3$ by Na or Mg; when Nb_2O_5 in HClAq is reduced by Zn the solution becomes brown, and a solid separates, which is probably Nb_3O_5. Moist Nb_2O_5 reacts as an acid-forming oxide; niobates are formed by fusing Nb_2O_5 with basic acids or carbonates (*v. Niobates*, p. 506). The mol. w. of none of the oxides of Nb is known with certainty.

Niobic oxide Nb_2O_5 (*Niobic anhydride. Niobium pentoxide*).

Occurrence.—Niobates occur in a few rare minerals, *e.g. columbite, tantalite*, and *samarskite*.

Preparation.—1. $NbOCl_3$ is agitated with water, the insoluble $Nb_2O_5.xH_2O$ is washed till free from HCl, dried at 100°, and heated to incipient redness. The solution after treating $NbOCl_3$ with water contains much Nb_2O_5; the oxide is obtained by adding slight excess of NH_3Aq, warming till every trace of NH_3 is removed, collecting the pp., washing till free from HCl, and drying.—2. Dilute H_2SO_4Aq is added to a boiling solution of $NaNbO_3$, the ppd. $Nb_2O_5.xH_2O$ is thoroughly washed and heated.—3. Impure Nb_2O_5 is fused with $KHSO_4$, the fused mass is treated with water, and the pp. is washed and heated.—4. Nb_2O_5 is obtained in crystals by dissolving in molten borax, heating in a porcelain oven, washing, and drying (Nordenskjöld, *P.* 114, 612; Ebelmen, *A. Ch.* [3] 33, 34; Knop, *Z. K.* 12, 610; also by strongly heating Nb_2O_5 (from $NbOCl_3$) in a slow current of HCl (Deville, *C. R.* 66, 180). For preparation of Nb_2O_5 from *columbite v.* Niobium, *Preparation*, p. 505.

Properties.—A white powder; becomes yellow when heated, and goes white on cooling. Insoluble in water. S.G. 4·4 to 4·53 (Marignac, *A. Ch.* [4] 8, 5). The crystals of Nb_2O_5 are flat, right-angled tablets; they are optically active (Nordenskjöld, *P.* 114, 612; *cf.* Ebelmen, *A. Ch.* [3] 33, 34; Knop, *A.* 159, 56). S.H. ·118 at 0° to 210·5°, ·124 at 0° to 301·5°, ·134 at 0° to 449°. (Krüss a. Nilson, *B.* 20, 1691).

Reactions.—1. Dissolves in hot conc. *sulphuric acid*; the solution may be diluted without ppn., but on heating all the Nb_2O_5 is ppd.; the pp. contains H_2SO_4.—2. Boiling *hydrochloric acid* dissolves only traces of Nb_2O_5; the residue is easily soluble in water, and this solution is ppd. on boiling with H_2SO_4Aq (Wöhler, *P.* 48, 93; Marignac, *A. Ch.* [4] 8, 15; 13, 20; H. Rose, *P.* 112, 484).—3. Easily dissolved by cold *hydrofluoric acid*.—4. Soluble in *caustic potash* solution.—5. *Caustic soda* does not dissolve Nb_2O_5 but the product is soluble in water. Nb_2O_5 which has been strongly heated is insoluble in H_2SO_4, HClAq, or HFAq; it is dissolved by molten alkalis.—6. Reduced by *hydrogen* to

NbO_2 at full red heat.—7. Moist Nb_2O_5 dissolved in HClAq is reduced by *zinc* with formation of a blue liquid which then becomes brown and deposits brown flocks, probably of Nb_3O_5 (Marignac, *A.Ch.* [4] 13, 5).—8. Strongly heated with *hydrogen sulphide*, or *carbon disulphide*, an oxysulphide is formed, probably Nb_2OS_3 (Delafontaine, *Ar. Sc.* 27, 167).—9. Heated with *ammonia*, Nb nitride (*q.v.*) is formed.—10. Mixed with *carbon* and heated in *chlorine* or *bromine*, $NbCl_5$ (or $NbBr_5$) is formed along with some $NbOCl_3$ (or $NbOBr_3$).—11. Fused with *basic oxides* or *carbonates*, niobates (*q. v.*) are produced.

Combinations.—1. With *water* to form various hydrates (*v. infra*).—2. Nb_2O_5 appears to combine with some acids, but no definite compounds have yet been isolated; *e.g.* the pp. obtained by decomposing $NbOCl_3$ by water in presence of Na_2HPO_4 contains H_3PO_4, and the pp. obtained by adding water to Nb_2O_5 in H_2SO_4 and boiling contains H_2SO_4 (*v.* Blomstrand, *Acta Univ. Lund.* 1864).

Hydrates of niobic oxide. Various hydrates of Nb_2O_5 are known. By fusing Nb_2O_5 with $KHSO_4$, boiling with water, dissolving the pp. in HClAq, and ppg. by NH_3Aq, Santesson (*Bl.* [2] 24, 52) obtained a flocculent pp. containing 8·04 to 8·41 p.c. H_2O, agreeing with the formula $3Nb_2O_5.4H_2O$. The solid obtained by ppg. $NaNbO_3Aq$ by H_2SO_4Aq and drying at 100° has the composition $Nb_2O_5.7H_2O$, according to Santesson (*l.c.*). The hydrate obtained by decomposing $NbOCl_3$ by water is amorphous; that formed by the action of moist air on $NbOCl_3$ is said to be crystalline (H. Rose, *P.* 112, 557). The hydrates of Nb_2O_5 react as weak acids (*v. Niobates*, p. 506).

Niobous oxide NbO (*Niobium monoxide*). By reducing $NbOF_3.2KF$ with Na, H. Rose obtained a black powder which he thought to be Nb (*P.* 104, 312). This substance was recognised as an oxide by Delafontaine (*Ar. Sc.* 27, 167). Prepared by strongly heating $NbOF_3.2KF$ with Na, under KCl, and washing with cold water. S.G. 6·3 to 6·67. Obtained in crystals by passing vapour of $NbOCl_3$ over heated Mg wire (Deville a. Troost, *C. R.* 60, 1221; *v.* also Deville, *C. R.* 66, 183). Black, lustrous, regular crystals. Moist NbO is soluble in boiling dilute HClAq, or in HFAq; H is said to be evolved. KOHAq dissolves NbO, forming K niobate. Molten $KHSO_4$ forms Nb_2O_5; heated in Cl $NbOCl_3$ is produced.

Niobium dioxide NbO_2 (*Niobium tetroxide* [Nb_2O_4]). A black powder with blue reflection; insol. water and acids. Formed by heating Nb_2O_5 in a stream of H to full white heat (Delafontaine, *Ar. Sc.* 27, 167).

Wöhler (*P.* 48, 93) noticed that Zn reduces a solution of Nb_2O_5 in HClAq, with production of blue and then brown coloured substances. Marignac (*A. Ch.* [4] 13, 5) obtained a blue-brown pp. by boiling $Nb_2O_5.xH_2O$ with HClAq, dissolving the residue in water, and reducing by Zn.

Niobium, oxybromide of, $NbOBr_3$. A voluminous, crystalline, yellowish solid, obtained by passing Br vapour over a heated mixture of Nb_2O_5, with a little charcoal (H. Rose, *P.* 104, 442). Sublimes without melting. Heated in CO_2 gives Nb_2O_5 and $NbBr_5$. Decomposed by water, giving $Nb_2O_5.xH_2O$ and HBrAq.

Niobium, oxychloride of, $NbOCl_3$. Mol. w. 216·1. Obtained, along with $NbCl_5$, by heating Nb_2O_5 mixed with charcoal in a stream of Cl; also by heating Nb_2O_5 in a stream of CO_2 charged with vapour of $NbCl_5$ (Deville a. Troost, *C. R.* 60, 1221). A white, lustrous mass; sublimes at c. 400° without melting. V.D. at 440° to 810° = 114 (D. a. T., *l.c.*). Heated strongly in CO_2, $NbCl_5$ and Nb_2O_5 are formed; the same products are formed by heating in H (Blomstrand, *Acta Univ. Lund.*, 1864). Sol. alcohol; decomposed by water to $Nb_2O_5.xH_2O$ and HClAq.

Niobium, oxyfluoride of, $NbOF_3$. Small crystals, optically active; resemble ZrF_4; obtained by strongly heating Nb_2O_5, mixed with a large excess of CaF_2 in HCl (Joly, *C. R.* 81, 1266). $NbOF_3$ forms various compounds with metallic fluorides (*v. Fluoxyniobates*, p. 507).

Niobium, oxysulphide of, Nb_2OS_3. A black powder; obtained by passing H_2S or CS_2 vapour over strongly heated Nb_2O_5. The product of these reactions was supposed by H. Rose to be a sulphide of Nb (*P.* 111, 193; *v.* also Rose a. Hermann, *J. pr.* 111, 393). Delafontaine (*Ar. Sc.* 27, 167) showed the substance to be an oxysulphide; Rammelsberg (*J. pr.* 108, 95) thought the composition was NbOS or $Nb_7O_7S_8$.

Niobium, salts of. No compounds obtained by replacing the H of acids by Nb have yet been isolated. There are indications that Nb_2O_5 combines with some acids (*v. Niobic oxide, Combinations*, No. 2, *supra*). M. M. P. M.

NITRANILIC ACID *v.* Di-nitro-di-oxy-quinone.

NITRANILINE *v.* Nitroaniline.

NITRATES. *Salts of nitric acid*, HNO_3. The greater number of the nitrates are normal salts; many basic nitrates also exist. The general formula for normal nitrates may be written $M^n.nNO_3$, where M^n denotes a metal of n valency. The normal nitrates may also be regarded as composed of a basic and an acidic radicle; on this view, they are classed under the general formulæ $M_2O.N_2O_5$, $MO.N_2O_5$, $M_2O_3.3N_2O_5$, $MO_2.2N_2O_5$. The simplest way of looking at the composition of the basic nitrates is to regard them as compounds of the acidic radicle N_2O_5 with more than the normal quantity of base; thus normal lead nitrate is $PbO.N_2O_5$, and basic lead nitrate is $3PbO.N_2O_5$. Several basic nitrates may be formulated as salts of the hypothetical orthonitric acid H_3NO_4, which bears the same relation to ordinary, or meta, nitric acid that orthophosphoric bears to metaphosphoric acid; thus basic lead nitrate $3PbO.N_2O_5$ may be written $Pb_3(NO_4)_2$.

Some nitrates occur native; *e.g.* $Ca(NO_3)_2$, $Mg(NO_3)_2$, KNO_3, $NaNO_3$. Alkali nitrates are found in river, spring, and drainage waters, and in the juices of some plants. With regard to the formation of nitrates in the soil *v.* Nitrification, this vol. Nitrates are prepared by dissolving metals, metallic oxides or carbonates, in nitric acid; also, in some cases, by double decomposition from the alkali nitrates.

Most nitrates are crystalline salts. As no nitrate has been gasified, the formulæ of these salts are not necessarily molecular. The normal nitrates are soluble in water; a few, *e.g.* $Bi(NO_3)_3$, are decomposed by water with production of insoluble basic nitrates. Nitrates are decomposed

by heat; a few give off HNO_3, but in almost all cases O is evolved, along with oxides of N and H_2O; the final residue is generally a metallic oxide corresponding with the nitrate used; $AgNO_3$ leaves a residue of Ag. Heated with combustible bodies, nitrates cause deflagration or explosion; if the combustible body be an acid-forming element, or a compound capable of forming an acid by oxidation, a salt is formed composed of the metal of the nitrate and the acid produced from the combustible body. Thus K_2SeO_4 is formed by deflagrating KNO_3 with Se, and K_2MnO_4 by deflagrating KNO_3 with an oxide or salt of Mn. Alkali nitrates are reduced to NH_3 by the action of potash and zinc, or by a pair of metals one of which is distinctly more electro-positive than the other, *e.g.* by Cu and Zn, Fe and Zn, Pt and Zn, &c. Alkali nitrates are also reduced to NH_3 by the action of common putrefactive organisms in presence of peptones and air; also by Pt black charged with O, in the presence of dextrose (*v.* Loew, *B.* 23, 675). Nitrates are reduced to nitrites, N_2O, NO, and N, by organisms present in the soil (*v.* Warrington, *C. J.* 45, 669; 53, 742 [references are given here to other memoirs]; 59, 484; Munro, *C. J.* 49, 667).

The greater number of the nitrates are insoluble in conc. nitric acid. A few dissolve in a large quantity of the acid; according to Ditte (*A. Ch.* [5] 18, 320) these nitrates combine with HNO_3 to form acid salts, *e.g.* $KNO_3.2HNO_3$, $NH_4NO_3.HNO_3$, $KNO_3.3HNO_3$, $RbNO_3.5HNO_3$. Some other hydrated nitrates dissolve in warm HNO_3Aq when dehydrated; on cooling, hydrates are deposited containing less water than those which crystallise from water; to this class of nitrates belong $Mg(NO_3)_2$, $Mn(NO_3)_2$, $Zn(NO_3)_2$, $Al(NO_3)_3$, $Cu(NO_3)_2$ (Ditte, *l.c.*).

The methods of detecting and estimating nitrates are numerous; reference must be made to *Manuals of analysis*.

Aluminium nitrates. The *normal* salt, $Al(NO_3)_3.9H_2O$, obtained by dissolving AlO_3H_3 in HNO_3Aq, and evaporating, crystallises in oblique rhombic prisms. Melts at 73°; deliquescent; c. sol. H_2O and HNO_3Aq (Ordway, *A.* 76, 247; Salm-Horstmar, *J.* 1850. 301; Thorey, *Russ. Zeitschr. Pharm.* 10, 321). The salt does not react with HCl gas (Thomas, *C. J.* 33, 367). *Basic* Al nitrates are obtained by digesting $Al(NO_3)_3$ with AlO_3H_3 (Ordway, *l.c.*).

Ammonium nitrate NH_4NO_3. According to Tissandier (*C. R.* 82, 388) this salt is frequently present in rain-water. It is obtained by adding a slight excess of NH_3Aq to HNO_3Aq and evaporating; also by passing the electric discharge through a mixture of H, N, and O; by passing H_2S into dilute HNO_3Aq; by the interaction of certain metals, *e.g.* Sn, with HNO_3Aq. NH_4NO_3 crystallises in various forms according to the temperature; the crystals formed at 36° are trimetric, those formed at 87° are rhombohedral, and monometric crystals are produced at 120° (Lehmann). The specific heats, volume-changes, and heats of transformation, of the various modifications have been determined by Bellati a. Romanese (*Nuovo Cimento*, [3] 21, 5; abstract in *C. J.* 54, 106). S.G. 1·707 (Kopp, *A.* 36, 1); 1·709 (Schiff, *A.* 112, 88); for other results *v.* Clarke's *Specific Gravity Table*, new ed. 110. NH_4NO_3 dissolves in H_2O with a large disappearance of heat. S. at 18° c. 200; saturated solution contains 47·8 p.c. NH_4NO_3, and boils at 164°. E. sol. alcohol. Deliquesces in air, losing NH_3 and acquiring an acid reaction. Melts at c. 152°; decomposition begins at c. 210° and becomes explosive at c. 300°; products are H_2O and N_2O, but part of salt volatilises (Berthelot, *C. R.* 82, 932); heated very rapidly, NH_3, NO, and NH_4NO_2 are also formed (B.). According to B. (*l.c.*) NH_4NO_3 may be sublimed unchanged, by placing the fused salt in a basin covered with filter paper, over which is a paper cylinder filled with coarse fragments of glass, and heating gently not above 190°–200°. NH_4NO_3 condenses considerable quantities of NH_3, forming a liquid varying in composition according to temperature and pressure (*v.* Divers, *Pr.* 21, 107; Raoult, *C. R.* 77, 788). At −10°, and 760 mm., the liquid $NH_4NO_3.2NH_3$ is formed; heated to 28·5° a solid remains, $NH_4NO_3.NH_3$ (R., *l.c.*); *cf.* Mendelejeff (*B.* 23, 3464), who regards $NH_4NO_3.NH_3$ and $NH_4NO_3.2NH_3$, as amides obtained from $NO.OH.ONH_4.ONH_4$ and $NO(OHN_4)_3$, which are the NH_4 salts of hypothetical orthonitric acid $NO(OH)_3$. The liquid compounds of NH_4NO_3 and NH_3 react with many salts, the reactions generally resembling those of NH_4NO_3 and dry NH_3 combined (for details *v.* Divers, *l.c.*). NH_4NO_3 absorbs dry HCl, forming NH_4Cl; after a time a little Cl and NO are evolved (Thomas, *C. J.* 33, 367). The Cu-Zn couple reduces NH_4NO_3Aq to NH_3 and NH_4NO_2; at B.P. NO is evolved (Gladstone a. Tribe, *C. J.* 33, 150).

Antimony nitrate. The compound $Sb_4O_6.N_2O_5$ is said to be formed by dissolving Sb_4O_6 in cold fuming HNO_3 (Péligot, *C. R.* 23, 709).

Barium nitrate $Ba(NO_3)_2$. Crystallises in tetartohedral forms belonging to the regular system (Scacchi, *J.* 1860. 13; Baumhauer, *Z. K.* 1, 51; Lewis, *P. M.* [5] 3, 453). S.G. 3·22 to 3·24 (Kremers, *J.* 5, 15; for other determinations *v.* Clarke's *Specific Gravity Table* (new ed.), 111). H.F. [Ba, O, N^2O^5 Aq] = 187,020 (?) (*Th.* 3, 518). Melts at c. 593° (Carnelley, *C. J.* 33, 278). S. 5 at 0°, 7 at 10°, 9·2 at 20°, 11·6 at 30°, 14·2 at 40°, 17·1 at 50°, 20·3 at 60°, 23·6 at 70°, 27 at 80°, 30·6 at 90°, 32·2 at 100°; saturated solution boils at 101·9°; S.G. and pctge. composition of $Ba(NO_3)_2Aq$ are as follows (Mulder):—

S.G.	P.c. $Ba(NO_3)_2$	S.G.	P.c. $Ba(NO_3)_2$
1·009	1	1·05	6
1·017	2	1·06	7
1·025	3	1·069	8
1·034	4	1·078	9
1·042	5	1·087	10

$Ba(NO_3)_2$ is only slightly soluble in water containing HCl or HNO_3; insol. alcohol.

$Ba(NO_3)_2$ is prepared by adding to $BaCO_3$, or crude BaS, enough HNO_3Aq to decompose almost the whole of the salt, filtering, and crystallising; also by mixing equivalent weights of $BaCl_2$ and $NaNO_3$ in solution, and recrystallising the $Ba(NO_3)_2$ which separates (Bolley, *C. C.* 1860. 330; Kuhlmann, *D. P. J.* 150, 57, 108, 415). $Ba(NO_3)_2$ melts at a moderate temperature; at red heat it evolves O, N, and NO_2, and leaves BaO; according to Rammelsberg (*B.* 2, 147; 7, 542) the residue

contains more O than BaO, and has the composition Ba_3O_4. $Ba(NO_3)_2$ is not acted on by HCl gas (Thomas, *C. J.* 33, 367).

Beryllium nitrates. The composition of these salts is doubtful. They are very soluble in water and difficult to crystallise. By double decomposition from $BeSO_4$Aq, and evaporating, Ordway (*J. pr.* 76, 22) obtained deliquescent crystals approximating to the composition $Be(NO_3)_2.3H_2O$. By heating at 100° the crystals lost half of their nitric acid, and a basic salt remained, soluble in water. Other soluble basic salts seem to be formed by adding a little NH_3Aq to a solution of the normal salt, and by digesting the normal salt with $BeO.xH_2O$.

Bismuth nitrates. The *normal* salt has the composition $Bi(NO_3)_3.10H_2O$ according to Gladstone (*J. pr.* 44, 179) and Heintz (*J. pr.* 45, 102); according to the more recent work of Yvon (*C. R.* 84, 1164) the crystallised salt has the composition $2Bi(NO_3)_3.11H_2O$. The normal salt is formed by dissolving Bi, Bi_2O_3, or $Bi_2(CO_3)_3$ in HNO_3Aq, filtering through asbestos or powdered glass, and evaporating to the crystallisation-point. Forms large deliquescent crystals; S.G. 2·823 at 13° (Clarke's *Table of Specific Gravities* (new ed.), 112). Crystals are very caustic; they melt easily in the water of crystallisation; decomposition begins at c. 75°–80° with production of basic salts (*v. infra*). Decomposed by HCl gas, giving $BiCl_3$ and also much Cl, along with NO, H_2O, and possibly other oxides of N and Cl (Thomas, *C. J.* 33, 367). Various *basic* salts have been described. According to Graham (*A.* 29, 16) $2(BiO.NO_3).H_2O$ is formed by heating the normal salt to 80°, and is not decomposed below 260° (*cf.* Ruge, *J.* 1862. 163). Yvon (*C. R.* 84, 1164) assigns the composition $4(BiO.NO_3).3H_2O$ to the salt obtained by heating the normal salt to 120°, and also to the product of the action of water on the normal salt. Many basic salts, $xBi_2O_3.yN_2O_5.zH_2O$, seem to be produced by decomposing $Bi.3NO_3$, or a solution of Bi in HNO_3Aq, by water; the composition of the most stable of these *subnitrates* is $BiO.NO_3.H_2O$; in other cases x, y, and z have such values as 5, 4, and 9, or 5, 3, and 8, or 6, 5, and 9. The composition of these basic salts varies with the temperature of the water used, the amount of washing given to the pp., and the length of time the pp. is allowed to remain in contact with the acid liquid above it. The compositions of these salts, and the preparation of a salt of constant composition for medicinal use, have been examined chiefly by Phillips (*J. Ph.* 18, 688), Duflos (*Ar. Ph.* [2] 23, 307), Herberger (*R. P.* 55, 289, 306), Ullgren (*B. J.* 17, 169), Dulk (*R. P.* 33, 1), Becker (*Ar. Ph.* 55, 31, 129), Janssen (*Ar. Ph.* 68, 1, 129), Ruge (*J.* 1862. 163), and Yvon (*C. R.* 84, 1164).

Cadmium nitrate $Cd(NO_3)_2.4H_2O$. White, prismatic, deliquescent, needles; by dissolving Cd, CdO, or $CdCO_3$ in HNO_3Aq and evaporating. S.G. 2·45 at 14°, 2·46 at 20° (Laws, *Am. S.* [3] 14, 281). H.F. $[Cd,O^2,N^2O^4,4H^2O] = 125,170$; $[Cd, O, N^2O^5Aq] = 86,000$ (*Th.* 3, 518). Melts at 59·5°, and boils at c. 132° (Ordway, *Am. S.* [2] 27, 14). Reacts with HCl gas to produce $CdCl_2$, evolving Cl and NO (Thomas, *C. J.* 33, 367). Wells (*Am.* 9, 304) describes a *basic* salt; to this salt he has assigned the composition $2CdO.N_2O_5.3H_2O$; obtained by digesting hot $Cd(NO_3)_2$Aq with CdO, and allowing to cool.

Cæsium nitrate $CsNO_3$. Obtained by dissolving Cs_2CO_3 in HNO_3Aq, and evaporating; the *habitus* of the crystals depends on the rate of evaporation. Melts below red heat; when strongly heated evolves O, and forms $CsNO_2$. S. 10·58 at 3·2°; very slightly sol. in alcohol (Bunsen, *P.* 119, 1).

Calcium nitrate $Ca(NO_3)_2.4H_2O$. Occurs in soils when conditions are favourable to production of HNO_3, and Ca salts are also present. This salt is prepared in some countries by the slow decomposition of animal and vegetable matter. S.G. 1·79 when liquid, and 1·9 when solid, at 15·5° (Ordway, *J.* 12, 115). S.G. of $Ca(NO_3)_2 = 2·5$ at 17·9° (Favre a. Valson, *C. R.* 77, 579). H.F. $[Ca,O^2,N^2O^4,4H^2O] = 218,440$; $[Ca,O,N^2O^5Aq] = 177,160$. Prepared by dissolving CaO or $CaCO_3$ in HNO_3Aq, and evaporating; if the evaporation is continued to dryness the anhydrous salt is obtained. The hydrated salt crystallises with difficulty in deliquescent, six-sided prisms; melts at 44°; boils at 132°, remaining clear till c. one-third of the water has gone, when the anhydrous salt is deposited (Ordway, *Am. S.* [2] 27, 14). The dry salt $Ca(NO_3)_2$ melts at 561° (Carnelley, *C. J.* 33, 278). Decomposed at high temperature, giving off O and NO; the partially decomposed salt is phosphorescent (*Baldwin's phosphorus*); not acted on by HCl gas (Thomas, *C. J.* 33, 367).

Cerium nitrates. *Cerous nitrate*, $Ce(NO_3)_3.6H_2O$, is obtained as a pale rose-coloured, deliquescent, crystalline mass, by dissolving Ce_2O_3, or CeO_2 in presence of reducing substances, in HNO_3Aq, evaporating, and drying over H_2SO_4 (Lange, *J. pr.* 82, 129). Gives off $3H_2O$ at 150°, and decomposes at 200°. Forms several double salts with nitrates MNO_3 and $M(NO_3)_2$, *e.g.* $Ce(NO_3)_3.2KNO_3.2H_2O$, $2Ce(NO_3)_3.3Mg(NO_3)_2.24H_2O$. These double nitrates have been examined by Lange (*l.c.*) and Holzmann (*J. pr.* 84, 76), and more recently by Zschiesche (*J. pr.* 107, 65). They are obtained by crystallising a mixed solution of $Ce(NO_3)_3$ and the other nitrate; and also by dissolving CeO_2 in HNO_3, adding the other nitrate and a little alcohol, and evaporating. Should the metal of the nitrate which is added be capable of forming a higher oxide than that corresponding to the nitrate used, a little of this oxide is sometimes formed at the expense of the O of the CeO_2, and the reduction from $Ce(NO_3)_4$ to $Ce(NO_3)_3$ proceeds without addition of alcohol; thus, addition of $Mn(NO_3)_2$ to CeO_2 dissolved in HNO_3Aq produces $2Ce(NO_3)_3.3Mn(NO_3)_2.24H_2O$, with simultaneous formation of a little MnO_2. The double cerous nitrates are also formed by dissolving the various metals in an acid solution of CeO_2 in HNO_3Aq; reduction is effected to $Ce(NO_3)_3$. *Ceric nitrate*, $Ce(NO_3)_4$. Said to be obtained as a reddish-yellow mass by evaporating CeO_2 in HNO_3Aq; decomposed by hot water forming a basic salt. Combines with KNO_3 and NH_4NO_3 to form $2Ce(NO_3)_4.4MNO_3.3H_2O$ (Berzelius, *P.* 1, 29.)

Chromium nitrates. The *normal* salt, $Cr(NO_3)_3.9H_2O$, is obtained by dissolving CrO_3H_3 in HNO_3Aq, evaporating, and crystallising from warm water; the crystals, which form with difficulty, are purple oblique prisms, melting at

37° to a green liquid which boils at 125·5° (Ordway, *Am. S.* [2] 9, 30; 27, 14). Various *basic* salts are described by Loewel (*Ph. C.* 1845. 580), Ordway (*Am. S.* [2] 26, 197), and Siewert (*A.* 126, 86); they are formed by heating the normal salt, by dissolving CrO_3H_3 in solution of the normal salt, and by boiling HNO_3Aq with excess of CrO_3H_3.

Cobalt nitrates. The *normal* salt, $Co(NO_3)_2.6H_2O$, forms red, prismatic, deliquescent crystals; S.G. 1·83 at 14° (Boedeker); melts below 100°; at higher temperatures gives off H_2O and oxides of N, and leaves black Co_3O_4. Produced by dissolving Co, or $CoCO_3$ in HNO_3Aq, and evaporating. Easily sol. water. Franz (*J. pr.* [2] 5, 274) gives the following table showing p.c. $Co(NO_3)_2$ in aqueous solutions at 17·5°:—

P.c. $Co(NO_3)_2$	S.G.
5	1·0462
10	1·0906
15	1·1378
20	1·1936
25	1·2538
30	1·319
35	1·3896
40	1·4662
Saturated at 17·5°	1·5382

Thomsen gives H.F. [$Co, O^2, N^2O^4, 6H^2O$] 123,330; [Co, O, N^2O^5Aq] = 84,540. When HCl gas is passed over $Co(NO_3)_2$, $CoCl_2$, oxides of N, and Cl are formed (Thomas, *C. J.* 33, 367). Combines with cerous nitrate to form $Co(NO_3)_2.Ce(NO_3)_2.8H_2O$ (Lange, *J. pr.* 82, 129).

Basic salts are obtained by adding NH_3Aq to $Co(NO_3)_2Aq$ under different conditions (*v.* Winkelblech, *A.* 13, 148, 253; Habermann, *M.* 5, 442).

Copper nitrates. The *normal* nitrate, $Cu(NO_3)_2.3H_2O$, is obtained by dissolving Cu or CuO in HNO_3Aq, and evaporating. The solution is at first green owing to production of $Cu(NO_2)_2$. Blue prismatic crystals; S.G. 2·174 (Hassenfratz, *A.* 28, 3). The salt $Cu(NO_3)_2.6H_2O$ is deposited below 20°. H.F. [$Cu, O^2, N^2O^4, 6H^2O$] = 96,950 (*Th.* 3, 518). The hexahydrated salt effloresces in air, losing $3H_2O$; it melts at 38°, and decomposes at 65°, forming a basic salt. The trihydrated salt melts at 114·5°, and decomposes at 170°. At red-heat, $Cu(NO_3)_2$ evolves N oxides and leaves CuO; it is deliquescent, easily sol. water, but ppd. again by conc. HNO_3Aq. Franz gives following table (*J. pr.* [2] 5, 274):—

S.G. of $Cu(NO_3)_2Aq$	P.c. $Cu(NO_3)_2$
1·0942	10
1·2037	20
1·3299	30
1·4724	40
1·5404	44

$Cu(NO_3)_2$ is rapidly decomposed by HCl, with formation of $CuCl_2$, Cl, NO, and probably N (Thomas, *C. J.* 33, 367).

Basic nitrates of Cu are produced by boiling $Cu(NO_3)_2Aq$ with KNO_3Aq, or by passing N_2O_3 into H_2O holding CuO_2H_2 in suspension; the product is said to be $4CuO.N_2O_5.3H_2O$ (Vogel a. Reinhauer, *J.* 1859. 216). For other basic salts *v.* Graham, *T.* 1837. 47; Casselmann, *Fr.* 4, 24; Tutschew, *Z.* 6, 109.

Didymium nitrate $Di(NO_3)_3.6H_2O$. Rose-red crystals; by dissolving Di_2O_3 in HNO_3Aq and crystallising; S.G. 2·249; loses $6H_2O$ at 200°. Easily sol. water and alcohol; forms double salts with $Co(NO_3)_2$, $Ni(NO_3)_2$, and $Zn(NO_3)_2$ (*v.* Marignac, *A. Ch.* [3] 38, 148; Hermann, *Rep. Chim. pur.* 1861. 53; Frerichs a. Smith, *A.* 191, 346; Cleve, *Bl.* [2] 43, 361).

Erbium nitrate $Er(NO_3)_3.6H_2O$. Large crystals; sol. water and alcohol. Decomposed by heat forming a basic salt $2Er_2O_3.3N_2O_5.9H_2O$ (Höglund, *Bl.* [2] 18, 193, 279; Cleve, *C. R.* 91, 381).

Gallium nitrate $Ga(NO_3)_3$. Obtained by dissolving Ga in HNO_3Aq, evaporating at 100°, drying in an exsiccator, and heating in a dry air-stream to 40°. Decomposes at 110°, and at 200° leaves Ga_2O_3 (de Boisbaudran).

Gold nitrates. By dissolving $Au_2O_3.xH_2O$ in HNO_3Aq, a very unstable salt is obtained; Schottländer gives the formula $5(AuO.NO_3).H_2O$ as approximately correct (*A.* 217, 312). The compound $Au(NO_3)_3.HNO_3.3H_2O$, which may be called *auronitric acid*, is obtained in large crystals by dissolving $Au_2O_3.xH_2O$ in HNO_3Aq, with special precautions. This compound forms shining, yellow, triclinic octahedra; S.G. 2·84; it is readily decomposed by heat to $2Au_2O_3.N_2O_5.2H_2O$ (Schottländer, *A.* 217, 312). Several salts are known derived from auronitric acid; they are obtained by dissolving $HNO_3.Au(NO_3)_3$ along with various nitrates in HNO_3Aq, and evaporating. The K salts are $KAu(NO_3)_4$ and $HK_2Au(NO_3)_6$ (Schottländer, *l.c.*).

Indium nitrate $2In(NO_3)_3.9H_2O$. Large needle-shaped crystals; by dissolving excess of In in HNO_3Aq, and evaporating in an exsiccator. Loses $6H_2O$ at 100°: at red heat forms a basic salt, then In_2O_3 (Winkler, *J. pr.* 94, 1; 102, 273).

Iron nitrates. According to Scheurer-Kestner (*C. R.* 47, 927), Fe reacts with HNO_3Aq S.G. 1·034 to form $Fe(NO_3)_2$ and NH_4NO_3, with acid S.G. 1·073 $Fe(NO_3)_3$ is also formed, with acid S.G. 1·115 only $Fe(NO_3)_3$ is produced, and with more conc. acid basic salts begin to be formed.

Ferrous nitrate $Fe(NO_3)_2.6H_2O$ is best prepared by dissolving FeS in cooled HNO_3Aq S.G. less than 1·12; the liquid is made as nearly neutral as possible by addition of FeS, decanted, evaporated slowly, and strongly cooled. The crystals may be kept unchanged at low temperatures in the mother-liquor. S. 200 at 0°, 300 at 25° (Ordway, *Am. S.* [2] 40, 325).

Ferric nitrate $Fe(NO_3)_3.9H_2O$ (Ordway, *Am. S.* [2] 26, 197; 27, 14). Prepared by dissolving Fe in HNO_3Aq S.G. 1·29 till about 10 p.c. Fe is taken up by the acid, then adding an equal volume of HNO_3Aq S.G. 1·43; oblique rhombic prisms are deposited on cooling. S.G. 1·6835 at 20°; nearly colourless; slightly deliquescent; very soluble in water; very slightly soluble in cold HNO_3Aq; melts 47·2°; acid begins to be given off at 100°; boils 125°; completely decomposed at red heat (Ordway, *l.c.*). Hausmann obtained $Fe(NO_3)_3.6H_2O$ (*A.* 89, 109; *v.* also Widenstein, *J. pr.* 84, 243). Scheurer-Kestner obtained a dihydrated salt (*J.* 1862. 193).

Numerous *basic ferric nitrates* were obtained by Ordway (*l.c.*) by dissolving FeO_3H_3 in $Fe(NO_3)_3Aq$, and evaporating (*v.* also Hausmann, *A.* 89, 109; and Scheurer-Kestner, *J.* 1862. 193). Basic salts are also produced by heating $Fe(NO_3)_3Aq$. Basic ferric nitrates are slowly resolved by boiling water to normal salt and Fe_2O_3; the change proceeds most rapidly by heating in a sealed tube.

Several *ferric aceto-nitrates*, *e.g.* $Fe(NO_3)(C_2H_3O_2)_2.3H_2O$, $Fe(NO_3)_2(C_2H_3O).8H_2O$ have been prepared and described by Scheurer-Kestner (*A. Ch.* [3] 63, 422).

Lanthanum nitrate $La(NO_3)_3.6H_2O$. Large prismatic, deliquescent, crystals; easily sol. water and alcohol. May be fused without decomposition at c. 40°, but at rather higher temperature HNO_3 is removed and a basic salt formed: completely decomposed at red heat (Ordway). Two *double salts*, $2La(NO_3)_3.3Ni(NO_3)_2.36H_2O$, and $2La(NO_3)_3.3Zn(NO_3)_2.69H_2O$, are described by Frerichs a. Smith (*A.* 191, 359).

Lead nitrates. The *normal* salt, $Pb(NO_3)_2$, crystallises in octahedra from a solution of PbO or $PbCO_3$ in boiling very dilute HNO_3Aq. S.G. 4·472 at 4° (Playfair a. Joule, *C. J.* 1, 137); 4·41 at 15·5° (Holker, *P. M.* [3] 27, 214; *v.* also Schröder, *P.* 106, 226; Ditte, *B.* 15, 1438). H.F. $[Pb, N^2, O^6] = 105,500$; $[Pb, O^2, N^2O^4] = 109,470$; $[Pb, O, N^2O^5Aq] = 68,070$ (*Th.* 3, 518). S. 39 at 0°, 48·3 at 10°, 60·6 at 25°, 80 at 45°, 101 at 65°, 120·5 at 85°, 138·9 at 100° (Kremers, *P.* 92, 497). S. in alcohol, S.G. ·9282, 4·96 at 4°, 5·82 at 8°, 8·77 at 22°, 12·8 at 40°, 11·49 at 50° (Gerardin, *A. Ch.* [4] 5, 129). Insol. conc. HNO_3Aq. $Pb(NO_3)_2$ is decomposed at low red heat giving PbO, O, and NO_2. In HCl gas, $PbCl_2$ is formed with evolution of NO and Cl (Thomas, *C. J.* 33, 367). Forms a compound with lead phosphate, viz. $Pb(NO_3)_2.Pb_3(PO_4)_2.2H_2O$ (Gerhardt, *A.* 68, 286).

Many *basic lead nitrates* have been described. The salt $2PbO.N_2O_5.H_2O$, which formula may be written $Pb.OH.NO_3$, is obtained by boiling $Pb(NO_3)_2Aq$ with PbO, filtering hot, and allowing to cool (Berzelius, *P.* 19, 312; Pelouze, *J. pr.* 25, 486; Persoz, *A. Ch.* [3] 58, 191). S.G. 5·93 (Ditte, *C. R.* 94, 1180). Several other basic salts are known; according to Wakeman a. Wells (*Am.* 9, 299) the only recrystallisable basic salt, besides $Pb.OH.NO_3$, is $10PbO.3N_2O_5.5H_2O$.

Lithium nitrate $LiNO_3$. By neutralising HNO_3Aq with LiOH or Li_2CO_3, and evaporating. Rhombic prisms; S.G. 2·334 (Kremers, *P.* 92, 520). H.F. $[Li,N,O^3] = 111,615$; $[Li,O,NO^2] = 113,620$; $\frac{[Li^2,O,N^2O^5Aq]}{2} = 97,005$ (*Th.* 3, 518). Melts at 264° (Carnelley, *C. J.* 33, 275). Easily sol. water and alcohol. Kremers (*P.* 114, 41) gives following table:—

S.G. $LiNO_3Aq$ at 19·5°	P.c. $LiNO_3$
1·0769	14·2
1·1346	26·7
1·193	40·6
1·255	57·5
1·3154	77·4

$LiNO_3$ slowly reacts with dry HCl, a small quantity of Cl and NO being evolved (Thomas, *C. J.* 33, 370).

The *hydrated salt* $LiNO_3.5H_2O$ is said to be obtained by crystallising below 10° (Troost, *A. Ch.* [3] 51, 134).

Magnesium nitrate $MgNO_3.6H_2O$. Occurs in mother-liquor from saltpetre plantations; also in some well-waters of Stockholm, according to Berzelius. Prepared by neutralising HNO_3Aq by *magnesia alba*, and evaporating. Very deliquescent monoclinic crystals (Marignac, *J.* 1856. 336). S.G. 1·464 (Playfair a. Joule, *C. S. Mem.* 2, 401). H.F. $[Mg,O^2,N^2O^4,6H^2O] = 214,530$. $[Mg,O,N^2O^5Aq] = 176,480$ (*Th.* 3, 518). Very soluble water and alcohol. Oudemans (*Fr.* 7, 419) gives the table:—

P.c. $Mg(NO_3)_2 6H_2O$	S.G. $Mg(NO_3)_2Aq$
1	1·0034
5	1·0202
10	1·0418
15	1·0639
20	1 0869
25	1·1103
30	1·1347
35	1·1649
40	1·1909
45	1·2176
49	1·2397

According to Graham (*T.* 1837. 47), $5H_2O$ are removed from $Mg(NO_3)_2.6H_2O$ at c. 330° (M.P. of lead), and the monohydrated salt can be fused without change, but is decomposed at red heat, leaving MgO. Einbrodt (*A.* 65, 115) found that acid began to be evolved before five-sixths of the water was removed, hence he regarded the existence of $Mg(NO_3)_2.H_2O$ as very doubtful. By heating $Mg(NO_3)_2.6H_2O$ until water ceases to come off, a *basic* salt $3MgO.N_2O_5$ is obtained, according to Chodnew (*A.* 71, 241). Reacts with HCl gas to form $MgCl_2$, Cl and O and H_2O being evolved (Thomas, *C. J.* 33, 370).

Manganese nitrate $Mn(NO_3)_2.6H_2O$. Small monoclinic crystals (Hannay, *C. J.* 33, 269). Obtained by dissolving $MnCO_3$ in HNO_3Aq, also by dissolving MnO_2 in HNO_3Aq in sunlight or presence of deoxidisers, and evaporating. S.G. 1·8199 when solid at 21°; 1·8104 when liquid at 21° (Ordway, *J.* 12, 113). H.F. $[Mn,O^2,N^2O^4,6H^2O] = 157,700$; $[Mn,O,N^2O^5Aq] = 117,720$ (*Th.* 3, 518). Decomposed by heat, giving MnO_2, Mn_2O_3, or Mn_3O_4, according to the temperature. Reacts with HCl gas to form $MnCl_2$, with evolution of Cl and NO (Thomas, *C. J.* 33, 370). According to Schultz-Sellac (*Z.* 1870. 646) the salt $Mn(NO_3)_2.3H_2O$ crystallises from solution in conc. HNO_3Aq.

Mercury nitrates. *Mercuric nitrate*, $2Hg(NO_3)_2.H_2O$, is obtained by dissolving HgO in excess of slightly warmed HNO_3Aq, and evaporating over H_2SO_4; after some minutes the liquid above the crystals has the composition $Hg(NO_3)_2.2H_2O$ (Millon, *A. Ch.* [3] 18, 361). Ditte (*J.* 1854. 366) obtained $Hg(NO_3)_2.8H_2O$ by cooling to −15° a nearly neutral conc. solution of HgO in HNO_3Aq.

Basic mercuric nitrates are readily formed by heating the normal salt; the chief are $2HgO.N_2O_5.3H_2O$ (Ditte, *l.c.*); $2HgO.N_2O_5.2H_2O$ (Marignac, *J.* 1855. 415); $3HgO.N_2O_5.H_2O$, obtained by the prolonged action of water on any of the other basic salts.

Mercuric nitrate forms several *double salts*.

With HgI_2, the compounds $Hg(NO_3)_2.HgI_2$, $Hg(NO_3)_2.2HgI_2$, and $2Hg(NO_3)_2.3HgI_2$ are formed (Preuss, *A.* 29, 326; Liebig, *A.* 72, 79). These iodo-nitrates are decomposed by water, with separation of HgI_2 and solution of $Hg(NO_3)_2$. With HgS, the compound $Hg(NO_3)_2.2HgS$ is formed; by digesting freshly ppd. HgS with $Hg(NO_3)_2Aq$, also by passing into $Hg(NO_3)_2Aq$ less H_2S than suffices to decompose it wholly.

Mercurous nitrate. The nitrates derived from Hg_2O have been examined chiefly by Mitscherlich (*P.* 9, 387), Lefort (*A.* 56, 247), Marignac (*A. Ch.* [3] 27, 332), and Gerhardt (*A.* 72, 74). $HgNO_3$ is formed by the reaction of excess of Hg with HNO_3Aq, but if the action is continued basic salts are produced. Basic salts are also obtained by decomposing $HgNO_3$ by water.

The *normal salt*, $HgNO_3.2H_2O$, is obtained in colourless monoclinic crystals by reacting on excess of Hg with cold HNO_3Aq S.G. c. 1·2. To prevent admixture of basic salts it is advisable to allow the acid and Hg to remain in contact until crystals cease to be formed, then to warm gently, filter, and allow to crystallise. S.G. 4·78 (Playfair a. Joule, *C. S. Mem.* 2, 401). The crystals effloresce somewhat in air; they are dissolved without change in a little water, but dilution produces basic salts. By heating $HgNO_3$ with water HgO and NO_2 are formed. HgCl is formed when HCl is passed over $HgNO_3$, and Cl and NO are evolved (Thomas, *C. J.* 33, 370).

Basic mercurous nitrates are formed by warming with Hg the mother-liquor from the preparation of the normal salt, and by treating the normal salt with water. To the salt obtained by the first of these methods Gerhardt gave the formula $3Hg_2O.2N_2O_5.H_2O$; Marignac gave the formula $4Hg_2O.3N_2O_5.H_2O$. The other basic salts are: (1) $2Hg_2O.N_2O_5.H_2O$ (Gerhardt), obtained by the action of a little boiling water on $HgNO_3$; Marignac formulates this salt as $5Hg_2O.3N_2O_5.2H_2O$. (2) $2Hg_2O.N_2O_5.H_2O$ (Gerhardt, Marignac), obtained by adding much water to $HgNO_3Aq$.

Mercurous nitrate forms *double salts* with NH_4NO_3, $Pb(NO_3)_2$, $Ba(NO_3)_2$, and $Sr(NO_3)_2$. The compositions of these salts are expressed by the formulæ $2HgNO_3.4NH_4NO_3.5H_2O$ (Rammelsberg, *P.* 109, 397); $2M(NO_3)_2.2Hg_2O.N_2O_5$, where M = Pb, Ba, or Sr (Städeler, *A.* 87, 129).

Mercuroso-mercuric nitrate, $Hg_2O.2HgO.N_2O_5$. This salt is formed by the gradual oxidation of $HgNO_3$ in air. It is best obtained by boiling $1\frac{1}{2}$ parts HNO_3Aq, S.G. 1·2, with 1 part Hg till all Hg is dissolved, and maintaining the solution near its B.P. The salt separates as a yellow powder; after a time a white basic mercurous nitrate begins to form (Wittstock; Gerhardt, *A.* 72, 74; Brooks, *P.* 66, 63). Rubbed with NaCl, HgCl and oxychloride are formed, and on addition of water $HgCl_2$ goes into solution. Treated with HCl gas both HgCl and $HgCl_2$ are formed with evolution of Cl and NO (Thomas, *C. J.* 33, 370). The salt may be regarded as derived from orthonitric acid—$NO(OH)_3$—by replacing H by Hg^I and H_2 by Hg^{II}

$$\left[NO(OHg)(O_2Hg) = \frac{Hg_2O.2HgO.N_2O_5}{2}\right].$$

Nickel nitrates. The *normal salt*, $Ni(NO_3)_2.6H_2O$, is obtained, in emerald-green, deliquescent, monoclinic crystals, by dissolving Ni, NiO, or $NiCO_3$, in HNO_3Aq, and evaporating. Melts at 56·7°, and boils at 136·7°, remaining clear till $3H_2O$ is gone off (Ordway, *Am. S.* [2] 26, 197; 27, 14). S.G. 2·065 at 14°, 2·037 at 22° (Clarke's *Specific Gravity Table* [new ed.], 112). H.F. $[Ni, O^2, N^2O^4, 6H^2O] = 124,720$; $[Ni, O, N^2O^5Aq] = 83,420$ (*Th.* 3, 518). Several *double salts* of $Ni(NO_3)_2$ are known:— with $Ce(NO_3)_2$, $Di(NO_3)_3$, and $La(NO_3)_3$ (*v.* CERIUM NITRATES, DIDYMIUM NITRATE, LANTHANUM NITRATE). With *ammonia* forms

$$Ni(NO_3)_2.4NH_3.2H_2O$$

(Laurent, *A. Ch.* [3] 36, 354); and

$$Ni(NO_3)_2.6NH_3.1\tfrac{1}{2}H_2O$$

(F. Rose, *Ammon. Kobaltverbind.* [Heidelberg, 1871], 27). Also combines with *nickel chloride* and *ammonia* to form

$$6(Ni(NO_3)_2.4NH_3.H_2O).(NiCl_2.6NH_3).10H_2O$$

(Schwarz, *W. A. B.* 1850. 272).

The *basic salt* $8NiO.N_2O_5.5H_2O$ is ppd. as a white powder by adding boiling NH_3Aq to a solution of the normal salt (Habermann, *M.* 5, 440).

Palladium nitrates. The *normal salt* $Pd(NO_3)_2.xH_2O$ forms brown-yellow rhombic prisms; very deliquescent; obtained by dissolving Pd in cold HNO_3Aq, evaporating to a syrup at the ordinary temperature, and allowing to stand in a warm place (Fischer, *P.* 10, 607). By dissolving the normal salt in water, and diluting, the Pd is gradually ppd. as a *basic salt.* Basic salts are also obtained by evaporating Pd in HNO_3Aq at c. 100° to 120°, and treating the residue with water (Fischer, *l.c.*; Kane, *B. J.* 24, 236).

Platinum nitrates. A brown salt, probably $Pt(NO_3)_4$, is obtained by dissolving $PtO_2.xH_2O$ in HNO_3Aq, or by decomposing $Pt(SO_4)_2Aq$ with $Ba(NO_3)_2Aq$, and evaporating (Berzelius).

Potassium nitrate KNO_3. (*Nitre. Saltpetre.*) Melts at 339° (Carnelley, *C. J.* 33, 277). S.G. 2·0958 to 2·1078 at 4° (Playfair a. Joule, *C. J.* 1, 137); 2·059 at 0° (Quincke, *P.* 135, 642); 1·072 at M.P. (Braun, *P.* 154, 190). H.F.

$$[K, O, NO^2] = 121,485; \left[\frac{K^2, O, N^2O^5Aq}{2}\right] = 96,050$$

(*Th.* 3, 518). Heat of solution = −7967 at 15° −7814 at 34°, −7541 at 53° (Tilden, *Pr.* 38, 401). S.H. 13° to 98° = ·23875 (Regnault, *A. Ch.* [3] 1, 129). S. 13·3 at 0°, 21 at 10°, 31·2 at 20°, 44·5 at 30°, 63·9 at 40°, 85·9 at 50°, 110·9 at 60°, 139 at 70°, 172 at 80°, 206 at 90°, 247 at 100° (Mulder, *J.* 1866. 65; *v.* also Tilden a. Shenstone, *T.* 175, 23). Schiff gives the following tables (*A.* 107, 87, 293; for more extended tables *v.* Gerlach, *Fr.* 8, 286):—

Weight of alcohol in 100 parts	Weight of KNO_3 in 100 parts solution saturated at 15°
0	20·5
10	13·2
20	8·5
30	5·6
40	4·3
50	2·8
60	1·7
80	0·4

S.G. of KNO_3Aq at 21°	Weight of KNO_3 in 100 parts solution
1·1683	24·93
1·1073	16·62
1·0695	11·08
1·051	8·31
1·0337	5·54
1·017	2·77

S. in glycerin S.G. 1·225 = 10 (Vogel, *N.R.P.* 16,557). KNO_3 is dimorphous; it usually crystallises in trimetric prisms, $a:b:c = \cdot589:1:\cdot701$; if a drop of KNO_3Aq is allowed to crystallise slowly under the microscope, rhombohedral crystals are formed (Frankenheim, *P.* 92, 354). If the rhombohedral crystals are touched by a prismatic crystal while the crystallisation is proceeding, they are changed to prismatic; the prismatic may be changed to rhombohedral by heating nearly to the melting-point.

Occurrence.—In small quantities in all vegetable soils; also in most spring and river waters (Boussingault, *C. R.* 44, 108). Nitre is found in the soil of caves, in different parts of the world, wherein animal or vegetable matter undergoes putrefaction, and where alkalis or alkaline earths are present to combine with the nitric acid produced (*v.* Nitrification, p. 521). Nitre is also found as an efflorescence on the surface of the soil in parts of India, Arabia, South America, and other warm countries; the percentage of KNO_3 in a Bengalese soil was found by Davy to be 8·3. KNO_3 occurs in the juices of certain plants; notably in the leaves of the castor-oil plant.

Formation.—1. By the oxidation of nitrogenous matter in presence of air, moisture, and potash (*cf.* Nitrification, p. 521).—2. By the action of K_2CO_3 or KOH on $Ca(NO_3)_2$, or $NaNO_3$. 3. By the oxidation of NH_3 in presence of moisture, air, and ferric oxide, and combination of the HNO_3 formed with KOH (Pesci, *G.* 1875. 307).

In the artificial preparation of nitre by oxidation of nitrogenous matter in soils, the first step is to prepare a soil rich in N-containing materials; this is done by mixing porous soil, preferably that left from the lixiviation of a former nitre-bed, with farm-yard manure, animal and vegetable refuse, and wood ashes or calcareous matter, and watering this with urine. This soil is then formed into a mound under a shed, and the process of nitrification is allowed to proceed for perhaps a couple of years; air must be freely admitted, and great care must be taken to keep the soil neither too wet nor too dry. About 5lbs. crude nitre are obtained, on an average, from 1,000lbs. of such soil (for more details *v.* Dictionary of Applied Chemistry).

Preparation.—1. By purifying crude nitre prepared from the washings of *saltpetre earth*. The liquor from the saltpetre earth contains $Ca(NO_3)_2$, $Mg(NO_3)_2$, with smaller quantities of KNO_3 and $NaNO_3$, and also alkaline chlorides; K_2CO_3 (wood-ashes) is added, the liquid is filtered and evaporated; the crude KNO_3 is then treated with enough boiling water to dissolve all KNO_3 but not all the NaCl present—S. of KNO_3 at 100° = 247, S. of NaCl at 100° = 39—the liquid is boiled for a considerable time, when NaCl separates with $CaCO_3$ and $MgCO_3$; the liquid is then run off, and while crystallising it is constantly stirred to insure formation of small crystals containing little mother-liquor; the crystals are recrystallised, washed with saturated KNO_3Aq (to dissolve the last traces of alkaline chlorides), and again crystallised.—2. From *Chili-saltpetre* ($NaNO_3$), by adding this salt to hot conc. K_2CO_3Aq, when Na_2CO_3 separates and KNO_3 remains in solution. The mother-liquor is evaporated as long as Na_2CO_3 continues to separate, then run off and allowed to crystallise, with constant stirring.—3. By neutralising pure HNO_3Aq with pure KOHAq or K_2CO_3Aq, evaporating, and crystallising.

Properties.—A white, crystalline salt; dimorphous; S.G. c. 2·1; easily sol. water, solution tastes cool and bitter; melts below red heat to a colourless liquid which solidifies on cooling to a white fibrous mass, known as *mineral crystal* or *salprunellæ*. At red heat evolves O, and N as temperature increases. Deflagrates when heated with combustible bodies (for physical properties *v.* beginning of article).

Reactions.—1. Decomposed by *heat*; at c. 300°-400° O is evolved, and KNO_2 formed; as temperature increases N is evolved, and finally a mixture of K_2O and K_2O_4 remains.—2. Evolves O when *heated in presence of combustible substances* such as P, S, Zn, C, &c. Hence the use of KNO_3 in gunpowder; and as an oxidiser when molten.—3. Heated with *copper foil*, nearly pure K_2O is formed; a similar change occurs when KNO_3 is heated with *iron*.—4. Most *elements* are oxidised by heating with KNO_3; if the oxide produced is acidic, a K salt of the corresponding acid is produced.—5. *Organic compounds* are generally burnt (to CO_2 and H_2O) by heating with KNO_3.—6. Reduced by the *copper-zinc* couple, in presence of water, at first to KNO_2 and then to NH_3; a similar reduction takes place by *hydrogen occluded* by Pd, Pt, or Cu (Gladstone a. Tribe, *C. J.* 33, 139, 306).—7. Reacts with *hydrogen chloride gas* to form KCl, evolving Cl and N oxides (Thomas, *C. J.* 33, 367). For methods by which nitre may be valued approximately, or completely analysed, reference must be made to *Manuals of Analysis*; for an account of the technical applications of nitre reference should be made to Dictionary of Applied Chemistry.

Rhodium nitrate $Rh(NO_3)_3.2H_2O$ (?). A gum-like, very deliquescent, mass, obtained by dissolving $Rh_2O_3.3H_2O$ in HNO_3Aq, and evaporating at 100° till HNO_3 ceases to be evolved (Claus, *J. pr.* 34, 428; Berzelius).

Rubidium nitrate $RbNO_3$. Obtained in long needles, or six-sided prisms (according to rate of evaporation) by neutralising HNO_3Aq by Rb_2CO_3 and evaporating. S. 20·1 at 0°, 43·5 at 10°. When heated evolves O (Kirchoff a. Bunsen, *P. M.* [4] 22, 55). According to Ditte (*C. R.* 89, 641) an *acid salt*, $2RbNO_3.5HNO_3$, is obtained by dissolving $RbNO_3$ in $HNO_3.H_2O$; this salt is decomposed by water or heat.

Samarium nitrate $Sm(NO_3)_3.6H_2O$. Pale yellow prisms; e. sol. water; S.G. 2·375 (Cleve, *C. N.* 48, 74; 51, 145).

Scandium nitrate $Sc(NO_3)_3$(?) Small plates; by evaporating at 100° a solution of Sc_2O_3 in HNO_3Aq. Decomposed by heat, giving a basic salt soluble in water (Nilson, *B.* 13, 1444).

Silver nitrate $AgNO_3$. (*Lunar caustic.*) S.G. 4·238 to 4·328 (Schröder, *P.* 107, 113). S. 121·9 at 0°, 227·3 at 19·5°, 500 at 54°, 714 at 85°, 1111 at 110° (Kremers, *P.* 92, 497); S. 1622·5 at 125°, 1941·4 at 133° (Tilden a. Shenstone, *T.* 175, 23). Saturated solution boils at 125°. S. in boiling alcohol = 25. Melts at 218° (Carnelley, *C. J.* 33, 276). H.F. [Ag, O, NO^2] = 30,745; [Ag, N, O^3] = 28,740 (*Th.* 3, 517). Crystallises in trimetric system; $a:b:c$ = ·9433:1:1·37. S.H. 16° to 99° = ·14352 (Regnault, *A. Ch.* [3] 1, 129).

Preparation. — Pure Ag is dissolved in HNO_3Aq, the solution is evaporated to dryness, the residue is heated gently till all HNO_3 is removed, when it is dissolved in water and crystallised. If solution of Ag in HNO_3Aq proceeds in the cold the liquid becomes blue from solution of N_2O_3, but no gas is evolved; on warming, NO escapes rapidly. $AgNO_3$ may be prepared from Ag which contains Cu by saturating warm fairly conc. HNO_3Aq with the metal, adding enough KOHAq to a part of the solution to ppt. Ag_2O along with CuO, digesting the pp. with the rest of the solution, whereby the remaining CuO is ppd., filtering, and evaporating the filtrate.

Properties.—White trimetric crystals; solution in water is perfectly neutral to litmus paper, has a metallic taste, and is poisonous; melts below red heat; is a powerful caustic, at once destroying flesh when applied to it. $AgNO_3$ is readily reduced by organic matter in light.

Reactions.—1. Decomposed by *heat*, leaving Ag.—2. With *hydrogen chloride* gas forms AgCl and HNO_3, with evolntion of a very little Cl and NO (Thomas, *C. J.* 33, 371).—3. With *organic matter*, *e.g.* paper, dust, &c., forms Ag in presence of sunlight.—4. $AgNO_3Aq$ is slowly and very partially decomposed by *hydrogen* with ppn. of Ag (Russell, *C. J.* [2] 12, 3).—5. *Uranous oxide*, UO_2, ppts. Ag, with production of $UO_2(NO_3)_2$ (Isambert, *C.R.* 80, 1087).

Combinations.—1. With *ammonia*, to form $AgNO_3.2NH_3$; by supersaturating conc. $AgNO_3Aq$ with NH_3; decomposes above 100°, giving off NH_3 and N (Marignac, *P.* 9, 413; Mitscherlich, *A. Ch.* [2] 72, 288; Kane, *P.* 20, 153). Dry $AgNO_3$ absorbs NH_3 to form $AgNO_3.3NH_3$ (H. Rose, *J.* 1857. 256).—2. With *silver bromide*, to form $AgNO_3.AgBr$; by dissolving freshly ppd. AgBr in very conc. hot $AgNO_3Aq$ (Risse, *A.* 111, 42). AgCl seems to form a similar compound.—3. With *silver iodide*, to form several compounds. $2AgNO_3.AgI$ is obtained by boiling very conc. $AgNO_3Aq$ with AgI, pouring off, and allowing to cool (Risse, *A.* 171, 23; Riche, *A.* 111, 39; *cf.* Weltzien, *A.* 101, 127; Kremers, *J. pr.* 71, 54; Preuss, *A.* 29, 329; Schnauss, *Ar. Ph.* [2] 82, 260; Hofmann, *A.* 171, 23; Stürenberg, *Ar. Ph.* [2] 143, 12).—4. With *ammonium* and *potassium nitrates* to form $AgNO_3.MNO_3$(M = NH_4 or K) (Ditte, *C. R.* 101, 878).

Sodium nitrate $NaNO_3$. (*Cubic saltpetre, Chili saltpetre*). S.G. 2·266 at 4° (Playfair a. Joule, *C. S. Mem.* 2, 401); 2·246 at 15·5° (Holker, *P. M.* [3] 27, 213); 1·878 at melting-point (Braun, *P.* 154, 190). Melts at c. 316° (Carnelley, *C. J.* 33, 276). H.F. [Na, N, O^3] = 111,250; [Na, O, NO^2] = 113,255; $\left[\frac{Na^2,O,N^2O^5Aq}{2}\right]$ = 91,310 (*Th.* 3, 518). Heat of solution −4786 at 16°, −4255 at 54° (Tilden, *Pr.* 38, 401). S. 72·9 at 0°, 80·8 at 10°, 87·5 at 20°, 94·9 at 30°, 102 at 40°, 112 at 50°, 122 at 60°, 134 at 70°, 148 at 80°, 162 at 90°, 180 at 100°, 200 at 110°; saturated solution freezes at −17·5° (Rüdorff, *B.* 2, 68), contains 216·4 parts $NaNO_3$ in 100 water, and boils at 119·7° (Mulder, *J.* 1866. 65; *cf.* Ditte, *C. R.* 80, 1164; Maumené, *C. R.* 58, 81; 81, 107). Schiff (*A.* 110, 75) gives a table showing S.G. and p.c. composition of $NaNO_3Aq$. S. in alcohol (61·4 p.c.) at 26° = 21·2 (Pohl, *W. A. B.* 6, 600; *v.* also Wittstein, *Viertelj. Zeit. Pharm.* 12, 109). 75 parts $NaNO_3$ added to 100 parts water at 13·2° lower the temperature through 18·5°. 50 parts $NaNO_3$ mixed with 100 parts snow lower the temperature to −17·5°.

Occurrence.—In large quantities in Chili, Peru, and some other parts of South America.

Preparation.—1. The crude salt is purified by repeated solution and crystallisation; or it is recrystallised once or twice, the first portions of each crop of crystals being rejected, then heated with HNO_3Aq, whereby chlorides are transformed into nitrates and again crystallised. 2. By neutralising HNO_3Aq with NaOHAq or Na_2CO_3Aq, and evaporating.

Properties.—White obtuse rhombohedrons, having much the aspect of cubes; hence the name *cubic saltpetre*. Absorbs water from moist air. Melts c. 316°, and solidifies to white mass on cooling; decomposes at higher temperature similarly to, but more readily than, KNO_3; deflagrates with charcoal, &c., but less quickly than KNO_3.

Reactions.—Decomposed by *heat* at c. 350°–380°, evolving O, and at higher temperature N also.—2. *Heated in presence of oxidisable bodies*, produces oxides, which, if acidic, form Na salts of corresponding acids.—3. With *hydrogen chloride* forms NaCl, and evolves NO and Cl (Thomas, *C. J.* 33, 367).

Strontium nitrate $Sr(NO_3)_2$. Prepared by adding to $SrCO_3$ enough HNO_3Aq to dissolve nearly all the salt, filtering, and crystallising. Separates without water of crystallisation from hot conc. solutions; from cold and more dilute solutions crystals of $Sr(NO_3)_24H_2O$ are obtained (Souchay a. Lenssen, *A.* 99, 45). The anhydrous salt crystallises in octahedrons, S.G. 2·98 at 16·8° (Favre a. Valson, *C. R.* 77, 579). The hydrate forms triclinic crystals, $a:b:c$ = ·5895:1: ·808, S.G. 2·249 at 15·5° (F. a. V., *l.c.*) H.F. [Sr,N,O^3] = 109,910 (*Th.* 3, 517). S. anhydrous salt 20 in cold water, 200 in boiling water. Melts at red heat with decomposition, leaving SrO. Does not react with HCl gas (Thomas, *C. J.* 33, 371). A compound with Sr acetate, viz. $Sr(NO_3)_2.Sr(C_2H_3O)_2.3H_2O$, is obtained by allowing a mixed solution of the salts to evaporate (von Hauer, *J. pr.* 74, 432).

Tellurium nitrate. The compound $8TeO_2.2N_2O_5.3H_2O$ is obtained by dissolving Te in excess of hot HNO_3Aq S.G. greater than 1·15; the salt crystallises in forms which are probably orthorhombic; soluble in HNO_3Aq; easily decomposed by water with separation of TeO_2 (Klein, *A. Ch.* [6] 5, 59).

Thallium nitrates. *Thallous nitrate*, $TlNO_3$, is obtained by dissolving Tl in not very conc. HNO_3Aq, keeping as small an excess of acid as possible, and evaporating. Rhombic prisms, S.G. 5·5 (Lamy a. Des Cloizeaux, *N.* 1, 116). S. 10·6 at 15°, 43·5 at 58°, 588 at 107° (Crookes, *C. J.* 17, 141; Lamy, *C. R.* 54, 1255). Insol. alcohol. Melts at 205° without decomposition and solidifies to a glass S.G. 5·8 (Lamy, *l.c.*) H.F. $[Tl,N,O^3] = 58,150$ (*Th.* 3, 517). Strongly heated in a crucible leaves $TlNO_2$ and Tl_2O_3 (Carstanjen, *J. pr.* 102, 65, 129).

Thallic nitrate $Tl(NO_3)_3$. Separates in large deliquescent crystals from solution of TlO.OH in HNO_3Aq S.G. 1·4; according to Strecker (*A.* 135, 207) the crystals contain $6H_2O$, and according to Willm (*A. Ch.* [4] 5, 5) $8H_2O$. Decomposed at c. 100°.

Thorium nitrate $Th(NO_3)_4.12H_2O$. Large, translucent tables; very hygroscopic; lose $8H_2O$ over H_2SO_4. Forms a very soluble double salt with KNO_3.

Tin nitrates. No definite salt has been isolated. Stannous oxide dissolves in very dilute cold HNO_3Aq, but the solution decomposes on heating with separation of SnO_2 (*cf.* Ditte, *A. Ch.* [5] 27, 145). Sn dissolves in cold very dilute HNO_3Aq, with production of $NH_4.NO_3$ and probably $Sn(NO_3)_2$. Freshly ppd. SnO_2 dissolves in HNO_3Aq: on heating SnO_2 is ppd.

Titanium nitrate. By evaporating a solution of TiO_2 in HNO_3Aq over lime, Merz obtained lustrous plates $5TiO_2.N_2O_5.6H_2O$; soluble in cold water (*J. pr.* 99, 157).

Uranium nitrate. By dissolving U or an oxide of U in HNO_3Aq, and evaporating, large, yellow, rhombic crystals are deposited having the composition $UO_2(NO_3)_2.6H_2O$ = *uranyl nitrate*. S.G. 2·807 (Boedeker). Effloresces somewhat in dry air; melts at 59·5°, and boils at 118° (Ordway, *J.* 1859. 114). A trihydrated salt, $UO_2(NO_3)_2.3H_2O$, was obtained by Schultz-Sellack (*Z.* [2] 6, 646) by evaporating a strongly acid solution of the ordinary salt over H_2SO_4 and KOH. Reacts with HCl to form U oxychloride with evolution of Cl and NO (Thomas, *C. J.* 33, 371).

Vanadium nitrates. No definite salt has been isolated. By dissolving VO or VO_2 in HNO_3Aq, a blue solution is obtained which cannot be evaporated without decomposition (Berzelius). By dissolving V_2O_5 in HNO_3Aq, and allowing to evaporate, a reddish residue is obtained (Berzelius).

Yttrium nitrate $Y(NO_3)_3.6H_2O$. Large translucent crystals; by evaporating over H_2SO_4, a solution of Y_2O_3 in HNO_3Aq (Cleve, *Bl.* [2] 21, 344). Heated till NO_2 is evolved, the *basic* salt $2Y_2O_3.3N_2O_5.9H_2O$ is obtained (*v.* Bahr a. Bunsen, *A.* 137, 1).

Zinc nitrate $Zn(NO_3)_2.6H_2O$. Zn dissolves in HNO_3Aq with formation of NH_4NO_3 and $Zn(NO_3)_2$; from very dilute HNO_3Aq, N_2O is evolved. The salt is prepared by evaporating a solution of Zn, ZnO, or $ZnCO_3$, in HNO_3Aq. Large 4-sided prisms; deliquescent; very soluble water and alcohol; melt at 36·4° and boil at 131° (Ordway, *Am. S.* [2] 27, 14); lose $2H_2O$ *in vacuo* over H_2SO_4 (Vogel a. Reischauer, *N. J. P.* 11, 137); lose all H_2O by heating to 105° in stream of dry air (Pierre, *A. Ch.* [3] 16, 247). S.G. 2·063 at 13° (Clarke's *Table of Specific Gravities* (new ed.) 110). H.F. $[Zn,O^2,N^2O^4,6H^2O] = 142,180$; $[Zn,O,N^2O^5Aq] = 102,510$ (*Th.* 3, 518). The S.G. of $Zn(NO_3)_2Aq$ and p.c. of $Zn)NO_3)_2$ are given by Franz (*J. pr.* [2] 5, 274):—

S.G.	P.c.	S.G.	P.c.
1·0496	5	1·3268	30
1·0968	10	1·3906	35
1·1476	15	1·4572	40
1·2024	20	1·5258	45
1·264	25	1·5984	50

$Zn(NO_3)_2$ with HCl gas gives $ZnCl_2$, evolving Cl and NO (Thomas, *C. J.* 33, 371). Many *basic nitrates of zinc* are known; they are obtained by heating the normal salt, by treating HNO_3Aq with a large excess of Zn, and by digesting hot $Zn(NO_3)_2$ with ZnO (*v.* Schindler, *N. J. P.* 11, 137; Vogel a. Reischauer, *ibid.*; Ordway, *Am. S.* [2] 27, 14; Grouvelle, *A. Ch.* [3] 19, 137; Wells, *Am.* 9, 304).

Zirconium nitrates. The *normal salt* $Zr(NO_3)_4$ is said to be obtained by evaporating a solution of $ZrO_2.xH_2O$ in excess of HNO_3Aq; by heating to 100°, the *pyro-salt* ZrN_2O_7 is formed; and by boiling a dilute aqueous solution of this, the *basic salt* $3ZrO_2.2N_2O_5$ is produced.

M. M. P. M.

NITRATION *v.* NITRO- COMPOUNDS.

NITRIC ACID. HNO_3. (*Spirit of nitre.* When dilute, *aquafortis.*) Mol. w. 62·89 (*v. infra*). [c. −47°] (Berthelot, *Bl.* [2] 29, 3). (86°) (Mitscherlich, *P.* 18, 152; Millon, *J. pr.* 29, 337). S.G. 1·552 at 12·5° (Mitscherlich, *l.c.*); 1·552 at 15° (Millon, *l.c.*). V.D. (mixed with dry air) at 40·5° = 34·3 (Playfair a. Wanklyn, *C. J.* 15, 142; *v. infra*). S.H. of $HNO_3.10H_2O = ·768$, $HNO_3.20H_2O = ·849$, $HNO_3.50H_2O = ·93$, $HNO_3.100H_2O = ·963$, $HNO_3.200H_2O = ·982$ (Thomsen, *P.* 142, 337). H.F. $[H,N,O^3] = 41,510$; $[H,O,NO^2] = 43,515$; $[H,O^2,NO] = 63,085$;

$$\left[\frac{N^2,O^5,H^2O}{2}\right] = 7,330;$$

$$\left[\frac{N^2O,O^4,H^2O}{2}\right] = 16,200;$$

$$\left[\frac{2NO,O^3,H^2O}{2}\right] = 28,905;$$

$$\left[\frac{2NO^2,O,H^2O}{2}\right] = 9,335;$$

$[N^2,O^5,Aq] = 29,820$; $[N^2O^3Aq,O^2] = 36,640$; $[2NO^2,O,Aq] = 33,830$; $[N^2O,O^4,Aq] = 47,560$; $[2NO,O^3,Aq] = 72,970$; $[H,N,O^3,Aq] = 49,090$; $[HNO^2Aq,O] = 18,320$ (*Th.* 2, 199). H.V. 7250 (Berthelot, *C. R.* 90, 1510). For E.C. of HNO_3Aq at different dilutions *v.* Ostwald (*J. pr.* [2] 32, 300). Affinity of HNO_3Aq approximately the same as HClAq. M.M. 1·18 (Perkin, *C. J.* 55, 680).

Occurrence.—In small quantities in rain-water, varying from c. ·1 to c. 16 pts. per million pts. of rain; for measurements *v.* Goppelsröder, (*Fr.* 10, 259; 11, 16); Warington (*C. J.* 55, 537; references are given to various other results). Ekin (*C. J.* [2] 9, 64) found HNO_3 in the spring-water of an uncultivated hill near Bath, not exposed to contact with organic matter. Salts of HNO_3 occur in almost all soils, although not generally in large quantities; and also in the juices of many plants.

Nitric acid has been known from early times. Geber mentions it (8th cent.); Glauber (17th cent.) gave directions for its preparation from

nitre by the use of H_2SO_4. Lavoisier showed that this acid contained O; Cavendish proved the presence of N in it, and obtained it by passing electric sparks through moist O and N.

Formation.—1. By burning H in O in presence of air (Lavoisier; Kolbe, *A.* 119, 176; Hofmann, *B.* 3, 658). The experiments of L. T. Wright (*C. J.* 35, 42) tend to show, although they do not absolutely prove, that the HNO_3 is formed by oxidation of NH_3, not of N.—2. By passing electric sparks for some time through a mixture of moist N and O (Böttger, *J. pr.* 73, 494; Perrot, *C. R.* 49, 204; Buff a. Hofmann, *A.* 113, 140).—3. By exploding air with electrolytic gas ($H_2 + O$) (Bunsen). Hempel's experiments (*B.* 23, 1455) show that HNO_3 is formed when air is burnt with O and electrolytic gas under pressure of several atmos. Hempel also proves that considerable quantities of HNO_3 are formed when C is burnt in compressed air in presence of strongly compressed O.—4. By burning air in coal-gas (Ilosva, *Bl.* [3] 2, 734); or coal-gas in air (Wright, *C. J.* 35, 42).—5. According to Berthelot (*C. R.* 108, 543), a very little HNO_3 is formed when ether and P are slowly oxidised by air in presence of water.—6. Nitrates are formed by the oxidation of nitrogenous animal or vegetable matter in the soil (*v.* NITRIFICATION). 7. Ozone produces NH_4NO_2 from NH_3, and NH_4NO_2 easily oxidises to NH_4NO_3 (Carius, *A.* 174, 31; Schönbein, *J. pr.* 75, 99; Weith a. Weber, *B.* 7, 1745; Wöhler, *A.* 136, 256).—8. By oxidising NH_3 in presence of moisture; *e.g.* by passing NH_3 and air over Pt black heated to c. 300°; by distilling $(NH_4)_2SO_4$ and conc. H_2SO_4 with $K_2Cr_2O_7$; or distilling $(NH_4)_2SO_4$ with $KMnO_4$ and dilute H_2SO_4Aq (Tessié du Mothay, *W. J.* 1871. 260).—9. HNO_3 is a product of the reaction of NO_2 with H_2SO_4; and $NaNO_3$ is formed by acting on NaOHAq with N_2O_3 (Lunge, *B.* 12, 1058).—10. By heating $MnCl_2$ or $MnSO_4$ with $NaNO_3$ (Kuhlmann, *W. J.* 1862. 239).—11. By decomposing $Ba(NO_3)_2Aq$ or $Pb(NO_3)_2Aq$ by H_2SO_4Aq, filtering, and concentrating by evaporation.—12. By heating $NaNO_3$ with AlO_3H_3 or SiO_2 (Wagner, *D. P. J.* 183, 76).

Preparation.—1. A mixture of 101 pts. thoroughly purified and dry KNO_3, in coarse powder, and 98 pts. pure H_2SO_4 is heated in a capacious glass retort, the neck of which passes some way into a glass receiver which is kept cold. The distillate is again distilled till one-third has passed over, when a quantity of conc. H_2SO_4 equal to the contents of the retort is added (when the retort is cold), the receiver is changed, and distillation is continued; the distillate is again distilled at as low a temperature as possible, to get rid of H_2SO_4; the distillate thus obtained is gently warmed, and a current of perfectly dry CO_2 is passed through it until it is quite colourless; oxides of N are thus removed. HNO_2 may be removed by distilling with a little urea, which decomposes HNO_2, giving CO_2, H_2O, and N.—2. Commercial acid is distilled, after addition of a little KNO_3 to decompose H_2SO_4, until a few drops give no pp., when diluted, with $AgNO_3$; the receiver is then changed and distillation continued.

Preparation of fuming nitric acid.—The red fuming acid consists of a solution of NO_2 in HNO_3; it is a more powerful oxidiser than the ordinary acid. It is prepared by heating c. 202 pts. KNO_3 with 98 pts. H_2SO_4 and continuing the distillation as long as liquid comes over; the second stage of the process, which is represented by the equation $KHSO_4 + KNO_3 = K_2SO_4 + HNO_3$, occurs only at a temperature so high that part of the HNO_3 is decomposed with formation of NO_2. A better method is to arrange the materials so that a portion of the HNO_3 is reduced to NO_2 as soon as it is formed; this may be done by mixing 100 pts. KNO_3 with $3\frac{1}{2}$ pts. starch, placing the mixture in a large retort the beak of which passes inside a glass tube 3 to 4 feet long which tube dips into a glass receiver kept very cold, and adding 100 pts. H_2SO_4 S.G. 1·85. The process goes on almost without the application of heat. About 60 pts. red fuming acid are obtained from 100 pts. KNO_3 (Brunner, *Rép. Chim. app.* 3, 188).

Properties.—Perfectly pure HNO_3 has not been isolated; Roscoe obtained an acid with from 99·5 to 99·8 p.c. HNO_3 (*A.* 116, 211). Nitric acid is a colourless, highly corrosive liquid; according to Berthelot it solidifies at c. $-47°$; the B.P. is 86°, but decomposition begins below this temperature; at c. 256° the change $2HNO_3 = 2NO_2 + H_2O + O$ is complete. The following table shows the process of decomposition by heat (Carius, *B.* 4, 828):—

t	S.G. of vapour		P.c. decomposition	c.c. of O from 1 g. HNO_3
	Air=1	H=1		
86°	2·05	29·6	9·53	8·43
100	2·02	29·1	11·77	10·41
130	1·92	27·6	18·78	16·62
160	1·79	25·8	28·96	26·22
190	1·59	23·0	49·34	43·69
220	1·42	20·4	72·07	63·79
250	1·29	18·6	93·03	82·30
256	1·25	18·0	100·0	88·47
265	1·24	17·9		
312	1·23	17·8		

By mixing the vapour from HNO_3 with dry air, Playfair a. Wanklyn (*C. J.* 15, 142) found the V.D. at $40·5° = 34·3$, that calculated from HNO_3 being 31·5. HNO_3 is slowly and partially decomposed by sunlight, giving NO_2, O, and H_2O; so that when exposed to sunlight the acid becomes yellow and contains NO_2. Solution of HNO_3 in water, and dilution of the liquid, are accompanied by production of heat; Thomsen (*Th.* 3, 66) gives the following table:—

x	$[HNO^3, xH^2O]$	$[HNO^3.xH^2O, xH^2O]$
·5	2005	1280
1	3285	
1·5	4160	1550
2·5	5276	1389
3	5710	
5	6665	653
10	7318	140
20	7458	−22
40	7436	−15
80	7421	29
100	7439	
160	7450	45
320	7493	

If these results are plotted, and a curve drawn, with the horizontal lines showing molecules of H_2O and the vertical lines showing quantities of heat, the curve shows no signs of irregularity; hence, Thomsen concludes that the heat of solution and dilution of HNO_3 does not indicate the formation of any definite hydrates of HNO_3. Considering the results which have followed a very close and extended examination of the heat of dilution of H_2SO_4 (*v.* especially Pickering, *C. J.* 57, 64), it seems inadvisable to draw conclusions in favour of, or against, the formation of hydrates of HNO_3, from the limited number of thermal observations made by Thomsen. Berthelot (*Bl.* [2] 22, 530) has also measured the heat produced on adding water to HNO_3 already diluted with known quantities of water, and concludes that a hydrate $HNO_3.2H_2O$ exists in aqueous solutions of HNO_3. Perkin has determined the magnetic rotatory power of HNO_3 and $HNO_3.xH_2O$ (*C. J.* 55, 680); his results are:—M.M. $HNO_3 = 1·18$; M.M. $HNO_3 + 2·67H_2O = 3·656$. Now by deducting 2·67 (M.M. of $2·67H_2O$) from 3·656, we get ·986 as the M.M. of HNO_3 in presence of $2·67H_2O$; but pure HNO_3 gave M.M. 1·18; hence the water has reduced the M.M. of HNO_3 by ·194. From these results, Perkin concludes that HNO_3 and H_2O combine to form H_3NO_4.

The electrical conductivity of HNO_3Aq for increasing dilution has been measured by Kohlrausch a. Grotrian (*P. M.* [4] 49, 417) and by Ostwald (*Z. P. C.* 1, 74). Conductivity increases slightly with dilution, but soon reaches a maximum. The behaviour of HNO_3Aq in this respect is characteristic of that of the strong monobasic acids (*cf.* also Bouty, *C. R.* 106, 654). Roscoe (*C. J.* 13, 150) has shown that distilling HNO_3Aq at 760 mm. results in production of an acid containing 68 p.c. HNO_3; the formula $2HNO_3.3H_2O$ requires 70 p.c., and $HNO_3.2H_2O$ requires 63·6 p.c., HNO_3; the liquid of constant B.P. is therefore not a definite hydrate. This liquid boils at 120·5° under 735 mm. pressure. By distilling at 150 mm. pressure, Roscoe obtained an acid containing 67·6 p.c. HNO_3; at 70 mm. (B.P. 65°–70°) the acid contained 66·7 p.c. HNO_3; at pressure greater than 760 mm. rather more than 68 p.c. HNO_3 was present in the acid of constant B.P. The percentage of HNO_3 in the liquid obtained by passing dry air into HNO_3Aq containing from 64 to 68 p.c. HNO_3, varies with temperature; the higher the temperature the greater the percentage of HNO_3. For every mixture of HNO_3 and H_2O there is a fixed temperature, whereat HNO_3 and H_2O evaporate in the same proportion as they are present in the residual acid; for 66·2 p.c. HNO_3 this temperature is 100°, for 64·5 p.c. it is 60° (Roscoe, *l.c.*; for older observations *v.* Millon, *J. pr.* 29, 349; Smith, *Ph. C.* 1848. 203). When HNO_3 and H_2O are mixed, the maximum contraction takes place for the ratio $2HNO_3{:}3H_2O$ (Kolb, *A. Ch.* [4] 10, 140).

Kolb (*A. Ch.* [4] 10, 136) gives the following table, showing weight of HNO_3 is 100 pts. of HNO_3Aq (p) at 0° and 15°. The numbers marked with an asterisk were directly determined by adding a weighed excess of $CaCO_3$, and weighing the residue:—

p	S.G.		Contraction
	at 0°	at 15°	
100·00	1·559	1·530	0·0000
99·84*	1·559*	1·530*	0·0004
90·42*	1·558*	1·530*	0·0010
99·52*	1·557*	1·529*	0·0014
97·89*	1·551*	1·523*	0·0065
97·00	1·548	1·520	0·0090
96·00	1·544	1·516	0·0120
95·27*	1·542*	1·514*	0·0142
94·00	1·537	1·509	0·0182
93·01*	1·533*	1·506*	0·0208
92·00	1·529	1·503	0·0242
91·00	1·526	1·499	0·0272
90·00	1·522	1·495	0·0301
89·56*	1·521*	1·494*	0·0315
88·00	1·514	1·488	0·0354
87·45*	1·513*	1·486*	0·0369
86·17*	1·507*	1·482	0·0404
85·00	1·503	1·478	0·0433
84·00	1·499	1·474	0·0459
83·00	1·495	1·470	0·0485
82·00	1·492	1·467	0·0508
80·96*	1·488*	1·463*	0·0531
80·00	1·484	1·460	0·0556
79·00	1·481	1·456	0·0580
77·66	1·476	1·451	0·0610
76·00	1·469	1·445	0·0643
75·00	1·465	1·442	0·0666
74·01*	1·462*	1·438*	0·0688
73·00	1·457	1·435	0·0708
72·39*	1·455*	1·432*	0·0722
71·24*	1·450*	1·429*	0·0740
69·96	1·444	1·423	0·0760
69·20*	1·441	1·419*	0·0771
68·00	1·435	1·414	0·0784
67·00	1·430	1·410	0·0796
66·00	1·425	1·405	0·0806
65·07	1·420*	1·400*	0·0818
64·00	1·415	1·395	0·0830
63·59	1·413	1·393	0·0833
62·00	1·404	1·386	0·0846
61·21*	1·400*	1·381*	0·0850
60·00	1·393	1·374	0·0854
59·59*	1·391*	1·372*	0·0855
58·88	1·387	1·368	0·0861
58·00	1·382	1·363	0·0864
57·00	1·376	1.358	0·0868
56·10*	1·371*	1·353*	0·0870
55·00	1·365	1·346	0·0874
54·00	1·359	1·341	0·0875
53·81	1·358	1·339	0·0875
53·00	1·353	1·335	0·0875
52·33*	1·349*	1·331*	0·0875
50·99	1·341*	1·323*	0·0872
49·97	1·334	1·317	0·0867
49·00	1·328	1·312	0·0862
48·00	1·321	1·304	0·0856
47·18*	1·315*	1·298*	0·0850
46·64	1·312	1·295	0·0848
45·00	1·300	1·284	0·0835
43·53*	1·291*	1·274*	0·0820
42·00	1·280	1·264	0·0808
41·00	1·274	1·257	0·0796
40·00	1·267	1·251	0·0786
39·00	1·260	1·244	0·0755
37·95*	1·253*	1·237*	0·0762
36·00	1·240	1·225	0·0740

p	S.G. at 0°	S.G. at 15°	Contraction
35·00	1·234	1·218	0·0729
33·86*	1·226*	1·211*	0·0718
32·00	1·214	1·198	0·0692
31·00	1·207	1·192	0·0678
30·00	1·200	1·185	0·0664
29·00	1·194	1·179	0·0650
28·00*	1·187*	1·172*	0·0635
27·00	1·180	1·166	0·0616
25·71	1·171*	1·157*	0·0593
23·00	1·153	1·138	0·0520
20·00	1·132	1·120	0·0483
17·47*	1·115	1·105	0·0422
15·00	1·099	1·089	0·0336
13·00	1·085	1·077	0·0316
11·41*	1·075	1·067*	0·0296
7·22*	1·050	1·045*	0·0206
4·00	1·026	1·022	0·0112
2·00	1·013	1·010	0·0055
0·00	1·000	1·999	0·0000

On adding water to the fuming red nitric acid, the liquid becomes green, then blue, and finally colourless when dilute; red vapour of NO_2 is evolved, the more rapidly the higher is the temperature. The NO_2 present in the fuming acid is slowly decomposed by the added water, giving HNO_2, which colours the liquid blue (the green colour being the result of the yellow caused by NO_2 and the blue caused by HNO_2); on further dilution NO is evolved, and only HNO_3 remains:

$$(1)\ 2NO_2 + H_2O = HNO_3 + HNO_2;$$

$$(2)\ 3HNO_2 = HNO_3 + 2NO + H_2O.$$

Reactions.—1. *Heat* decomposes HNO_3 to NO_2, H_2O, and O; the decomposition is complete at c. 256° (Carius, *B.* 4, 828).—2. *Light* slowly decomposes HNO_3 in the same way as heat; hence very conc. HNO_3Aq kept in an open place always contains some NO_2.—3. The products of *electrolysis* of HNO_3Aq vary with the dilution of the acid; with acid $2HNO_3{:}3H_2O$ no H is evolved at first, after a little NO comes off, and then H begins, while the NO slowly ceases; as dilution increases H is evolved and products of reduction —N_2O_3, NO, N, and NH_3—are produced, the more rapid the electrolysis the greater is the quantity of H evolved; very dilute acid evolves H only without the formation of reduced products (Bourgoin, *J. Ph.* [4] 13, 266 [abstract in *C. J.* [2] 9, 885]; Gladstone a. Tribe, *C. J.* 35, 172).—4. Conc. HNO_3Aq is rapidly reduced by *hydrogen occluded* by Pt or Pd, with oxidation of the H (G. a. T., *l.c.*).—5. HNO_3Aq is also reduced by many *metals*; the products vary with temperature, concentration of the acid, and the nature of the metal. Mg with 68 p.c. acid *plus* an equal quantity, or twice the quantity, of water, produces H along with gaseous reduction-products (G. a. T., *C. J.* 35, 178). The gaseous reduction-products are generally N_2O, NO, and N; these gases are formed by the reaction with HNO_3Aq of *e.g.* Al, Cd, Co, Cu, In, Fe, Pb, Mg, Ni, Ag, Tl, Sn, Zn (Acworth, *C. J.* 28, 828; Acworth a. Armstrong, *C. J.* 32, 54). It appears to be the case that the greater the heat of formation of a metallic oxide the more completely is HNO_3Aq reduced by the metal (*cf.* Thomsen, *Th.* 3, 547). Al, Cd, Fe, Mg, Pb, Sn, Zn, and the alkali metals produce NH_4NO_3 and NH_2OH, but no nitrous acid or nitrites; Bi, Cu, Hg, and Ag produce nitrites, but no NH_4NO_3 or NH_2OH (Divers, *C. J.* 43, 443; for the combined action of HNO_3Aq and H_2SO_4Aq on Zn *v.* Divers a. Shimidzu, *C. J.* 47, 597). In most cases nitrates of the metals are formed, but sometimes these are decomposed with the final formation of oxides, *e.g.* Sb, Sn, and W (*v.* also Veley, *Pr.* 48, 458). Ta, Ti, Au, and most of the Pt metals do not react with HNO_3Aq.—6. All the solid *non-metals* are oxidised by nitric acid.—7. *Oxidisable compounds* are oxidised by HNO_3Aq; *e.g.* ferrous compounds are changed to ferric, stannous to stannic, arsenious to arsenic; sulphides generally yield sulphates and nitrates.—8. *Hydriodic acid* and *iodides* yield H_2O, NO, and I.—9. *Hydrochloric acid* gives H_2O, NOCl, and Cl (*v. aqua regia* under Chlorhydric acid, vol. ii. p. 8; *Reactions* No. 17).—10. *Organic compounds* are oxidised by HNO_3Aq; straw, hay, cotton, &c., are inflamed by the conc. acid (Kraut, *B.* 14, 301). Many organic compounds, especially those of the benzenoid class, form nitro- derivatives, H being replaced by NO_2.—11. With *starch*, N_2O_3 or a mixture of this with NO_2 is produced; HNO_3Aq S.G. 1·3 to 1·35 gives almost pure N_2O_3; if the S.G. is greater than 1·35 NO_2 is also produced; if S.G. is less than 1·3 the chief gaseous product is NO (Lunge, *B.* 11, 1229, 1641).

Combinations.—1. With *water*; it is still undecided whether a hydrate or hydrates of HNO_3 are produced when HNO_3 is dissolved in water; *v. Properties*, p. 519.—2. With *ammonia* to form NH_4NO_3.—3. With dry *sulphur dioxide* to form $SO_2.NO_2.OH$ (*v.* Nitrogen derivatives of sulphur acids in vol. iv.).—4. With some *nitrates* to form acid salts; according to Ditte (*A. Ch.* [5] 18, 320), the nitrates which combine with HNO_3 when dissolved in excess of the acid are those of NH_4, K, Rb, and Tl.—5. With *nitric anhydride* to form $(HNO_3)_2N_2O_5$ ($= H_2N_4O_{11}$; *v. Dinitric acid, infra*).

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Dinitric acid $H_2N_4O_{11}$ ($= (HNO_3)_2.N_2O_5$). Weber (*J. pr.* [2] 6, 342) obtained this compound by adding very conc. colourless HNO_3 to melted N_2O_5, and cooling to c. 8° (for details of preparation *v.* Weber, *l.c.*). A bluish yellow liquid, solidifying at c. 5°; S.G. 1·642 at 18°. Fumes in air; dissolves in water with production of much heat; when gently warmed N_2O_5 is evolved. It is very dangerous to keep the compound in sealed tubes as explosions generally occur. Acts as a powerful oxidiser; forms NO_2 derivatives with many carbon compounds. The relation of this acid to nitric acid is probably similar to that of disulphonic to sulphonic acid: $H_2SO_4 + SO_3 = H_2S_2O_7$; $2HNO_3 + N_2O_5 = H_2N_4O_{11}$. M. M. P. M.

NITRIDES. *Compounds of N with one other more positive element.* The term is generally applied to the binary compounds of N with B, P, Si, and the metals. The metallic nitrides have for the most part the composition denoted by the formulæ RN, R_2N, or R_3N; R = monovalent metal. They are mostly obtained by the action of ammonia on metallic oxides or chlorides; frequently also by the direct action of atmospheric

nitrogen on metals at the moment of separation from their oxides by charcoal. Some metallic nitrides are also obtained by the reaction of metals or oxides of metals with hydrazoïc acid, HN_3 (*q.v.* p. 559). Most of them have a metallic aspect, are easily decomposed by heat, sometimes with explosion; some of them, however, withstand a very high temperature without decomposition. Many of them are reduced to metals by strongly heating in hydrogen or ammonia-gas; heated with water or hydrate of potassium they often yield metallic oxides and ammonia; they burn when heated in the air. They unite with other metallic compounds, especially with metalamides. The chief metallic nitrides are those of Al, Cu, Cr, Fe, Mg, Hg, Mo, Ni, Nb, Pt, K, Na, Ta, Th, ?Sn, Ti, W, U, Y, Zn, and Zr. For descriptions of the nitrides *v.* the several metals enumerated above. M. M. P. M.

NITRIFICATION. Nitre occurs in many parts of the earth. In some places it is found as an efflorescence on the surface of the soil; it is formed on the sides of caves (generally those frequented by animals), on the walls of old stables, and in the soil surrounding some of the villages in North India (*v.* Palmer, *C. J.* [2] 6, 318). Nitre also occurs in Algeria, Spain, &c.; and very large deposits of $NaNO_3$ are found in Peru. Nitrates are found in all, or almost all, soils, especially in those which are fertile and well manured. Nitrates are obtained by the artificial oxidation of nitrogenous matters in soils, by arranging the conditions so that there is first an accumulation of nitrogenous compounds, and then a slow oxidation in presence of moisture and some base which combines with the HNO_3 as it is produced (*v. Potassium nitrate, Formation*, p. 515).

That HNO_3 is formed by the oxidation of nitrogen compounds has been abundantly proved (*e.g.* by Boussingault, *C. R.* 82, 477). There is no convincing experimental proof that the N of the air is oxidised to HNO_3, under normal naturally occurring conditions. L. T. Wright (*C. J.* 35, 42) found that HNO_3 is formed by burning H in air, but that if special precautions are taken to remove all NH_3 from the air, HNO_3 is not formed. Boussingault (*C. R.* 76, 22) found that there was no increase in the total N in a quantity of soil rich in N compounds, after keeping in a closed vessel full of air for 11 years, although there was a marked increase in the nitrates in the soil. Various experimenters have proved that NH_3 can be oxidised to HNO_3, *e.g.* by ozone, by $KMnO_4$ and H_2SO_4, &c. (*v.* Nitric acid, *Formation*, p. 518). Experiments conducted at Rothamsted have proved conclusively that nitrates are formed in a fertile soil from NH_4 salts applied to the soil. The following table, taken from the article Nitrification in the first edition of this Dictionary (Supp. iii. p. 1399), exhibits very clearly the oxidation of NH_4 salts to nitrates in the soil:—

Nitrogen existing as nitrates in one million parts of drainage water.

Dates on which drainage water was collected	Plots which received no NH_4 salts				Plots which received 400lbs. NH_4 salts per acre, between March 10 and 13						
	3 and 4	5	16	17	7	10	11	12	13	14	18
February 16, 1879	3·4	3·7	4·2	3·3	3·5	5·2	4·8	4·1	3·8	4·8	4·2
April 7, 1879	3·6	2·9	3·6	2·3	39·0	45·4	41·8	25·4	29·4	33·0	40·4

In 1862, Pasteur suggested that the oxidation of nitrogen compounds in the soil to nitrates is accomplished by a living organism. In 1877 Schloesing a. Muntz (*C. R.* 84, 301; 85, 1018) showed that nitrification did not take place in sewage slowly filtered through a column of pure sand and limestone until after 20 days, that nitrification then proceeded rapidly, but was completely stopped by allowing vapour of chloroform free access to the surface of the sand and limestone; 7 weeks after the application of $CHCl_3$, a little vegetable earth, which was known to nitrify easily, was placed on the surface of the sand, and then nitrification began again. S. a. M. also showed that heating soil to 100° destroyed the power of that soil to produce nitrates from nitrogenous matter.

Warington has conducted, at Rothamsted, an extensive, laborious, and accurate, series of experiments on nitrification in soils; his memoirs are to be found in *C. J.* 33, 44; 35, 429; 45, 637 [numerous references here to other workers]; 47, 758; 51, 118; 53, 751; *cf.* also Munro, *C. J.* 49, 632. The results fully confirm the view that the production of nitrates in soils from nitrogenous compounds is due to the activity of a living organism. Summarising the results, Warington says (*C. J.* 45, 461): 'Nitrification in soils and waters is found to be strictly limited to the range of temperature to which the vital activity of low organisms is confined. Nitrification is also dependent on the presence of plant-food suitable to organisms of low character. Further proof is afforded by the fact that antiseptics are fatal to nitrification. The action of heat is equally confirmatory. By raising sewage or soil to the temperature of boiling water, its nitrifying power is entirely destroyed. Finally, nitrification can be started in boiled sewage, or in other sterilised liquids of suitable composition, by the addition of a few particles of surface soil, or a few drops of a solution which has lately nitrified; while, if no such addition is made, these liquids may be freely exposed to filtered air without nitrification taking place. . . . Schloesing has apparently given a final blow to the theory that air exists in a condensed state in the pores of a soil, and may on that account exert special oxidising powers, by his recent experiments (*Ann. de la Science agronomique*, 1884. 1), showing that the gases in a vegetable soil simply occupy the normal

volume due to temperature and atmospheric pressure.'

The result of Warington's examination of the classes of bodies that undergo nitrification in soils is, that all nitrogenous substances which yield ammonia by the action of organisms existing in fertile soils are nitrifiable (*C. J.* 45, 653).

The conditions under which nitrification proceeds in soils, sewage, &c., are as follows (W. *C. J.* 45, 654 *et seq.*) :—(1) A sufficient quantity of some base must be present to combine with the nitric acid. When the whole of the bases present are neutralised the nitrification stops, although nitrifiable compounds may still be present. There is a limit to the quantity of alkaline carbonate which can be present in a liquid undergoing nitrification. This fact renders impossible the nitrification of urine, except when diluted with water, because the first product of the action on urine of organisms in the soil is NH_4 carbonate, and unless this be present in very moderate quantity nitrification cannot proceed. Warington's experiments showed that 14 parts urine in 100 water did not nitrify when kept in contact with soil containing nitrifying organisms for 172 days. Addition of gypsum allows nitrification to proceed in cases where it would either not occur or be stopped by the presence of NH_4 carbonate (W., *C. J.* 47, 758; Pickard, *Ann. de Science agronomique*, 1884. 302; Joulie, *ibid.* 1884. 289). Thus, whereas a 14 p.c. urine solution did not nitrify after 172 days, a 30 p.c. solution, to which gypsum was added, nitrified after 78 days, and a 50 p.c. solution containing gypsum nitrified after 151 days. (2) In order that a nitrogenous liquid shall nitrify, the concentration of the liquid must not exceed a certain degree (for experiments *v. C. J.* 45, 662). (3) A sufficient quantity of the nitrifying organism must be present. The vigour of the organisms obtained in different cultivations differs considerably. A liquid which refuses to nitrify when seeded, because its concentration is excessive, may be caused to undergo nitrification by seeding it with a very vigorous organism, *i.e.* one which has been obtained by cultivation in a fairly conc. solution well supplied with nutriment. 'The plan that has proved most effective in producing rapid nitrification is to make use of the sediment lying at the bottom of the vessel in which the nitrification of a fairly strong solution has been conducted' (W., *l.c.* p. 665). (4) Stagnant liquids of considerable depth nitrify much less quickly than a shallow liquid of similar composition, or than a liquid which is poured over a porous solid and so brought into contact with fresh supplies of oxygen. (5) Some quantity of carbon in combination—'organic carbon'—is needed for the nourishment of the nitrifying organism, but no advantage accrues from the presence of more C than is required for this purpose (*cf.* Munro, *C. J.* 49, 651 *et seq.*). (6) Nitrification proceeds within certain limits of temperature; the organism seems to be destroyed at, or somewhat below, 100°; at 3°–5° nitrification proceeds much more slowly than at somewhat higher temperatures. (7) Light tends to decrease, or even stop, the process of nitrification (*v.* W., *C. J.* 33, 44). The product of nitrification is sometimes a nitrite, sometimes a nitrate, and sometimes both. The exact conditions under which nitrite and nitrate are formed have not yet been determined satisfactorily. In a later communication (*C. J.* 59, 484) Warington describes the isolation of two organisms: one of these oxidises ammonia to nitrous acid and has no effect on nitrites; the other produces neither nitrites nor nitrates in ammoniacal solutions, but in absence of ammonia rapidly converts nitrites into nitrates. P. F. Frankland and G. C. Frankland (*Pr.* 47, 296) seem to have isolated a bacillus, which grows slowly in broth, and which converts ammoniacal salts into nitrates.

With regard to the distribution of the nitrifying organisms in the soil, Warington's experiments show that the organisms are not evenly distributed below a depth of about 9 inches in clay-soils (*C. J.* 45, 649), and that nitrification occurs chiefly, if not altogether, in the surface-soil, and rarely in a clay-subsoil 2 or 3 feet from the surface (*C. J.* 51, 118). M. M. P. M.

NITRILES. Compounds of the form R.C⋮N where R is an organic radicle.

Formation.—1. By distilling potassium alkyl sulphates ($KRSO_4$) with potassium cyanide (Dumas, *C. R.* 25, 474).—2. From alkyl iodides and potassium cyanide in presence of dilute alcohol (Schlagdenhauffen, *C. R.* 48, 228; Henry, *C. R.* 104, 1181).—3. By dehydrating amides by distillation with P_2O_5 or P_2S_5 (Dumas, Malaguti, a. Leblanc, *A.* 64, 333).—4. By distilling organic acids with potassium or lead sulphocyanide. This reaction is most successful with aromatic acids (Krüss, *B.* 17, 1766).—5. By boiling the formyl derivatives of aromatic amines (*e.g.* (formanilide) with zinc-dust (Gasiorowski, *B.* 17, 73).—6. By the action of bromine and NaOH on the amide of the acid containing one C atom more: $X.CH_2.CONH_2 + 3Br_2 + 8NaOH = X.CN + 6NaBr + Na_2CO_3 + 6H_2O$. This reaction, which gives a means of descending the series, is particularly applicable to the higher homologues (yield from monoamide = 30 p.c.), but the lower the homologue the smaller is the yield, till in the case of valeramide hardly any nitrile at all is formed, the chief product of the reaction being butylamine (Hofmann, *B.* 17, 1406).—7. By distilling the formyl derivatives of aromatic monamines with zinc-dust, the yield being 10 p.c.–20 p.c. (Gasiorowski a. Merz, *B.* 18, 1008).—8. By warming the oxim of the corresponding aldehyde with Ac_2O.—9. Aromatic nitriles may be formed from diazo- compounds by Sandmeyer's reaction, using cuprous cyanide (Sandmeyer, *B.* 17, 2653).

Reactions.—1. Readily converted into NH_3 and the corresponding acid by heating with *acids* or *alkalis*. Cold conc. HClAq forms the intermediate amides.—2. *Alcohol* (1 mol.) and gaseous HCl form the salt of an imido-ether, *e.g.* $CH_3.CH(OEt){:}NH_2Cl$.—3. *Zinc* and dilute acids yield the corresponding amine (Mendius, *A.* 121, 129).—4. H_2S unites, forming a thio-amide, *e.g.* $CH_3.CS.NH_2$.—5. *Sodium* polymerises many fatty nitriles. Sodium acting on an alcoholic solution of aromatic nitriles often reduces them to the aromatic hydrocarbons or their hydrides (Bamberger a. Lodter, *B.* 20, 1702).—6. HBr combines with nitriles. The product is decomposed by water, fatty nitriles yielding the acid, while benzonitrile yields benzamide.—

7. *Hydroxylamine* unites, forming amidoxims $R.C(NH_2):NOH$.

Isonitriles *v.* CARBAMINES.

NITRILO - DIACETONAMINE *v.* ACETONAMINE.

NITRILO - PROPIONITRILE. A name for hydrocyanaldine *v.* vol. i. p. 104.

NITRITES. *Salts of nitrous acid*, HNO_2, *v. Nitrous acid* and *Nitrites*, under NITROGEN, p. 567.

NITRO- . *Use of this prefix applied to inorganic compounds:* for *nitro- compounds* and *nitro- salts v.* the element the nitro- compound of which is sought for, or the salts to the names of which *nitro-* is prefixed. Thus, *nitroferrocyanides* are described under *ferrocyanides*, a section of the group CYANIDES; *nitrochromate of potassium* is described under CHROMATES.

NITRO-ACENAPHTHENE $C_{12}H_9NO_2$. [155°] (J.); [102°] (A.). Formed by nitrating acenaphthene dissolved in HOAc (Jandrier, *C. R.* 104, 1858; Quincke, *B.* 20, 609; 21, 1454). Pale-yellow needles (by sublimation). Easily reduced by zinc and HCl to an amido- derivative, which yields a bluish-violet product on oxidation.

Dinitro-acenaphthene $C_{12}H_8(NO_2)_2$. [206°]. Yellow needles, formed at the same time as the preceding (Q.; *cf.* Berthelot, *Bl.* 8, 250).

NITRO-ACETIC ACID $CH_2(NO_2)CO_2H$ or $CH_2(ONO)CO_2H$.

Ethyl ether EtA'. (c. 155°). S.G. $\frac{0}{}$ 1·133. Formed from bromo- or iodo-acetic ether and silver nitrite at 130°. Extracted with ether Forcrand, *Bl.* [2] 31, 536; Steiner, *B.* 15, 1605; Lewkowitsch, *J. pr.* [2] 20, 163). Oil, smelling like nitrous ether. Yields amido-acetic ether on reduction. Splits up when boiled for a long time, yielding CO_2, oxalic ether, and NO.

NITROACETAMIDO - DI - METHYL-HYDROQUINONE *v. Acetyl-di-methyl derivative* of NITRO-AMIDO-HYDROQUINONE.

NITRO-ACET-ANILINE *v. Acetyl derivative* of NITRO-ANILINE.

NITRO-ACET-NAPHTHALIDE *v. Acetyl derivative* of NITRO-NAPHTHYLAMINE.

NITRO-ACETONITRILE. A name formerly given to fulminic acid (*v.* vol. ii. p. 317).

NITRO-ACETONYL-UREA

$CMe_2<\begin{smallmatrix}CO.NH\\N(NO_2).CO\end{smallmatrix}>$(?). [141°]. Obtained by nitrating acetonyl-urea (Franchimont a. Klobbie, *R. T. C.* 7, 241). Slender needles, sl. sol. water and benzene, sol. alcohol and ether. Decomposed by boiling water, forming α-oxy-isobutyric acid.

o-**NITRO-ACETOPHENONE** $C_8H_7NO_3$ *i.e.* $CH_3.CO.C_6H_4NO_2$ [1:2]. *Nitro-phenyl methyl ketone.* Formed, together with the *m*- isomeride, by nitration of acetophenone, especially at 40° (Engler, *B.* 18, 2238). Prepared by boiling o-nitro-benzoyl-acetoacetic ether with dilute H_2SO_4 for 8 hours, and extracting with ether (Gutkzeit, *A.* 221, 325). Oil, v. sol. alcohol. With PCl_5 it yields chloro-o-nitro-styrene. Boiling alcoholic ammonium sulphide converts it into indigo. $KMnO_4$ yields *o*-nitro-benzoic acid. Tin and HCl yield *o*-amido-acetophenone (242°–252°).

m-Nitro-aceto-phenone $CH_3.CO.C_6H_4NO_2$ [1:3]. [81°] (Buchka, *B.* 10, 1714). Formed by the action of *m*-nitro-benzoyl chloride on sodio-acetacetic ether and digesting the product with water (Gevekoht, *B.* 15, 2084). Obtained also by nitrating acetophenone in the cold. Needles, volatile with steam. Yields *m*-nitro-benzoic acid on oxidation.

Oxim [132°]. Forms a methyl-ether [64°] (Gabriel, *B.* 15, 3063).

p-Nitro-acetophenone $CH_3.CO.C_6H_4NO_2$ [1:4]. [81°]. Formed by the action of *p*-nitro-benzoyl chloride on sodio-acetacetic ether, and digesting the product with water (Gevekoht, *B.* 15, 2084). Formed also by warming *p*-nitro-phenyl-propiolic acid with dilute H_2SO_4, or by allowing its ether to stand with conc. H_2SO_4 at 40°, pouring the *p*-nitro-benzoyl-acetic acid which is formed into water, and expelling CO_2 by boiling (Drewson, *A.* 212, 160; Engler a. Zulke, *B.* 22, 203). Yellow prisms. Yields chloro-*p*-nitro-styrene with PCl_5. Yields *p*-amido-acetophenone [106°] on reduction by tin and HCl.

Phenyl-hydrazide $CH_3.C(N_2HPh).C_6H_4NO_2$. [132°].

NITRO-ACET-TOLUIDE *v. Acetyl derivative* of NITRO-TOLUIDINE.

NITRO-ACET-XYLIDE *v. Acetyl derivative* of NITRO-XYLIDINE.

DI-NITRO-ACETYLENE-DI-UREA $C_4N_6H_4O_6$ *i.e.* $CO<\begin{smallmatrix}NH.C(NO_2).NH\\NH.C(NO_2).NH\end{smallmatrix}>CO$. *Di-nitroglycoluril.* Formed by nitrating acetylene-di-urea (Franchimont a. Klobbie, *R. T. C.* 7, 18). Chars at 180°. On boiling with water it is decomposed into CO_2, water, and an isomeride of hydantoïc acid.

NITRO- ACIDS *v.* NITRO- COMPOUNDS.

(α)-**NITRO-ACRIDINE** $C_{13}H_8N_2O_2$ *i.e.* $C_{13}H_8(NO_2)N$. [214°]. Formed, together with the two following bodies, by nitrating acridine (Graebe a. Caro, *A.* 158, 275). Golden-yellow plates (by sublimation), insol. water, sl. sol. alcohol and ether. Its solution in dilute acids shows blue fluorescence. The hydrochloride crystallises in yellow prisms.

(β)-Nitro-acridine [154°]. Plates, v. sol. hot alcohol. Forms salts with acids.

Di-nitro-acridine $C_{13}H_7(NO_2)_2N$. Reddish-yellow tables, sl. sol. alcohol and ether. Does not dissolve in dilute acids.

TRI-NITRO-ACRIDINE CARBOXYLIC ACID $C_{13}H_5(NO_2)_3NCO_2H$. Formed by boiling methyl-acridine with HNO_3 (S.G. 1·33) (Bernthsen, *A.* 224, 40). Yellow prisms.

NITRO-ALDEHYDO-BENZOIC ACID $C_6H_3(CHO)(NO_2).CO_2H$ [1:2:4]. [160°].

Formed, together with a small quantity of $C_6H_3(CHO)(NO_2).CO_2H$ [1:3:4] [184°] by nitrating *p*-aldehydo-benzoic acid (Löw, *A.* 231, 368). Four-sided prisms (from water), v. sol. alcohol and ether. With acetone and NaOH it forms indigo-carboxylic acid.—AgA': sl. sol. water.

Ethyl ether EtA'.

NITRO-ALDEHYDO-CINNAMIC ACID $C_{10}H_7NO_5$ *i.e.* $C_6H_3(CH:CH.CO_2H)(NO_2)(CHO)$ [1:2:4]. [194°]. Formed by nitration of aldehydo-cinnamic acid (Löw, *A.* 231, 376). Prisms. V. sol. glacial acetic acid, acetone, and hot water, hardly sol. ether or chloroform. Does not give the indigo reaction with acetone and NaOH, so that NO_2 is probably not *ortho* to CHO.—AgA' aq.

Ethyl ether EtA'. [80°]. Prisms.

NITRO-ALIZARIN *v.* NITRO-DI-OXY-ANTHRAQUINONE.

DI-NITRO-ALLYL-ANILINE $C_9H_9N_3O_4$ *i.e.* $C_3H_5NHC_6H_3(NO_2)_2$. [76°]. Formed from bromo-

m-di-nitro-benzene, allylamine, and alcohol (Romburgh, *R. T. C.* 4, 192). Yellow needles.

Tri-nitro-allyl-aniline $C_9H_8N_4O_6$ *i.e.* $C_3H_5NHC_6H_2(NO_2)_3$. [80°]. Formed by the action of allylamine on chloro-tri-nitro-benzene (picryl chloride) (R.).

p-**NITRO-ALLYL-BENZOYL-ACETIC ETHER** $C_6H_4(NO_2).CO.CH(C_3H_5).CO_2Et$. [46°]. Formed from sodium *p*-nitro-benzoyl-acetic ether and allyl iodide (Perkin a. Bellenot, *C. J.* 49, 452).

NITRO-AMIDO-ACETAMIDE $C_2H_5N_3O_3$ *i.e.* $CH_2(NH.NO_2).CONH_2$. Formed by decomposing nitro-hydantoïn by boiling water (Franchimont a. Klobbie, *R. T. C.* 7, 239). Long prisms, decomposing at 130°.

NITRO - DI - AMIDO - BENZENE *v.* NITRO-PHENYLENE-DIAMINE.

NITRO - AMIDO - BENZENE SULPHONIC ACID $C_6H_6N_2SO_5$ *i.e.* $C_6H_3(NO_2)(NH_2)(SO_3H)$ [2:1:4]. o-*Nitraniline sulphonic acid.* Formed by heating (1, 2, 4)-bromo-nitro-benzene sulphonic acid with alcoholic NH_3 at 180° (Goslich, *A.* 180, 103) and by nitrating acetyl-*p*-amido-benzene sulphonic acid (Nietzki, *B.* 18, 294; 21, 3220). The same acid appears to be formed by sulphonating *o*-nitro-aniline (Post a. Hardtung, *B.* 13, 38). Yellow needles, extremely sol. water, m. sol. alcohol and HClAq. Boiling aqueous KOH converts it into $C_6H_3(NO_2)(OK)(SO_3K)$. HClAq at 180° yields o-nitro-aniline.

Salts.—KA'aq. S. 5 at 6°.—NH_4A'. S. 13 at 6°.—BaA'_2 $2\frac{1}{2}$aq. S. ·5 at 9°.—CaA'_2 $2\frac{1}{2}$aq (P. a. H.).—PbA'_2 2aq. S. 2 at 6°.

Chloride $C_6H_3(NO_2)(NH_2).SO_2Cl$. [60°].

Amide [156°]. Yellow needles.

Nitro-amido-benzene sulphonic acid $C_6H_3(NO_2)(NH_2)(SO_3H)$[1:2:4]. Formed by the action of HNO_3 (1 mol.) on acetyl-amido-benzene *m*-sulphonic acid (1 mol.) dissolved in conc. H_2SO_4 (Eger, *B.* 21, 2579; 22, 847). Yellow needles (from water), sl. sol. alcohol, almost insol. ether.—KA': golden-yellow plates (from water).—NaA': yellow needles, v. sol. water.

Nitro-amido-benzene sulphonic acid $C_6H_3(NO_2)(NH_2)(SO_3H)$ [3:1:6]. Formed by heating *m*-nitroaniline sulphate at 120°-170° with $ClSO_3H$ (Limpricht, *B.* 18, 2186). Long colourless prisms or glistening plates. Easily soluble in hot water, more sparingly in cold.

Salts.—A'K aq: long thin glistening red prisms or yellowish-red plates.—A'Na 2aq: small yellow plates.—A'_2Ca 4aq: easily soluble large orange tables or thick red prisms.—A'_2Ba aq: red tablets or prisms, sparingly soluble in cold water.

Nitro-amido-benzene sulphonic acid $C_6H_3(NO_2)(NH_2)(SO_3H)$[3:1:4]? Formed by heating *m*-nitro-aniline with fuming H_2SO_4 at 160° (Post a. Hardtung, *A.* 205, 102; *B.* 13, 40). Yellowish-brown prisms. — BaA' 2aq: long spikes. S. 14 at 100°. — CaA'_2 4aq: small needles, v. sol. water. This acid is perhaps identical with the preceding.

Nitro-amido-benzene sulphonic acid $C_6H_3(NO_2)(NH_2)(SO_3H)$[4:1:3]. Formed in small quantity by heating $C_6H_3Br(NO_2)(SO_3H)$ [1:4:3] with alcoholic ammonia at 160° (Thomas, *A.* 186, 132). Needles, v. sol. water.—BaA'_2 $1\frac{1}{2}$aq. S. ·15 at 15°.

Nitro-amido-benzene disulphonic acid $C_6H_2(NO_2)(NH_2)(SO_3H)_2$. Formed by the action of ammonium sulphide on di-nitro-benzene disulphonic acid obtained from nitro-benzene *m*-sulphonic acid (Limpricht, *B.* 8, 289). Very deliquescent mass.—BaA'' 2aq.

(*a*)-**NITRO-AMIDO-BENZOIC ACID** $C_7H_6N_2O_4$ *i.e.* $C_6H_3(NO_2)(NH_2).CO_2H$[2:5:1]. Mol. w. 182. Formed by boiling (*a*)-di-nitro-*m*-uramido-benzoic acid with water (Griess, *B.* 5, 198; 11, 1734). Yellow needles or prisms, m. sol. hot water, v. sol. hot alcohol. Yields nitro-oxy-benzoic acid [169°]. Yields on reduction a diamido-benzoic acid which forms *p*-phenylene-diamine on distillation.—BaA'_2 3aq.

(*β*)-Nitro-amido-benzoic acid $C_6H_3(NO_2)(NH_2).CO_2H$[4:3:1]. [298°]. Formed by boiling (*β*)-di-nitro-*m*-uramido-benzoic acid with water (Griess). Formed also by saponifying its acetyl derivative (Kaiser, *B.* 18, 2946). Red plates or needles. Yields on reduction a diamido-benzoic acid which forms o-phenylene-diamine on distillation.—CaA'_2 aq: red crystals, sl. sol. water.—BaA'_2 2aq.

Ethyl ether EtA'. [139°]. Red needles.

Formyl derivative [221°]. (Zehra, *B.* 23, 3634).

Acetyl derivative $C_6H_3(NO_2)(NHAc)CO_2H$. [206°]. Formed, together with the (2, 3, 1)-isomeride, by nitrating *m*-acetamido-benzoic acid below 0° (K.). Yellow tables.—CaA'_2 $7\frac{1}{2}$aq.—BaA'_2 7aq.

γ-Nitro-amido-benzoic acid $C_6H_3(NO_2)(NH_2)(CO_2H)$[2:3:1]. [157°]. Formed by boiling (*γ*)-di-nitro-*m*-uramido-benzoic acid with water (Griess, *B.* 2, 435; 5, 199). Formed also by saponifying its acetyl derivative which is prepared as above (K.). Long yellow needles, v. sol. hot water. Yields o-nitro-benzoic acid on elimination of NH_2 (Griess, *B.* 11, 1734). Yields on reduction a di-amido-benzoic acid which forms o-phenylene-diamine on distillation.—KA' 2aq.—BaA'_2 7aq.—HA'HCl, white crystals, decomposed by water.

Acetyl derivative $C_6H_3(NO_2)(NHAc).CO_2H$. [241°]. Colourless crystals.—CaA'_2 6aq.—BaA'_2 aq.

(*δ*)-Nitro-amido-benzoic acid $C_6H_3(NO_2)(NH_2).CO_2H$ [3:4:1]. [284°]. Formed by heating di-nitro-*p*-uramido-benzoic acid with water (Griess, *B.* 5, 855). Formed also by heating $C_6H_3(NO_2)(OMe).CO_2H$ [3:4:1] with aqueous ammonia at 140°-170° (H. Salkowski, *A.* 173, 52). Reddish-yellow needles (from alcohol), sl. sol. hot water. Yields, on reduction, di-amido-benzoic acid [210°]. Converted into *m*-nitro-benzoic acid by the diazo- reaction.—KA' aq: orange prisms.—BaA'_2 5aq.

Ethyl ether EtA'. [145°]. Formed by heating $C_6H_3Br(NO_2).CO_2Et$ [4:3:1] with alcoholic NH_3 for 3 hours at 150° (Grohmann, *B.* 23, 3449). Yellow crystals.

Amide $C_6H_3(NO_2)(NH_2).CONH_2$. [227°]. Formed by heating $C_6H_3Br(NO_2).CONH_2$ [4:3:1] with alcoholic NH_3 at 180° (G.). Lemon-yellow crystals, insol. water, sl. sol. alcohol.

Acetyl derivative $C_6H_3(NO_2)(NHAc).CO_2H$. [221°]. Formed by nitration of acetyl-*p*-amido-benzoic acid below 10° (Kaiser, *B.* 18, 2943). Thick yellow tables, v. sl. sol. cold water.—CaA'_2 2aq.—BaA'_2 $6\frac{1}{2}$aq.

(*ε*)-Nitro-amido-benzoic acid $C_6H_3(NO_2)(NH_2)(CO_2H)$ [5:2:1]. [263°].

Formation. — 1. By boiling di-nitro-o-uramido-benzoic acid with water (Griess, *B.* 11, 1730).—2. By heating $C_6H_3(NO_2)(OEt).CO_2Et$ with alcoholic NH_3 at 140° and boiling the resulting amide with baryta-water (Hübner, *A.* 195, 21).—3. By heating $C_6H_3Br(NO_2).CO_2H$ [2:5:1] with conc. NH_3Aq at 145° (Rahlis, *A.* 198, 112).—4. From its amide which is formed when nitro-isatoic acid is warmed with aqueous ammonia (Kolbe, *J. pr.* [2] 30, 477).

Properties.—Slender yellow needles, v. sol. boiling water. On elimination of NH_2 it yields *m*-nitro-benzoic acid.

Salts.—$KA'2aq$. — CaA'_2 3aq. — BaA'_2 3aq: v. sol. cold water, sl. sol. hot water.—PbA'_2 2aq.—$HA'HCl$: needles, decomposed by water.

Amide $C_6H_3(NO_2)(NH_2).CONH_2$. [200°–210°]. Yellow needles (from acetone).

(ζ)-Nitro-amido-benzoic acid $C_6H_3(NO_2)(NH_2)(CO_2H)$ [3:2:1]. [204°]. Formed by heating $C_6H_3(NO_2)(OEt)(CO_2Et)$ [3:2:1] with alcoholic NH_3 at 130°–160° and saponifying the resulting amide (Hübner, *A.* 195, 37). Yellow needles (from water). On elimination of NH_2 it yields *m*-nitro-benzoic acid.—KA'.— CaA'_2 2aq. —SrA'_2 2aq.—BaA'_2 2aq: purple needles, sl. sol. cold water. — $Pb(OH)A'$. — CuA'_2. — AgA'. — $HA'HCl$: needles.

Ethyl ether EtA'. [204°]. Plates.

Amide $C_6H_3(NO_2)(NH_2)(CONH_2)$. [109°]. Yellow plates, almost insol. water and alcohol.

(η)-Nitro-amido-benzoic acid $C_6H_3(NO_2)(NH_2).CO_2H$ [5:3:1]. [208°]. Formed by reducing *s*-di-nitro-benzoic acid with NH_3 and H_2S (Hübner, *A.* 222, 81). Small golden prisms (from water). On elimination of NH_2 it yields *m*-nitro-benzoic acid. Reduces to di-amido-benzoic acid which, when distilled with steam, forms phenylene *m*-diamine.—NaA' aq: red needles.—NH_4A' 3aq: bright-yellow needles. — BaA'_2 4aq. — CaA'_2 $5\frac{1}{2}$aq. — PbA'_2 $3\frac{1}{2}$aq. — AgA'aq.

Ethyl ether EtA'. [155°]. Yellow needles.

Di-nitro-o-amido-benzoic acid $C_7H_5N_3O_6$ *i.e.* $C_6H_2(NO_2)_2(NH_2).CO_2H$. Mol. w. 227. [256°]. Formed, together with its methyl ether, by heating $C_6H_2(NO_2)_2(OEt).CO_2Me$ with aqueous ammonia (H. Salkowski, *B.* 4, 870; *A.* 173, 40). Golden-yellow scales (from alcohol).—NH_4A' aq.

Methyl ether MeA'. [165°]. Needles.

Ethyl ether EtA'. [135°]. Laminæ.

Di-nitro-*p*-amido-benzoic acid $C_6H_2(NO_2)_2(NH_2)(CO_2H)$ [5:3:4:1]. *Chrysanisic acid.* [260°]. Formed by the action of aqueous ammonia upon $C_6H_2(NO_2)_2(OMe)CO_2H$, which is a product of the action of warm fuming HNO_3 on anisic acid (Cahours, *A. Ch.* [3] 27, 454; Beilstein a. Kellner, *A.* 128, 104). Formed also by oxidation of di-nitro-*p*-toluidine by chromic acid mixture (Friederici, *B.* 11, 1975). Plates (from alcohol), sl. sol. cold Aq.—NH_4A'.—AgA'.

Methyl ether MeA'. [144°]. Plates.

Ethyl ether EtA'. [114°]. Plates.

Acetyl derivative $C_6H_2(NO_2)_2(NHAc).CO_2H$. [270°]. Silky needles.

Nitro-di-amido-benzoic acid $C_7H_7N_3O_4$ *i.e.* $C_6H_2(NO_2)(NH_2)_2CO_2H$ [5:4:3:1]. Formed by reducing chrysanisic acid with H_2S and alcoholic NH_3 (B. a. K.). Minute red crystals, v. sol. alcohol, sl. sol. hot water. —NH_4A'aq. Monoclinic prisms; $a:b:c = 1{\cdot}073:1:1{\cdot}809$; $\beta = 77°32'$.

DI-NITRO-AMIDO-BENZYL-METHYL KETONE $C_9H_9N_3O_5$. [214°]. Formed by reducing tri-nitro-benzyl methyl ketone in alcoholic solution with the theoretical quantity of $SnCl_2$ and HCl (Dittrich, *B.* 23, 2724). Groups of golden-yellow needles (from alcohol).

NITRO-AMIDO-ISOBUTYL-BENZENE $C_4H_9.C_6H_3(NO_2)(NH_2)$ [1:2:3]. *Nitro-isobutyl-aniline.* [124°]. Formed by saponifying its acetyl derivative (Gelzer, *B.* 21, 2941). Yellow crystals, v. sol. boiling water.

Acetyl derivative $C_4H_9.C_6H_3(NO_2)(NHAc)$. [106°]. Obtained by nitrating $C_4H_9.C_6H_4.NHAc$. Yellow needles, v. sl. sol. boiling water.

Nitro-amido-isobutyl-benzene $C_4H_9.C_6H_3(NO_2)(NH_2)$ [1:3:4]. [106·5°]. Formed from its acetyl derivative and alcoholic potash (Gelzer, *B.* 20, 3254). Orange crystals, sl. sol. hot water.

Acetyl derivative $C_4H_9.C_6H_3(NO_2)(NHAc)$. [105°]. (252°). Yellow needles. Obtained from $C_4H_9.C_6H_4.NHAc$ [1:4] and fuming HNO_3 at 0°.

Di-nitro-amido-isobutyl benzene $C_6H_2(C_4H_9)(NO_2)_2(NH_2)$. [127°]. Got by heating di-nitro-isobutyl-phenol [93°] with NH_3Aq at 175° (Barr, *B.* 21, 1544). Yellow needles.

***p*-NITRO-DI-AMIDO-DI-ISOBUTYL-TRI-PHENYL-METHANE** $C_6H_4(NO_2).CH(C_6H_3(NH_2).C_4H_9)_2$. [126°]. Formed from *p*-nitro-benzoic aldehyde, *p*-amido-isobutyl-benzene, and conc. H_2SO_4 (Bischler, *B.* 21, 3207). Yellow needles. Its hydrochloride and platinochloride are both crystalline. Its di-acetyl derivative melts at 114°, and its di-benzoyl derivative at 126°.

***m*-Nitro-di-*p*-amido-di-isobutyl-tri-phenyl-methane** $C_{27}H_{33}N_3O_2$. [65°]. Formed from *m*-nitro-benzoic aldehyde, *p*-amido-isobutyl-benzene, and conc. H_2SO_4.

Di-benzoyl derivative [114°]. Plates.

(α)-NITRO-o-AMIDO-CINNAMIC ACID $C_9H_8N_2O_4$ *i.e.* $C_6H_3(NH_2)(NO_2).CH:CH.CO_2H$? [240°]. Formed from o-amido-cinnamic acid (1 pt.), conc. H_2SO_4 (15 pts.), and KNO_3 (3 pts.) at 0°. On dilution with water (β)-nitro-o-amido-cinnamic acid separates as brownish needles, while the (α)-compound may be ppd. by nearly neutralising the mother-liquor with NaOH (Friedländer a. Lazarus, *A.* 229, 241). Brown needles. Insol. benzene, ether, or petroleum, sl. sol. water, v. sol. alcohol and acetone. Dissolved by mineral acids, but ppd. by sodic acetate. With HCl at 150° it gives (α)-nitro-carbostyril (nitro-oxy-quinoline), which forms slender white needles; v. sl. sol. alcohol, glacial acetic acid, or acetone, and does not melt below 320°.

Ethyl ether EtA'. [160°]. Formed, along with (β)-nitro-carbostyril, by nitrating o-amido-cinnamic ether. Compact brown needles.

(β)-Nitro-o-amido-cinnamic acid $C_6H_3(NH_2)(NO_2).CH:CH.CO_2H$. [254°]. Prepared as above. Brownish yellow needles. Insol. dilute mineral acids, and in water. Sol. alkalis. With HCl at 150° it gives (β)-nitro-carbostyril [260°], which crystallises from glacial acetic acid in compact yellow needles.

(3:4:1)-Nitro-amido-cinnamic acid $C_6H_3(NO_2)(NH_2).C_2H_2.CO_2H$. [225°]. Formed by saponifying its acetyl derivative, which is

formed by nitration of acetyl-*p*-amido-cinnamic acid (Gabriel a. Herzberg, *B.* 16, 2021). Red needles. Sol. hot alcohol and acetic acid, less sol. water, nearly insol. benzene and ligroïn.

Acetyl derivative [261°–266°].

NITRO-AMIDO-o-CRESOL $C_6H_2Me(NO_2)(NH_2)(OH)$ [1:3:5:2]. [118°]. Obtained by nitrating $C_6H_2Me(CO_2H)(NHAc)(OH)$ [1:3:5:2] and saponifying the resulting acetyl derivative (Nietzki a. Ruppert, *B.* 23, 3478). Brownish-red needles (from alcohol).

Di-acetyl derivative $C_6H_2Me(NO_2)(NHAc)(OAc)$. [146°].

Nitro-amido-cresol. *Methyl ether.* $C_6H_2Me(NO_2)(NH_2)(OMe)$ [1:2:4:5]. [132°]. Formed from its acetyl derivative. Needles. On elimination of NH_2 and reduction it yields $C_6H_3Me(NH_2)(OMe)$ [111°]. Reduction yields $C_6H_2Me(NH_2)_2OMe$ [166°].

Acetyl derivative $C_6H_2Me(NO_2)(NHAc)(OMe)$. [156°]. Formed from $C_6H_3Me(NHAc)(OMe)$ in HOAc by treatment with HNO_3 (S.G. 1·48) (Limpach, *B.* 22, 789). Needles.

Nitro-ω-amido-cresol *Methyl ether of the acetyl derivative* $C_6H_3(CH_2.NHAc)(NO_2)(OMe)$ [1:3:4]. *Methyl derivative of acetyl-nitro-oxy-benzylamine.* [137°]. Formed by nitrating $C_6H_4(CH_2.NHAc)(OMe)$ in the cold (Goldschmidt a. Polonowska, *B.* 20, 2410). Prisms, v. sl. sol. hot water. Yields nitro-anisic acid on oxidation.

Di-nitro-amido-*m*-cresol $C_6HMe(NO_2)_2(NH_2)OH$. [151°] (L. a. D.); [156°] (E. a. O.). Formed by reducing tri-nitro-cresol $C_6HMe(NO_2)_3OH$ [1:2:4:6:3] with H_2S and alcoholic NH_3 (Kellner a. Beilstein, *A.* 128, 166; Liebermann a. Dorp, *A.* 163, 104; Emmerling a. Oppenheim, *B.* 9, 1094). Thin yellow needles (from hot water).

Di-nitro-amido-*m*-cresol $C_6HMe(NO_2)_2(NH_2)(OH)$ [1:2 or 5:4:6:3]. [160°]. Formed by nitrating $C_6H_2Me(CO_2H)(NHAc)(OH)$ (Nietzki a. Ruppert, *B.* 23, 3479). Large red needles. Perhaps identical with the preceding.

Mono-acetyl derivative. [225°].

Di-acetyl derivative. [175°].

NITRO-AMIDO-ISO-CYMENE $C_6H_2(NO_2)(NH_2)PrMe$ [*x*:5or6:3:1]. Formed from its phthalyl derivative by heating with conc. HCl for 24 hours at 180° (Kelbe a. Warth, *A.* 221, 176). Oil. Volatile with steam.

Benzoyl derivative $C_6H_2(NO_2)(NHBz)PrMe$. [177°]. Formed by nitration of the benzoyl derivative of amido-iso-cymene.

Phthalyl derivative $(C_6H_2(NO_2)PrMe)_2C_2O_2C_6H_4$. [167°]. Formed by nitration of the phthalyl derivative of amido-iso-cymene.

Di-nitro-amido-cymene $C_6HMePr(NO_2)_2(NH_2)$ [1:4:2:6:3]. [113°–115°]. From the ethyl ether of di-nitro-thymol and alcoholic NH_3 at 180° (Mazzara, *G.* 19, 160). Yellow tables (from dilute alcohol), sl. sol. hot water.

NITRO-*p*-AMIDO-ETHYL-BENZENE $C_6H_3(C_2H_5)(NO_2)(NH_2)$ [1:3:4]. [47°]. Yellowish-red prisms. Sol. alcohol, ether, benzene, chloroform, and CS_2, more sparingly in ligroïn. The acetyl compound is obtained by careful nitration of acetyl-*p*-amido-ethyl-benzene.

Acetyl derivative $C_6H_3(C_2H_5)(NO_2)(NHAc)$: [47°]; long yellow silky needles, extremely soluble in alcohol, ether, &c., less easily in ligroïn (Paucksch, *B.* 17, 769).

Di-nitro-*p*-amido-ethyl-benzene $C_6H_2(C_2H_5)(NO_2)_2NH_2$ [1:3:5:4]. [135°]. Orange-yellow prisms. Sol. benzene and chloroform, less easily in alcohol and ether. The acetyl derivative is obtained by nitration of acetyl-*p*-amido-ethyl-benzene.

Acetyl derivative $C_6H_2(C_2H_5)(NO_2)_2NHAc$: [182°]; needles.

NITRO-AMIDO-HYDROQUINONE.

Acetyl-di-methyl derivative $C_6H_2(NO_2)(NHAc)(OMe)_2$: [164°]; yellow needles. Formed by nitration of acetyl-amido-di-methyl-hydroquinone (Baessler, *B.* 17, 2121).

NITRO-AMIDO-HYDROTOLUQUINONE $C_6HMe(NO_2)(NH_2)(OH)_2$. Formed by reducing di-nitro-hydrotoluquinone with $SnCl_2$ (Kehrmann a. Brasch, *J. pr.* [2] 39, 389). Its *hydrochloride* crystallises in long yellow needles changing to small plates.

NITRO-AMIDO-MESITYLENE $C_6HMe_3(NO_2)(NH_2)$. [73°]. *Nitro-mesidine.* Formed by reducing di-nitro-mesitylene with alcoholic ammonium sulphide (Maule, *C. J.* 2, 116; *A.* 71, 137; Knecht, *A.* 215, 98; Klobbie, *R. T. C.* 6, 31).—B'HCl.—$B'_2H_2PtCl_6$.—$B'_3H_3PO_4$.

Acetyl derivative $C_6HMe_3(NO_2)(NHAc)$. [191°]. Formed by nitrating acetyl-mesidine (Biedermann a. Ledoux, *B.* 8, 58; Ladenburg, *B.* 7, 1133; *A.* 179, 163). Silky needles, m. sol. alcohol. Feeble base.

Benzoyl derivative $C_6HMe_3(NO_2)(NHBz)$. [168·5°]. Formed by nitrating benzoyl-mesidine (Schack, *B.* 10, 1711).

Nitro-di-amido-mesitylene $C_6Me_3(NO_2)(NH_2)_2$. [184°]. Formed, together with di-nitro-amido-mesitylene by reduction of tri-nitro-mesitylene by alcoholic ammonium sulphide (Fittig, *A.* 141, 139). Orange laminæ (from water) or monoclinic crystals (from alcohol); $a:b:c = 1·625:1:·417$; $\beta = 60° 4'$ (Lang, *A.* 141, 140; Hintze, *A.* 235, 183), v. sl. sol. cold water.—$B''H_2Cl_2$: tables.

Di-nitro-amido-mesitylene $C_6Me_3(NO_2)_2(NH_2)$. *Di-nitro-mesidine.* [194°]. Formed as above. Sulphur-yellow crystals (from alcohol), insol. water. Very feeble base, its hydrochloride being decomposed by water.

Acetyl derivative $C_6Me_3(NO_2)_2(NHAc)$. [275°]. S. (alcohol) 5 at 78°. Formed by nitrating the acetyl derivative of nitro-amido-mesitylene. Needles.

NITRO-AMIDO-DI-METHYL-ANILINE *v.* NITRO-PHENYLENE-DI-METHYL-DIAMINE.

TETRA-NITRO-DI-METHYL-DI-AMIDO-DI-PHENYL-METHANE. *Di-nitro-derivative* $CH_2(C_6H_2(NO_2)_2.NMe.NO_2)_2$. Formed by the action of HNO_3 (S.G. 1·48) on $CH_2(C_6H_4NMe_2)_2$ dissolved in HOAc (Romburgh, *R. T. C.* 7, 226). Decomposes at 218°. On boiling with aqueous KOH it gives off methylamine. CrO_3 in HOAc forms $CO(C_6H_2(NO_2)_2NMeH)_2$.

NITRO-AMIDO-METHYL-QUINOLINE $C_6H_4 \Big\langle \begin{array}{l} C(NH_2):C(NO_2) \\ N{=\!=\!=}CMe \end{array}$. [201°]. Formed by heating chloro-nitro-(*Py.* 3)-methyl-quinoline with alcoholic NH_3 at 190° (Conrad a. Limpach, *B.* 21, 1965). Yellow needles (from alcohol).

NITRO-AMIDO-(α)-NAPHTHOIC ACID $C_{11}H_8N_2O_4$ *i.e.* $C_{10}H_5(NO_2)(NH_2).CO_2H$. [c. 110°]. Formed by reducing di-nitro-naphthoic acid [215°] with H_2S and NH_3 (Ekstrand, *J. pr.* [2] 38, 271; *B.* 19, 1985). Needles (from water).

Nitro-amido-(β)-naphthoic acid $C_{10}H_5(NO_2)(NH_2).CO_2H$. [235°]. Formed by reducing di-nitro-(β)-naphthoic acid [226°] (Ekstrand, *J. pr.* [2] 42, 301). Stellate groups of small needles.—HA'HCl: needles.

Nitro-amido-(α)-naphthoic acid. *Acetyl derivative* $C_{10}H_5(NO_2)(NHAc)CO_2H$. [259°]. Formed by nitrating the acetyl derivative of (4'?, 1)-amido-naphthoic acid (Ekstrand, *J. pr.* [2] 38, 247). Yellow needles, v. sol. alcohol.

Nitro-amido-naphthoic acid $C_{10}H_5(NO_2)(NH_2)CO_2H$ [4':1':1]. *Anhydride* $C_{10}H_5(NO_2)<{NH \atop CO}>$ *Nitro-naphthostyril.* [300°]. Formed by nitrating naphthostyril (Ekstrand, *J. pr.* [2] 38, 180). Orange needles (from HOAc).

Di-nitro-amido-naphthoic acid. *Anhydride* $C_{10}H_4(NO_2)_2<{NH \atop CO}>$. [above 290°]. Formed by nitrating the preceding anhydride (E.). Plates, v. sl. sol. HOAc and alcohol.

NITRO-AMIDO-(α)-NAPHTHOL $C_{10}H_8N_2O_3$ *i.e.* $C_{10}H_5(NH_2)(NO_2)OH$. [130°]. Formed by reducing di-nitro-(α)-naphthol with ammonium sulphide (Ebell, *B.* 8, 564). Small yellowish needles, insol. water, sol. alcohol.

Benzoyl derivative $C_{10}H_7BzN_2O_3$. [158°]. Small red needles (from alcohol) (Hübner, *A.* 208, 332).

Nitro-di-amido-(α)-naphthol. *Tri-acetyl derivative* $C_{10}H_4(NO_2)(NHAc)_2OAc$. [235°]. Formed by nitrating $C_{10}H_5(NHAc)_2OAc$ [280°] (Meerson, *B.* 21, 1195). Yellow powder, yielding phthalic acid on oxidation by potassium permanganate. Fuming HClAq converts it into $C_{10}H_4(NO_2)(NH_2)<{O \atop N}>CMe$, whence boiling dilute potash forms $C_{10}H_4(NO_2)(OH)<{O \atop N}>CMe$ crystallising in brown needles [163°].

NITRO-AMIDO-NAPHTHOL SULPHONIC ACID $C_{10}H_8N_2SO_6$ *i.e.* $C_{10}H_4(NO_2)(NH_2)(OH)SO_3H$. Formed by reducing di-nitro-naphthol sulphonic acid with $SnCl_2$ (Lauterbach, *B.* 14, 2029). Golden-yellow plates, m. sol. hot water. Its alkaline solution is blood-red.

NITRO-AMIDO-TETRA-OXY-BENZENE $C_6(NO_2)(NH_2)(OH)_4$. Formed by partial reduction of di-nitro-di-oxy-quinone (nitranilic acid) with $SnCl_2$. Small violet needles, nearly insol. alcohol, ether, and benzene (Nietzki a. Benckiser, *B.* 16, 2094; 18, 500). Its alkaline solution is readily oxidised by the air to nitro-amido-di-oxy-quinone $C_6(NO_2)(NH_2)(OH)_2O_2$. Nitrous acid converts it into nitro-diazo-di-oxy-quinone $C_6(NO_2)(N_2OH)(OH)_2O_2$.

NITRO-o-AMIDO-PHENOL $C_6H_6N_2O_3$ *i.e.* $C_6H_3(NO_2)(NH_2).OH$ [6:2:1]. [111°]. Formed by reducing the corresponding di-nitro-phenol with ammonium sulphide (Post a. Stuckenberg, *A.* 205, 85). Red needles, sl. sol. water, v. sol. alcohol and ether. Gives a dirty-green colour with $FeCl_3$.—$B'_2H_2SO_4$: colourless pyramids.

Nitro-*o*-amido-phenol. *Methyl ether* $C_6H_3(NO_2)(NH_2)(OMe)$ [3:2:1]. [76°]. Formed from $C_6H_3(NO_2)_2(OMe)$ [118°] by heating with alcoholic ammonia at 190° (Bantlin, *B.* 11, 2106). Long yellow needles.

Nitro-o-amido-phenol $C_6H_3(NO_2)(NH_2).OH$ [4:2:1]. [142°]. Obtained by reducing the corresponding di-nitro-phenol with ammonium sulphide (Laurent a. Gerhardt, *Compt. Chim.* 1849, 468; *A.* 75, 68; Post a. Stuckenberg, *A.* 205, 71). Orange prisms (containing aq) melting at 80° to 90° or anhydrous crystalline crusts, melting at 142°; v. sol. hot water, alcohol, and ether.—$C_6H_5KN_2O_3C_6H_6N_2O_3$: dark-red nodules. —AgHA'': brownish-yellow pp. (L. a. G.).

Benzoyl derivative $C_6H_5BzN_2O_3$. [above 200°]. Yellow needles, sl. sol. alcohol.

Nitro-benzoyl derivative [218°].

Methyl ether $C_6H_3(NO_2)(NH_2)(OMe)$. *Nitro-anisidine.* Formed by reducing $C_6H_3(NO_2)_2(OMe)$ by alcoholic ammonium sulphide (Cahours, *A.* 74, 301). Long garnet-red needles, insol. cold, sol. boiling, water.—B'HCl. —$B'_2H_2PtCl_6$.—B'HBr.—$B'HNO_3$.—$B'_2H_2SO_4$.

Benzoyl derivative of the methyl ether $C_6H_3(NO_2)(NHBz)(OMe)$. Needles (from alcohol); m. sol. boiling alcohol.

Ethyl ether $C_6H_3(NO_2)(NH_2)(OEt)$. [97°]. Formed by heating the di-ethyl ether of di-nitro-di-oxy-*s*-di-phenyl-hydrazine (hydrazo-nitro-phenetole) with conc. HClAq (Andreae, *J. pr.* [2] 21, 318). Yellow needles, m. sol. water. Yields *p*-nitro-phenetole on elimination of amidogen.—B'HCl.

Nitro-o-amido-phenol $C_6H_3(NO_2)(NH_2)(OH)$[5:2:1]. *Carbonyl derivative* $C_6H_3(NO_2)<{NH \atop O}>CO$. [241°]. Obtained by nitrating carbonyl-*o*-amido-phenol (Chelmicki, *J. pr.* [2] 42, 441). Long yellow needles (from water). Converted by boiling KOHAq into nitro-pyrocatechin [170°].

Nitro-o-amido-phenol. *Acetyl derivative of the methyl ether* $C_6H_3(NO_2)(NHAc)(OMe)$. [143°]. Formed by nitrating $C_6H_4(NHAc)(OMe)$[1:2] (Mühlhäuser, *A.* 207, 242). Yellow needles (from alcohol).

Nitro-amido-phenol [134°]. Formed by boiling nitrated *m*-phenylene-diamine with aqueous KOH (Barbaglia, *B.* 7, 1259). Orange plates.

Nitro-*m*-amido-phenol. *Methyl ether* $C_6H_3(NO_2)(NH_2)(OMe)$[4:3:1]. [129°]. Formed by heating (4, 3, 1)-di-nitro-anisole with alcoholic NH_3 at 190° (Bantlin, *B.* 11, 2106). Yellow leaflets (by sublimation).

Nitro-*p*-amido-phenol $C_6H_3(NO_2)(NH_2)(OH)$ [3:4:1]. [148°]. Got by saponifying its acetyl derivative (Hähle, *J. pr.* [2] 43, 63). Dark-red prisms, forming a violet solution in alkalis.— KA'. HA'HCl: plates or prisms.

Di-acetyl derivative. [147°]. Formed from di-acetyl-*p*-amido-phenol and fuming HNO_3. Pale-yellow prisms (from dilute alcohol).

Methyl ether $C_6H_3(OMe)(NO_2)(NH_2)$. [123°]. Formed in small quantity by distilling $C_6H_3(OMe)(NO_2)NMe_3OH$, a crystalline compound got by mixing nitro-*p*-amido-phenol with NMe_4OH. Crystals. Yields $C_6H_3(OMe)(NO_2)(NHAc)$ and $C_6H_3(OMe)(NO_2)(NH_3Cl)$.

Nitro-*p*-amido-phenol $C_6H_3(NO_2)(NH_2)OH$. [206°]. Formed by boiling its *m*-nitro-benzoyl derivative with alkalis (Hübner, *A.* 210, 382). Colourless needles (containing aq) melting at

183° or anhydrous golden needles, melting at 206°.—KA′ $1\frac{1}{2}$aq : red silky needles.—NaA′ 2aq. —BaA'_2 4aq.

Nitro-benzoyl derivative $C_6H_3(NO_2)(NH_2)O.CO.C_6H_4NO_2$. [225°]. Formed by nitrating benzoyl-*p*-amido-phenol [228°]. Yellow needles (from HOAc).

Nitro-di-amido-phenol $C_6H_7N_3O_3$ *i.e.* $C_6H_2(NO_2)(NH_2)_2OH$[4:6:2:1]. Formed by reducing picric acid with aqueous ammonium sulphide (Griess, *A.* 154, 202). Long dark-yellow needles (containing aq) or narrow plates, sl. sol. water and alcohol, v. sl. sol. ether.—$(HA')_2H_2SO_4$ 5aq : yellowish needles.—BaA'_2 2aq : ruby-red needles.

Nitro-di-amido-phenol. *Dibenzoyl derivative* $C_6H_2(NO_2)(NHBz)_2OH$. [167°–170°]. Formed by nitrating di-benzoyl-(α)-diamido-phenol.

Nitro-di-amido-phenol. *Dibenzoyl derivative* $C_6H_2(NO_2)(NHBz)_2OH$. [201°]. Formed by nitrating (6, 2, 1)-di-amido-phenol (Post a. Stuckenberg, *A.* 205, 79). Long brown needles, sl. sol. alcohol.

Di-nitro-o-amido-phenol $C_6H_5N_3O_5$ *i.e.* $C_6H_2(NO_2)_2(NH_2)(OH)$[6:4:2:1]. *Picramic acid.* [170°]. S. ·14 at 22° (Darney, *Am.* 5, 36).

Formation.—1. By reduction of picric acid (Wöhler, *P.* 13, 488; Girard, *A.* 88, 281; *J.* 1855, 535; Pugh, *A.* 96, 83; Lea, *J.* 1861, 637. 2. By nitration of nitro-o-amido-phenol (Stuckenberg, *A.* 205, 75), or of benzoyl-o-amido-phenol (Hübner, *A.* 210, 392).

Properties.—Red needles. Converted by the diazo- reaction into $C_6H_3Cl(NO_2)_2$ [110°]. The salts do not explode when struck. Cyanogen passed into its alcoholic solution forms 'ethoxy-carbimidamido - dinitrophenol' $C_9H_{10}N_4O_6$ (Griess, *B.* 15, 448), a crystalline body converted by boiling HClAq into uramidodinitro-phenol.

Salts.—NaA′aq. S. 2·06 at 15·5°. Dark-red crystalline crusts (Smolka, *M.* 8, 391).—NH_4A' : orange-red tables. — KA′. — BaA'_2. — CuA'_2. MgA'_2 3aq. S. 5·58 at 17°.—ZnA'_2 aq. S. ·017 at 23°.—CdA'_2 aq. S. ·08 at 23°; ·314 at 100°. — $Hg_2A'_2$: red powder. — HgA'_2 aq : yellow needles. S. ·032 at 18°; ·08 at 100°.—PbA'_2 : red needles. S. ·038 at 20°; ·067 at 100°.—MnA'_2 2aq. S. 1·026 at 19°.—CoA'_2. S. ·031 at 100°.—NiA'_2. S. ·0286 at 100°.—AgA′.—HA′HCl : reddish-brown needles (Petersen, *Z.* 1868, 378). $(HA'HCl)_2PtCl_4$.

Acetyl derivative $C_6H_2(NH_2)(NO_2)_2(OAc)$. [193°] (Schiff, *B.* 19, 849).

Methyl ether $C_6H_2(NH_2)(NO_2)_2(OMe)$. Dark-violet needles (from alcohol), insol. cold Aq.

Di-nitro-*m*-amido-phenol $C_6H_2(NO_2)_2(NH_2)(OH)$ [6:4:3:1]. [225°]. Formed by warming di-nitro-aniline with alcoholic KCy (Lippmann a. Fleissner, *M.* 7, 96). Brownish-red crystals, v. sl. sol. water. Yields di-nitro-resorcin on warming with aqueous alkalis. Its salts explode on heating. — KA′. — BaA'_2. — HgA'_2 aq.

Di-nitro-amido-phenol $C_6H_2(NO_2)_2(NH_2)(OH)$. [202°]. Formed by the action of aqueous NH_3 on (δ)-tri-nitro-phenol (Henriques, *A.* 215, 334). —KA′ aq.

Di-nitro-amido-phenol $C_6H_2(NO_2)_2(NH_2)(OH)$ [6:2:4:1]. *Isopicramic acid.* [170°]. S. ·082 at 22°; ·81 at 100°. Formed by heating its benzoyl derivative with HClAq (Dabney, *Am.* 5, 33). Yellowish-brown needles (from water).—KA′ : bluish-black crystals (from alcohol). Explodes when heated.

Benzoyl derivative $C_6H_2(NO_2)_2(NHBz)(OH)$. [250°]. Formed by heating $C_6H_3(CO_2H)(NHBz)(OH)$ [1:5:2] dissolved in HOAc with HNO_3 at 80° (D.). Yellow plates (from alcohol).—KA′ aq.—BaA'_2 3aq.—CaA'_2 $4\frac{1}{2}$aq.—PbA'_2.

Di-nitro-o-amido-phenol. *Benzoyl derivative* $C_6H_2(NO_2)_2(NHBz).OH$ [4:3?:2:1]. [220°]. Formed by nitrating benzoyl-*o*-amidophenol in HOAc at −4° (Hübner, *A.* 210, 387). Greenish-yellow needles, insol. water. On treatment with $POCl_3$ it yields $C_6H_2(NO_2)_2{<}^{O}_{N}{>}C.C_6H_5$. [219°]. —KA′ 2aq.—$NH_4A'$ aq.—BaA'_2 5aq. — ZnA'_2 3aq. —AgA′ : red needles.

Di-nitro-o-amido-phenol. *Acetyl derivative of the methyl-ether* $C_6H_2(NO_2)_2(NHAc)(OMe)$. [157°]. Formed by nitration of o-acetanisidine (Mühlhäuser, *B.* 13, 921; *A.* 207, 234). Prisms.

Tri-nitro-amido-phenol. *Ethyl ether* $C_6H(NO_2)_3(NH_2)(OEt)$. Formed by heating $C_6H(NO_2)_3(OEt).NHCO_2Et$ with dilute H_2SO_4 Köhler, *J. pr.* [2] 29, 283). Small yellow needles (from alcohol).

o-**NITRO-*p*-AMIDO-DIPHENYL** $C_{12}H_{10}N_2O_2$ *i.e.* $C_6H_4(NO_2).C_6H_4NH_2$. [98°]. Formed by reducing *op*-di-nitro-diphenyl with ammonium sulphide (Schultz, *A.* 174, 225; 207, 350). Reddish-brown monoclinic crystals; *a:b:c* = 1·52:1:2·19; β = 69° 31′.—B′HCl : needles.

***p*-Nitro-*p*-amido-diphenyl** $C_6H_4(NO_2).C_6H_4.NH_2$. [198°]. Formed by reducing *pp*-di-nitro-diphenyl with alcoholic ammonium sulphide in the cold (Fittig, *A.* 124, 278; Schultz, *A.* 174, 222). Small red needles (from alcohol). Gives *p*-nitro-benzoic acid on oxidation.—$B'_2H_2PtCl_6$.

Nitro-*p*-amido-diphenyl. *Benzoyl derivative* $C_6H_5.C_6H_3(NO_2)(NHBz)$ [1:3:4]. [143°]. Formed by nitrating benzoyl-*p*-amido-diphenyl (Hübner, *A.* 209, 339). Needles (from HOAc). Reduced by tin and HOAc to

$$C_6H_5.C_6H_3{<}^{N}_{NH}{>}C.C_6H_5.\quad [198°].$$

Di-nitro-*p*-amido-diphenyl. *Benzoyl derivative* $C_{12}H_7(NO_2)_2NHBz$. [206°]. Formed by nitrating benzoyl-*p*-amido-diphenyl (Hübner). Dark-yellow needles (from HOAc).

Nitro-di-amido-diphenyl [4:1] $C_6H_4(NH_2).C_6H_3(NO_2)(NH_2)$ [1:2:4]. [143°]. Formed by mixing benzidine sulphate (28 g.) in H_2SO_4 (300 g.) with KNO_3 (10 g.) (Täuber, *B.* 23, 796). Long red needles.—$B''H_2SO_4$ $\frac{1}{2}$aq.

Di-nitro-di-*p*-amido-diphenyl $C_{12}H_{10}N_4O_4$ *i.e.*

$C_6H_3(NO_2)NH_2$ [1:3:4]
| . *Di-nitro-benzidine.*
$C_6H_3(NO_2)NH_2$ [1:3:4]

[221°]. Formed by nitration of di-acetyl-benzidine and saponification of the product with KOH (Brunner a. Witt, *B.* 20, 1024; *cf.* Strakosch, *B.* 5, 237). Obtained also by hydrolysis of di-nitro-di-phthalyl-benzidine (Bandrowski, *M.* 8, 471). Red needles. Sol. phenol, v. sl. sol. alcohol, insol. water. Its tetrazo-compound combines with α-naphthylamine-*p*-sulphonic acid to form a dye-stuff, which dyes

unmordanted cotton the shade of alizarine-violet. By $SnCl_2$ and HCl it is reduced to tetra-amido-diphenyl.

Di-acetyl derivative [above 300°].

Di-nitro-di-*p*-amido-diphenyl [197°]. Obtained, together with the preceding, by hydrolysis of di-nitro-di-phthalyl-benzidine (Bandrowski). Yellow needles (from alcohol).

Di-nitro-di-amido-diphenyl
[4:3:1]$C_6H_3(NH_2)(NO_2).C_6H_3(NO_2)(NH_2)$[1:2or3:4] *Di-nitro-benzidine.* [214°]. Formed by stirring KNO_3 (20·2 g.) into benzidine sulphate (28·2 g.) dissolved in H_2SO_4 (300 g.) (Täuber, *B.* 23, 795). Yellow plates (from alcohol). Its azo-compounds do not dye cotton.

NITRO-AMIDO-PHENYL-ACETIC ACID
$C_8H_8N_2O_4$ *i.e.* $C_6H_3(NO_2)(NH_2).CH_2CO_2H$ [2:4:1]. [186°]. Formed by reducing (4,2,1)-di-nitro-phenyl-acetic acid with aqueous ammonium sulphide (Gabriel a. Meyer, *B.* 14, 824). Reddish-yellow needles, v. sol. hot water and alcohol, sl. sol. ether. Forms salts with acids and bases. —HA′HCl: colourless needles.

Methyl ether MeA′. [94°].

Ethyl ether EtA′. [100°]. Yellow needles.

Nitro-amido-phenyl-acetic acid
$C_6H_3(NO_2)(NH_2)CH_2.CO_2H$ [3:4:1]. [144°]. Prepared by saponification of its nitrile (nitro-amido-benzyl cyanide) by boiling with HCl (Gabriel, *B.* 15, 836). Orange-yellow plates or needles. Sol. alcohol and ether, insol. CS_2. By the action of amyl nitrite and HCl it gives (3,4,1)-nitro-diazo-ω-nitroso-toluene $C_6H_3(N_2Cl)(NO_2)(CH_2.NO)$.

Nitrile $C_6H_3(NO_2)(NH_2).CH_2CN$. [118°]. Formed by saponifying its acetyl derivative with potash. Orange plates, sol. water and alcohol.

Acetyl derivative of the nitrile $C_6H_3(NO_2)(NHAc).CH_2CN$. [113°]. Formed by nitrating $C_6H_4(NHAc).CH_2CN$ (Gabriel). Flat yellow needles or plates, sol. alcohol and hot water.

m-Nitro-α-amido-phenyl-acetic acid
$C_6H_4(NO_2).CH(NH_2).CO_2H$. [172°]. Formed by adding HNO_3 (1 mol.) to a cold solution of α-amido-phenyl-acetic acid in H_2SO_4 (Plöchl a. Loë, *B.* 18, 1179). Silky needles, v. sol. hot water, insol. alcohol.—CuA'_2: pale-blue needles.

DI-NITRO-AMIDO-DIPHENYLAMINE
$C_{12}H_{10}N_4O_4$ *i.e.*
[4:1] $C_6H_4(NH_2).NH.C_6H_3(NO_2)_2$ [1:2:4]. [177°]. Formed by the action of chloro-di-nitro-benzene on *p*-phenylene-diamine in alcoholic solution in presence of NaOAc (Nietzki, *B.* 23, 1852). Brownish-red plates, sl. sol. alcohol. — $B'C_6H_2(NO_2)_3OH$: brown needles.

Acetyl derivative $C_{12}H_9AcN_4O_4$. [238°]. Red needles.

Di-nitro-amido-diphenylamine [172°]. Formed from *m*-phenylene-diamine and $C_6H_3Cl(NO_2)_2$ (Leymann, *B.* 15, 1237).

NITRO - AMIDO - PHENYL - ISOBUTYRIC ACID $C_{10}H_{12}N_2O_4$ *i.e.*
$C_6H_3(NO_2)(NH_2).CH_2.CHMe.CO_2H$. [138°]. Formed by reducing di-nitro-isobutyric acid with ammonium sulphide (Edeleanu, *C. J.* 53, 559). Bright-red plates. Reduced by long boiling with ammonium sulphide to the compound $\left[\begin{smallmatrix}4\\1\\3\end{smallmatrix}\right] C_6H_3(NH_2){<}\begin{smallmatrix}CH_2.CHMe\\ NH.CO\end{smallmatrix}$ [216°].

***p*-NITRO-*o*-AMIDO-PHENYL-CARBAMIC ETHER** $C_6H_3(NO_2)(NH_2).NH.CO_2Et$ [4:2:1]. [162°]. Formed by reduction of di-nitro-phenyl-urethane with hot aqueous NH_4HS (Hager, *B.* 17, 2630). Orange-red needles or prisms. V. sol. alcohol, v. sl. sol. water. On heating above its melting-point it loses EtOH, and is converted into nitro-phenylene-urea with the formula $C_6H_3(NO_2){<}\begin{smallmatrix}NH\\NH\end{smallmatrix}{>}CO$.

NITRO-AMIDO-PHENYL-ETHANE *v.* NITRO-AMIDO-ETHYL-BENZENE.

NITRO-AMIDO-DI-PHENYL-ETHYLENE
$C_{14}H_{12}N_2O_2$ *i.e.* $C_6H_4(NO_2).CH:CH.C_6H_4NH_2$. [230°]. Formed by reducing di-nitro-di-phenyl-ethylene with alcoholic ammonium sulphide (Strakosch, *B.* 6, 329). Purple plates (from nitrobenzene).—B′HCl: silky needles, decomposed by water.

Nitro-amido-di-phenyl-ethylene
[2:1] $C_6H_4(NO_2).CH:CH.C_6H_4(NH_2)$ [1:2]. Formed by reducing di-o-nitro-stilbene, formed by the action of alcoholic potash on o-nitro-benzyl chloride (Bischoff, *B.* 21, 2077). Amorphous mass, sol. ether and alcohol.

Di-nitro-amido-phenyl-ethylene *v.* DI-NITRO-AMIDO-STYRENE.

***p*-NITRO-DI-*p*-AMIDO-TRI-PHENYL-METHANE** $C_6H_4(NO_2).CH(C_6H_4.NH_2)_2$. Prepared by heating aniline sulphate (28 pts.) with *p*-nitro-benzoic aldehyde (15 pts.) and $ZnCl_2$ (20 pts.) at 100° (Fischer, *B.* 15, 677). Large garnet-red crystals (containing C_7H_8). Yields paraleucaniline on reduction with zinc and HCl. —$B''H_2Cl_2$: needles.

***m*-Nitro-di-*p*-amido-tri-phenyl-methane**
[3:1] $C_6H_4(NO_2).CH(C_6H_4.NH_2$ [1:4]$)_2$. [136°]. Prepared by heating *m*-nitro-benzoic aldehyde with aniline hydrochloride and $ZnCl_2$ (Fischer a. Ziegler, *B.* 13, 671). Light-yellow crystals, sol. ether. Crystallises with C_6H_6 in yellow concentric crystals [81°].

NITRO-AMIDO-PHENYL-(α)-NAPHTHYL-AMINE $C_{16}H_{13}N_3O_2$ *i.e.*
$C_{10}H_7.NH.C_6H_3(NO_2).NH_2$ [1:4:2]. [147°]. Formed by reducing di-nitro-phenyl-(α)-naphthylamine with alcoholic ammonium sulphide (Heim, *B.* 21, 2302). Dark-yellow needles (from dilute alcohol). Gives a dark-green solution in H_2SO_4.

Nitro-amido-phenyl-(β)-naphthylamine
$C_{10}H_7.NH.C_6H_3(NO_2).NH_2$ [1:4:2]. [195°]. Formed by reducing di-nitro-phenyl-(β)-naphthylamine (Heim, *B.* 21, 590). Needles or prisms, m. sol. alcohol. Dyes silk golden-yellow. Conc. H_2SO_4 forms a yellow solution turned green by heating.

Acetyl derivative $C_{16}H_{12}AcN_3O_2$. [200°]. Orange-red needles (from alcohol).

***p*-NITRO-α-AMIDO-PHENYL-PROPIONIC ACID** $C_9H_{10}N_2O_4$ *i.e.*
$C_6H_4(NO_2)CH_2.CH(NH_2).CO_2H$. Formed from α-amido-phenyl-propionic acid, H_2SO_4, and HNO_3 (Erlenmeyer a. Lipp, *A.* 219, 213). Fluffy white mass (from alcohol), or prisms in stars (containing 1½aq) (from water). Sl. sol. alcohol, m. sol. water, insol. ether, v. sol. ammonia. Neutral to litmus. Bitter-sweet taste. Turns brown at 220°, decomposes at 240°–245°. Gives, on oxidation by chromic mixture, *p*-nitro-benzoic acid. Boiled with KOH it gives off NH_3.—HA′HCl. Needles in rosettes.—CuA'_2 2aq.

Nitro-amido-β-phenyl-propionic acid
[3:4:1] $C_6H_3(NO_2)(NH_2)C_2H_4.CO_2H$. *Nitro-amido-*

hydrocinnamic acid. [145°]. Red crystals. Sol. water, alcohol, ether, and benzene. The acetyl derivative is formed by nitration of *p*-amido-β-phenyl-propionic acid.

Acetyl derivative [174°]. Long yellow needles. Sol. alcohol and benzene, sl. sol. cold water and ether (Gabriel, *B.* 15, 844).

Nitro-amido-phenyl-propionic acid [2:4:1] $C_6H_3(NO_2)(NH_2).CH_2.CH_2.CO_2H$. [139°]. Prepared by reduction of di-nitro-phenyl propionic acid with aqueous ammonium sulphide (Gabriel a. Zimmermann, *B.* 12, 601). Plates or flat needles. Sol. alcohol, ether, and acetic acid, insol. CS_2.

Di-nitro-amido-β-phenyl-propionic acid [5:3:4:1] $C_6H_2(NO_2)_2(NH_2)CH_2.CH_2.CO_2H$. [194°]. Formed by heating $C_6H_2(NO_2)_2(OMe).C_2H_4.CO_2H$ with ammonia in sealed tubes at 100° (Stöhr, *A.* 225, 87). Yellow needles, v. sl. sol. water. Does not form salts with acids.—NH_4A'.—$BaA'_2 1\frac{1}{2}aq$.

Methyl ether MeA'. [102°].

Ethyl ether EtA'. [95°].

DI-NITRO-AMIDO-PHENYL-TOLYL-AMINE $C_7H_6(NH_2).NH.C_6H_3(NO_2)_2$. [184°]. Formed from tolylene-diamine [99°] and $C_6H_3Cl(NO_2)_2$ (Leymann, *B.* 15, 1237). Red tables.

Formyl derivative [157°].

Acetyl derivative [164°].

***p*-NITRO-DI-o-AMIDO-PHENYL-DI-TOLYL-METHANE** $C_6H_4(NO_2).CH(C_7H_6.NH_2)_2$.

(α)-Isomeride. [172°]. Formed from *p*-nitro-benzoic aldehyde, *p*-toluidine, HClAq and alcohol (Bischler, *B.* 20, 3302). Crystallises from benzene in needles (containing C_6H_6), v. sl. sol. cold alcohol.—$B''H_2PtCl_6$.

(β)-Isomeride. [127°]. Formed from *p*-nitro-benzoic aldehyde, *p*-toluidine, and conc. H_2SO_4 (Bischler, *B.* 20, 3304). Yellow plates, v. sol. benzene and warm alcohol, sl. sol. ligroïn.—$B''H_2Cl_2$.—$B''H_2PtCl_6$.

Di-acetyl derivative [136°].

Di-benzoyl derivative [152°].

***m*-Nitro-di-o-amido-phenyl-di-tolyl-methane** [3:1]$C_6H_4(NO_2).CH(C_7H_6.NH_2)_2$.

(α)-Isomeride. [128°]. Formed by the action of HCl on a mixture of *m*-nitro-benzoic aldehyde and *p*-toluidine.

(β)-Isomeride. [86°]. Formed from *m*-nitro-benzoic aldehyde, *p*-toluidine and H_2SO_4 (Bischler, *B.* 21, 3207). Yellowish needles, v. sol. hot alcohol.—$B''H_2PtCl_6$.

Di-acetyl derivative. [104°].

Di-benzoyl derivative. [148°].

***p*-Nitro-di-*m*-amido-phenyl-di-tolyl-methane** [4:1]$C_6H_4(NO_2).CH(C_7H_6.NH_2)_2$. Prepared by heating *o*-toluidine sulphate with *p*-nitro-benzoic aldehyde and $ZnCl_2$ at 100° (Fischer, *B.* 15, 679). Small yellow crystals (containing C_6H_6).

***m*-NITRO-DI-AMIDO-PHENYL-DI-XYLYL-METHANE** $C_6H_4(NO_2).CH(C_6H_2Me_2.NH_2)_2$. [92°]. Formed by condensing *m*-nitro-benzoic aldehyde with *m*-xylidine (Bischler, *B.* 21, 3216). Plates.—$B''H_2Cl_2$: yellow plates.—$B''H_2PtCl_6$.

Acetyl derivative. [132°]. Needles.

Benzoyl derivative. [186°].

***p*-Nitro-di-o-amido-phenyl-di-xylyl-methane** $C_6H_4(NO_2).CH(C_6H_2Me_2.NH_2)_2$. [90°]. Formed by condensing *p*-nitro-benzoic aldehyde with *m*-xylidine by H_2SO_4 (B.). Yellow needles.—$B''H_2Cl_2$.—$B''H_2PtCl_6$.

Di-acetyl derivative. [88°].

Di-benzoyl derivative. [192°]. Needles.

DI-NITRO-DI-AMIDO-DIPHENYL SULPHONIC ACID $C_6H_3(NO_2)(NH_2).C_6H_2(NO_2)(NH_2).SO_3H$ [1:3:4:5]. Obtained from di-acetyl-di-amido-diphenyl sulphonic acid by nitration and saponification (Zehra, *B.* 23, 3460).—KA' aq.

Di-acetyl derivative. Yellow needles.

***s*-DI-NITRO-DI-AMIDO-QUINONE** $C_6(NO_2)_2(NH_2)_2O_2$ [1:4:2:5:3:6]. Prepared by dissolving *s*-di-amido-di-imido-benzene nitrate $C_6H_2(NH_2)_2(NH)_2(HNO_3)_2$ (1 pt.) in conc. H_2SO_4 (15 to 20 pts.) at about 10°. On adding lumps of ice to the mixture, the compound crystallises out in dark-yellow needles. It is practically insoluble in all indifferent solvents. Very weak base, whose salts are readily decomposed by water. By warming with dilute KOH, ammonia is evolved, and the K salt of nitranilic acid $C_6(NO_2)_2(OK)_2O_2$ separates out. By stannous chloride it is reduced to tetra-amido-hydroquinone $C_6(NH_2)_4(OH)_2$ [1:2:4:5:3:6] (Nietzki, *B.* 20, 2115).

NITRO-AMIDO-RESORCIN $C_6H_6N_2O_4$ *i.e.* $C_6H_2(NO_2)(NH_2)(OH)_2$. [170°]. Formed by reduction of di-nitro-resorcin with ammonium sulphide (Benedikt a. Hübl, *M.* 2, 325). Dark-brown crystals, sl. sol. water, v. sol. alcohol.—$B'_2H_2SO_4$: needles.

Di-nitro-amido-resorcin $C_6H(NO_2)_2(NH_2)(OH)_2$. [190°]. Obtained by reducing tri-nitro-resorcin (styphnic acid) with alcoholic ammonium sulphide (B. a. H.). Coppery leaflets, insol. water, sl. sol. alcohol.

DI-NITRO-*p*-AMIDO-STYRENE $C_6H_3(NO_2)(NH_2).CH:CH(NO_2)$. Formed by nitrating *p*-amido-cinnamic acid, CO_2 being split off (Friedländer a. Lazarus, *A.* 229, 247). Slender reddish-brown needles (from alcohol). Conc. H_2SO_4 gives off CO_2 forming a nitro-amido-benzoic aldehyde.

Acetyl derivative. [252°].

Di-nitro-amido-styrene $C_6H_2(NO_2)_2(NH_2).C_2H_3$. *Acetyl derivative.* [212°]; needles, sol. alcohol and acetic acid, sl. sol. hot water, nearly insol. ether; formed by nitration of acetyl-*p*-amido-cinnamic acid (Gabriel a. Herzberg, *B.* 16, 2041).

NITRO-AMIDO-TOLUENE *v.* NITRO-TOLUIDINE.

NITRO-AMIDO-TOLUENE *exo*-SULPHONIC ACID $C_6H_3(NO_2)(NH_2).CH_2SO_3H$. Formed by reducing $C_6H_3(NO_2)_2.CH_2SO_3H$ by NH_3 and H_2S (Mohr, *A.* 221, 226). Needles, sol. water.—KA'.—BaA'_2 2aq.

Nitro-amido-toluene sulphonic acid $C_6H_2Me(NO_2)(NH_2).SO_3H$ [1:2:4:5]. S. ·17 at 11°. Obtained by sulphonating (2,1,4)-nitro-toluidine (Foth, *A.* 230, 300). Yellow needles (from water).—KA'aq.—BaA'_2 4aq.

Nitro-amido-toluene sulphonic acid $C_6H_2Me(NO_2)(NH_2).SO_3H$ [1:3:2:5]. Formed from acetyl-o-toluidine by successive sulphonation and nitration (Nietzki a. Pollini, *B.* 23, 138).

NITRO-AMIDO-*p*-TOLUIC ACID $C_6H_2Me(NO_2)(NH_2)CO_2H$ [1:2?:3:4]. [245°]. Formed by saponifying its acetyl derivative (Niementowski, *J. pr.* [2] 40, 27). Yellow needles, sol. hot water.—KA' 2aq: reddish-yellow needles.

Acetyl derivative [210°]. Formed from

acetyl-amido-toluic acid and HNO_3 in the cold. Yellow needles, insol. water.

Nitro-amido-toluic acid $C_6H_2Me(NO_2)(NH_2)CO_2H$ [1:2:4:5]. [236°]. Formed by heating bromo-nitro-toluic acid with alcoholic NH_3 at 180° (Fileti a. Crosa, *G.* 18, 298). Silky yellow needles (containing aq).

DI-NITRO-DI-AMIDO-DITOLYL [3:5:4:1] $C_6H_2Me(NO_2)(NH_2).C_6H_2Me(NO_2)(NH_2)$ [1:3:5:4]. [267°]. Formed by saponifying its acetyl derivative (Gerber, *B.* 21, 746). Garnet-red needles.

Di-acetyl derivative. Obtained from di-amido-ditolyl. Crystals, decomposing at 320°.

NITRO-AMIDO-XYLENE *v.* NITRO-XYLIDINE.

NITRO-AMIDO-XYLENE SULPHONIC ACID $C_8H_{10}N_2SO_5$ *i.e.* $C_6HMe_2(NO_2)(NH_2)SO_3H$ [1:3:2or5:4:6]. Formed by nitration of *m*-xylidine sulphonic acid (Sartig, *A.* 230, 338). Slender needles (from water), sl. sol. cold water, insol. alcohol.—KA′ $1\frac{1}{2}$aq.—BaA′$_2$ $1\frac{1}{2}$aq.—PbA′$_2$ aq.

NITRO-AMYLENE $C_5H_9NO_2$ *i.e.* $CH_3.CH(NO_2).C_3H_5$. Formed from allyl iodide and potassium nitro-ethane (Gal, *J.* 1873, 333). Oil. May be reduced to $C_5H_9NH_2$ (85°).

Nitro-amylene $CH_3.C(NO_2):CMe_2$. [166°–170°]. Formed from di-methyl-ethyl-carbinol and conc. HNO_3 (Haitinger, *M.* 2, 289). Oil, sol. alcohol and ether. Dissolves in alkalis and gives a blue colour with KNO_2 and H_2SO_4. On heating with HClAq it gives NH_3, hydroxylamine, and acetic acid. On heating with water it yields nitro-ethane and a ketone. NaOEt gives a yellow pp.

NITRO-ANILIC ACID *v.* DI-NITRO-DI-OXY-QUINONE.

o-**NITRO-ANILINE** $C_6H_6N_2O_2$ *i.e.* $C_6H_4(NO_2).NH_2$ [2:1]. *o-Nitraniline.* Mol. w. 138. [71·5°].

Formation.—1. By heating *o*-bromo-nitro-benzene with alcoholic NH_3 (Walker a. Zincke, *B.* 5, 114).—2. Together with *p*-nitro-aniline by nitration of acetanilide and saponification of the product (Körner).—3. By heating *o*-nitro-anisole $C_6H_4(NO_2)(OMe)$ with ammonia at 200° (Salkowski, *A.* 174, 278).—4. By reduction of *o*-di-nitro-benzene (Rinne a. Zincke, *B.* 7, 1374).—5. By nitration of benzanilide and saponification of the product (Lellmann, *A.* 221, 6).

Preparation.—1. By splitting off the HSO_3 group from *o*-nitro-aniline-*p*-sulphonic acid by heating it with HCl under pressure. The sulphonic acid can be very readily prepared by sulphonation and nitration of acetanilide (Nietzki a. Benckiser, *B.* 18, 294).—2. Twelve pts. of *o*-nitro-phenol are heated with 20 pts. of aqueous NH_3 (35 p.c.) at 160°–170° for 16 hours; the product is crystallised from water; the yield being about 60 p.c. of the *o*-nitro-phenol employed (Merz a. Riz, *B.* 19, 1749).

Properties.—Orange needles, m. sol. hot water, v. sol. alcohol, v. e. sol. ether. Volatile with steam. Does not combine with chlorinated quinones (Niemeyer, *A.* 228, 322).

Salts.—B′HCl: plates. Decomposed by water into HCl and *o*-nitro-aniline.

Formyl derivative $C_6H_4(NO_2)(NHCHO)$. [122°]. Needles (Hübner a. Herff, *A.* 209, 367).

Acetyl derivative $C_6H_4(NO_2)(NHAc)$. [93°]. Yellow plates, m. sol. cold water.

Propionyl derivative [63°] (Smith, *Am.* 6, 172).

Benzoyl derivative. [94°]. Needles.

Oxalyl derivative *v.* OXALIC ACID.

m-**Nitro-aniline** $C_6H_4(NO_2).NH_2$ [3:1]. [114°]. (285°). S. ·114 at 20°; S. (alcohol) 7·05 at 20° (Carnelley a. Thomson, *C. J.* 53, 786).

Formation.—1. By reducing *m*-di-nitro-benzene with H_2S and alcoholic ammonia (Hofmann a. Muspratt, *A.* 57, 204; Beilstein a. Kurbatoff, *A.* 176, 44).—2. Together with *p*-nitro-aniline by adding HNO_3 to a solution of aniline in H_2SO_4 (Hübner, *A.* 208, 299).

Preparation.—A solution of $SnCl_2$ (3 mols.) in alcohol saturated with HCl is slowly allowed to drop into a well-cooled alcoholic solution of *m*-di-nitro-benzene (1 mol.) with continual agitation (Anschütz a. Heusler, *B.* 19, 2161).

Properties.—Long yellow needles. Colours pine-wood yellow. Gives no colour with bleaching powder.

Reactions.—1. *Cyanogen* passed into its alcoholic solution forms a compound with formula $C_6H_4(NO_2).NH.C(NH).C(NH).C_6H_4.NO_2$ (Senf, *J. pr.* [2] 35, 530).—2. *Cyanogen iodide* forms a green pp. of $(C_6H_4(NO_2)NH)_4C$ [286°] (Hübner, *B.* 10, 1719).—3. *Silver nitrate* forms a compound $(C_6H_4(NO_2)(NH_2))_4AgNO_3$ [125°] when added to its alcoholic solution (Mixter, *Am.* 1, 239).—4. *Chlorinated quinones* dissolved in benzene form dark-green crystalline additive compounds (Niemeyer, *A.* 228, 322).

Salts.—B′HCl. Pearly crystals, v. e. sol. water.—$B'_2H_2PtCl_6$. Yellow powder, v. e. sol. water and alcohol.—B′HBr: plates (Staedel a. Bauer, *B.* 19, 1940).—$B'_2H_2C_2O_4$: crystals.

Acetyl derivative $C_6H_4(NO_2)(NHAc)$. [150°]. (Meldola a. Salmon, *C. J.* 53, 778; [143°] (Meyer a. Stüber, *A.* 165, 183). Prisms.

Benzoyl derivative. [156°]. Plates.

p-**Nitro-aniline** $C_6H_4(NO_2)(NH_2)$ [4:1]. [147°]. S. ·077 at 20°; S. (alcohol) 5·84 at 20° (Carnelley a. Thomson, *C. J.* 53, 786).

Formation.—1. By nitration of the anilides of tartaric, succinic, or acetic acid, the product being saponified (Arppe, *A.* 90, 147; 93, 157; Hofmann, *Pr.* 10, 589; 12, 639), the *o*-nitro-aniline, which is formed at the same time, may be removed by steam-distillation (Körner).—2. By heating [4:1]$C_6H_4(NO_2)(OMe)$ with ammonia at 200° (Salkowski, *A.* 174, 281).—3. By reduction of *p*-di-nitro-benzene (Zincke a. Rinne, *B.* 7, 871).—4. By heating *p*-chloro-nitro-benzene with ammonia (Engelhardt a. Latschinoff, *Z.* 1870, 232).—5. By heating *p*-nitrophenol (6 pts.) with aqueous NH_3 (20 pts.) at 190°-200° for several hours; the yield being 58 p.c. (Merz a. Riz, *B.* 19, 1753).

Preparation.—1. Equal volumes of HNO_3 (S.G. 1·42) and H_2SO_4 are mixed and cooled. Acetanilide is gradually added as long as it will dissolve. The cold solution is set aside for half an hour, then poured into water, and the nitro-compound crystallised from boiling water. The nitro-acetanilide is saponified by boiling NaOH, and the nitraniline crystallised from water (Meldola, *C. J.* 43, 427).—2. 1 kilo. of acetanilide is slowly dissolved in 4 kilos. of H_2SO_4, kept cool by standing the vessel in a stream of cold water. 590 grms. of HNO_3 of S.G. 1·478 (=85 p.c.), or the corresponding quantity of ordinary HNO_3 (1·42) diluted with 1200 grms. of H_2SO_4 is then very gradually run in, taking care that the tem-

perature does not rise above 20°. After standing, the product is poured into cold water, and the yellow pp. of nitracetanilide which separates is filtered off and saponified by boiling with strong HCl. The yield is very satisfactory (Nölting a. Collin, *B.* 17, 262; R. J. Friswell, *priv. com.*).

Properties.—Long monoclinic needles (from water). May be readily sublimed. Not volatile with steam. Weak base, its salt being decomposed by water. Does not combine with chlorinated quinones. Cyanogen iodide at 120° forms $(C_6H_4(NO_2).NH)_4C$ [above 300°] (Hübner).

Salts.—B'HCl.—$B'_2H_2PtCl_4$.

Formyl derivative $C_6H_4(NO_2)(NHCHO)$. [194°]. Formed from formanilide and fuming HNO_3 at −17° (Osborn a. Mixter, *Am.* 8, 346).

Acetyl derivative $C_6H_4(NO_2)(NHAc)$. [207°]. Formed by nitrating acetanilide. Prisms. Gives *p*-nitro-phenol when boiled with conc. KOHAq (Wagner, *B.* 7, 76).

Benzoyl derivative [199°]. Needles.

Di-nitro-aniline $C_6H_5N_3O_4$ *i.e.* $C_6H_3(NO_2)_2(NH_2)$ [6:2:1]. Mol. w. 183. [138°]. S. (95 p.c. alcohol). ·52 at 12°. Obtained by heating the methyl or ethyl ether of *c*-di-nitro-phenol with aqueous ammonia (Salkowski a. Rehs, *B.* 7, 370; *A.* 174, 273). Yellow needles. Yields *m*-di-nitro-benzene on elimination of NH_2.

Acetyl derivative $C_6H_3(NO_2)_2(NHAc)$. [197°].

Di-nitro-aniline $C_6H_3(NO_2)_2(NH_2)$ [4:2:1]. [176°] (Barr); [188°] (Hentschel, *J. pr.* [2] 34, 427). S. (95 p.c. alcohol) ·76 at 21° (S.); (88 p.c. alcohol) 5·8 (Rudneff, *Z.* 1871, 202).

Formation.—1. By the action of alkalis on di-nitro-phenyl-citraconimide (Gottlieb, *A.* 85, 17). — 2. By heating (1,2,4)-chloro-di-nitrobenzene with alcoholic ammonia (Clemm, *J. pr.* [2] 1, 145).—3. By heating [4:2:1] $C_6H_3(NO_2)_2(OMe)$ with NH_3Aq at 100° (Salkowski, *B.* 5, 872; 6, 139).—4. By heating (4,2,1)-di-nitro-phenol (3 g.) with ammonia (10 c.c. of 27 p.c.) for 16 hours at 175° (Barr, *B.* 21, 1542).

Properties.—Light-yellow prisms; v. sl. sol. boiling water. Does not form salts.

Reactions.—1. Elimination of NH_2 yields *m*-di-nitro-benzene.—2. Conc. KOHAq forms di-nitro-phenol [114°] (Willgerodt, *B.* 9, 979).—3. Alcoholic KCy added slowly forms di-nitro-amido-phenol [225°] (Lippmann a. Fleissner, *M.* 7, 95).

Acetyl derivative $C_6H_3(NO_2)_2(NHAc)$. [120°]. Formed by nitration of acetanilide (Rudneff, *Z.* 1871, 202; Ladenburg, *B.* 17, 148).

Tri-nitro-aniline $C_6H_4N_4O_6$ *i.e.* $C_6H_2(NO_2)_3(NH_2)$ [6:4:2:1]. *Picramide.* Mol. w. 228. [188°]. Formed by the action of ammonia on (1,2,4,6)-chloro-tri-nitro-benzene (Pisani, *A.* 92, 326) or on picric ethers (Liebermann a. Palm, *B.* 8, 278). Formed also by dissolving *p*-bromo-aniline in cooled HNO_3 (S.G. 1·5) (Hager, *B.* 18, 2578). Yellow plates with blue shimmer (from alcohol) or monoclinic tables (from HOAc). Tin and HCl reduce it to tri-amido-phenol (Hepp, *A.* 215, 350). Nitrous ether does not attack it. Boiling potash yields picric acid.

Combinations. — $(C_6H_4N_4O_6)C_6H_6$. Yellow prisms, which separate from its solution in benzene (Mertens, *B.* 11, 843).—$B'C_7H_8$.—$B'C_{11}H_{10}$. $B'C_6H_5NH_2$. [124°] (Hepp, *Bl.* [2] 30, 4 *A.* 215, 359).

References. — Bromo, Chloro-, and Iodo-nitro-aniline.

NITRO-ANILINE-SULPHONIC ACID *v.* Nitro-amido-benzene-sulphonic acid.

NITRO-ANISIC ACID *v. Methyl derivative* of Nitro-oxy-benzoic acid.

NITRO-ANISOLE *v. Methyl ether* of Nitro-phenol.

NITRO-ANTHRAQUINONE $C_{14}H_7NO_4$ *i.e.* $C_6H_4<^{CO}_{CO}>C_6H_3(NO_2)$ $\begin{bmatrix}1\\2 & 3\end{bmatrix}$. Mol. w. 253. [220°]. Prepared by nitrating anthraquinone dissolved in H_2SO_4 by HNO_3 in the cold (Roemer, *B.* 15, 1786; Liebermann, *B.* 16, 54). Yellow plates (by sublimation) or prismatic needles (from HOAc); sol. benzene, aniline, and chloroform, sl. sol. alcohol and ether. On reduction and treatment with nitrous acid it yields erytho-oxy-anthraquinone.

Nitro-anthraquinone $C_6H_4<^{CO}_{CO}>C_6H_3NO_2$ $\begin{bmatrix}1\\2 & 4\end{bmatrix}$. [230°]. Formed by boiling anthraquinone for half an hour with HNO_3 (S.G. 1·5) (Böttger a. Petersen, *J. pr.* [2] 6, 367; *B.* 6, 20; *A.* 166, 147). Formed also by nitration of di-bromo-anthracene (Claus a. Hertel, *B.* 14, 978). Yellow needles (by sublimation), insol. water, v. sl. sol. ether and alcohol, m. sol. benzene and HOAc. Yields alizarin on fusion with potash. Conc. H_2SO_4 (12 pts.) at 200° forms 'imido-oxy-anthraquinone' $C_{28}H_{16}N_2O_6$, which sublimes in rose-coloured needles.

Di-nitro-anthraquinone $C_{14}H_6N_2O_6$ *i.e.* $\begin{bmatrix}3 & 1\\ & 2\end{bmatrix}C_6H_3(NO_2)<^{CO}_{CO}>C_6H_3(NO_2)\begin{bmatrix}1\\2 & 6\end{bmatrix}$. Mol. w. 298. [above 300°]. Prepared by allowing anthraquinone (10 g.) dissolved in H_2SO_4 mixed with HNO_3 (10 g. of S.G. 1·48) to stand for several days. It is also formed by nitrating o-nitro-anthraquinone (Roemer, *B.* 16, 363). Yellow crystals (by sublimation), sol. nitro-benzene, sl. sol. xylene and HOAc, nearly insol. alcohol and ether. On reduction and treatment with nitrous acid it yields di-oxy-anthraquinone (anthrarufin). On heating with H_2SO_4 at 200° it yields four colouring matters, $C_{28}H_{17}N_3O_9$, $C_{28}H_{17}N_3O_{12}$, $C_{28}H_{18}N_4O_7$, and $C_{28}H_{17}N_3O_9$.

Di-nitro-anthraquinone $C_{14}H_6N_2O_6$. [256°–260°]. Formed by boiling anthraquinone with a mixture of equal volumes of H_2SO_4 and HNO_3 (S.G. 1·5), or by boiling anthracene with fuming nitric acid (Böttger a. Petersen, *A.* 160, 147; 166, 154). Minute monoclinic, almost colourless, crystals, insol. water, sl. sol. alcohol, v. sl. sol. ether. H_2SO_4 converts it at 200° into violet 'di-imido-di-oxy-anthraquinone' $C_{14}H_8N_2O_4$.

Di-nitro-anthraquinone $C_{14}H_6N_2O_6$. *Fritzsche's Reagent.* [280°]. Formed, together with anthraquinone, by heating anthracene with dilute nitric acid at 90°. On crystallisation from alcohol it separates first (Fritzsche, *N. Petersb. Acad. Bull.* 22, 43; *Z.* 1869, 114; *cf.* Anderson, *A.* 122, 302). Prepared by adding HNO_3 (30 g.) to a solution of chrysene (50 g.) containing anthracene in alcohol (5,000 c.c.), and heating on a water-bath. The crystals of the chrysene compound (*v. infra*) which then separate are oxidised by CrO_3 in HOAc, which attacks the chrysene and leaves the di-nitro-anthraquinone (Schmidt, *J. pr.* [2] 9, 263).

Properties.—Yellow needles (from boiling HOAc), v. sl. sol. alcohol and ether. Sublimes in colourless serrated plates. Forms very characteristic compounds with aromatic hydrocarbons. H_2SO_4 at 200° forms $C_{14}H_8N_2O_4$, a black powder.

Combinations. — $C_{14}H_6N_2O_6$(PhCH:CHPh): orange-red plates.—$C_{14}H_6N_2O_6(C_{14}H_{10})$: violet monoclinic laminæ, obtained by dissolving di-nitro-anthraquinone (9 pts.) and anthracene (10 pts.) in crude xylene (100 pts.).—With chrysene: $C_{14}H_6N_2O_6(C_{18}H_{12})$. Slender red needles [294°], sl. sol. boiling HOAc.

NITRO - ANTHRAQUINONE - CARBOXYLIC ACID $C_{14}H_6O_2(NO_2).CO_2H$. [above 300°]. Formed by nitration of anthraquinone-carboxylic acid (Liebermann a. Glock, *B.* 17, 891). Small needles. Dissolves in H_2SO_4 with a violet colour.

(α)-NITRO-ANTHRAQUINONE-SULPHONIC ACID $C_{14}H_7NSO_7$ *i.e.*
$C_6H_4{<}{\substack{CO\\CO}}{>}C_6H_2(NO_2)(SO_3H)\ \left[\substack{1\\6}\ 2{:}3\right]$. [255° uncor.]. Prepared by nitration of anthraquinone-sulphonic acid with a mixture of HNO_3 (1·5) and H_2SO_4, the (β)-isomeric acid which is formed simultaneously remains dissolved whilst the α acid separates out (Claus, *B.* 15, 1514; 17, 1276; Lifschütz, *B.* 17, 899; *cf.* Liebermann, *B.* 16, 55). Small white plates (from dilute HNO_3) or very fine silky needles (from hot water). Strong acid. On fusion with KOH it gives alizarin.

Salts.—A′Na aq: long needles, sol. hot water, nearly insol. cold water and alcohol.—A′K: small needles.—$A'NH_4$ ½aq: felted needles.—A'_2Ca: microscopic needles, sl. sol. water.—A'_2Ba: needles.

Chloride: [194° uncor.]. Yellow concentric needles. Nearly insol. alcohol and ether.

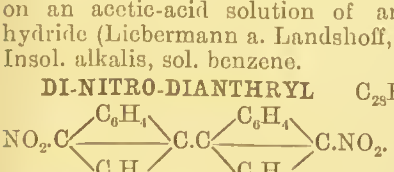
(β) - Nitro - anthraquinone - sulphonic acid $C_{14}H_6O_2(NO_2)(SO_3H)$. [250° uncor.]. Crystalline powder. V. sol. water and alcohol. Strong acid. Formed as above. Fusion with KOH gives no alizarin.

Salts.—K, Na, and NH_4 salts are extremely soluble. — $A'_2Ba\,3\frac{1}{2}aq$: needles.—$A'_2Pb\,2aq$: white needles (Claus, *B.* 15, 1516).

Nitro-anthraquinone-(α)-di-sulphonic acid [182°]. Formed by nitration of the lead salt of anthraquinone-(α)-di-sulphonic acid with HNO_3 and H_2SO_4 (Claus a. Schneider, *B.* 16, 907). Yellow prisms. Sol. water, alcohol, and acetic acid; insol. ether, chloroform, and ligroin.

DI-NITRO-ANTHRONE $C_{14}H_8N_2O_5$. [116°]. Formed as a by-product in the preparation of hydroanthracene-nitrite by the action of HNO_3 on an acetic-acid solution of anthracene-di-hydride (Liebermann a. Landshoff, *B.* 14, 472). Insol. alkalis, sol. benzene.

DI-NITRO-DIANTHRYL $C_{28}H_{16}N_2O_4$ *i.e.*



[337°].

Formed by nitration of dianthryl in acetic acid solution (Gimbel, *B.* 20, 2433). Yellow stellate needles. V. sol. benzene and chloroform, sl. sol. alcohol and acetic acid. On reduction it gives di-amido-dianthryl [309°]. By CrO_3 and acetic acid it is oxidised readily to anthraquinone. Bromine forms $C_{28}H_{16}Br_2$ [above 300°] (Sachse, *B.* 21, 2512).

NITRO-ARACHIC ACID $C_{20}H_{39}(NO_2)O_2$. [70°]. Formed by mixing arachic acid with HNO_3 and H_2SO_4 (Tassiuari, *B.* 11, 2031). Sl. sol. cold alcohol, v. sol. ether.

NITRO-ARBUTIN *v.* Arbutin.

TETRA-NITRO-AURINE $C_{19}H_{10}(NO_2)_4O_3$. [c. 140°]. Formed by nitration of aurine (Ackermann, *B.* 17, 1625). Brownish-yellow microscopic needles. V. sol. alcohol, nearly insol. water, benzene, chloroform, and ether. Dissolves in alkalis with a dark-red colour.

Salts.—$A''Ag_2$: brown pp.—A″Ba: black powder.

Ethyl ether $A''Et_2$: [c. 105°]; yellow crystals, v. sol. alcohol and benzene, insol. water and carbonated alkalis.

NITRO - AZO- compounds *v.* Azo- compounds.

Nitro-diazo- compounds *v.* Di-azo- compounds.

NITRO-AZOXY- compounds *v.* Azoxy- compounds.

NITRO-BARBITURIC ACID $C_4H_3N_3O_5$ *i.e.* $CO{<}{\substack{NH.CO\\NH.CO}}{>}CH.NO_2$. *Dilituric acid.* Formed by the action of nitric acid on hydurilic acid and on barbituric acid (Schlieper, *A.* 56, 23; Baeyer, *A.* 127, 211; 130, 140). Colourless dimetric efflorescent prisms (containing 3aq), v. sol. hot water forming an intense yellow solution, m. sol. alcohol, insol. ether. Bromine and water at 100° decompose it into di-bromo-barbituric acid and HNO_3. HIAq reduces it to amido-barbituric acid. Its solution gives a white pp. with ammonium salts.

Salts.—The salts are very stable, the acid not being separated by mineral acids.—NH_4H_2A''': crystalline pp., v. sl. sol. cold water.—$NaH_2A'''2aq$: silky needles.—KH_2A'''. Ppd. by adding HCl to a solution of the acid in potash.—K_2HA''': yellow needles, insol. alcohol and conc. KOHAq. Explodes when heated.—$BaH_2A'''Cl$ aq.—$Ca(H_2A''')_2 4aq$.—$Cu(H_2A''')_2 6aq$.—$Fe(H_2A''')_2 8aq$.—$Fe(H_2A''')_3 9aq$.—$AgH_2A'''aq$.—Ag_3A'''.

NITRO-BENZALDOXIM *v.* *Oxim* of Nitro-benzoic aldehyde.

NITRO-BENZAMIDE *v.* *Amide* of Nitro-benzoic acid.

m-**NITRO-BENZAMIDINE** $C_6H_4(NO_2).C(NH).NH_2$. Formed from nitro-benzoic imido-ethyl ether (Tafel a. Enoch, *B.* 23, 1552). Colourless mass (from ether), v. sol. water.—B′HCl. [240°]. Tables, v. sol. water.

m-**NITROBENZAMIDOXIM** $C_7H_7N_3O_3$ *i.e.* $C_6H_4(NO_2).C(NOH).NH_2$. [174°]. Formed from *m*-nitro-benzonitrile and hydroxylamine (Schöpff, *B.* 18, 1063). Orange needles, v. sol. warm water. $ClCO_2Et$ forms $C_6H_4(NO_2).C(NH_2).NO.CO_2Et$ [153°]. Acetic anhydride produces the azoxim $C_6H_4(NO_2).C{<}{\substack{N.O\\N}}{>}CMe$ [109°]. — B′HCl. — $B'_2H_2PtCl_6$.

Ethyl ether $C_7H_6EtN_3O_3$. Prisms.—B′HCl.

Benzyl ether $C_7H_6(CH_2Ph)N_3O_3$. [58°].

p-Nitro-benzamidoxim $C_6H_4(NO_2).C(NH_2).NOH$. [169°]. Formed from *p*-nitro-benzonitrile and hydroxylamine (Weise, *B.* 22, 2418). Yellow needles, sol. acids and alkalis. Reduces Fehling's solution and ammoniacal $AgNO_3$. M. sol. hot water and alco-

hol. Can be distilled. With Ac_2O it yields $C_6H_4(NO_2).C\lessgtr^{N.O}_{N}\gtrless CMe$ [144°], while aldehyde forms $C_6H_4(NO_2).C\lessgtr^{N.O}_{NH}\gtrless CH.CH_3$ [153°]. $ClCO_2Et$ produces $C_6H_4(NO_2).C(NH_2).NO.CO_2Et$ [169°], which on heating yields the compound $C_6H_4(NO_2).C\lessgtr^{N.O}_{NH}\gtrless CO$ [286°]. Sodium diazo-benzene sulphonate produces the compound $C_6H_4(NO_2).C\lessgtr^{N.O}_{NH}\gtrless C(NH_2).C_6H_4NO_2$ [151°] (Stieglitz, *B.* 22, 3157). $COCl_2$ reacts in benzene solution, forming $(C_6H_4(NO_2).C(NH_2).NO)_2CO$ [232°].—B'HCl. [185°].

Ethyl ether $C_6H_4(NO_2).C(NH_2).NOEt$, [60°]. Formed from the Na salt and EtI. With nitrous acid it yields $C_6H_4(NO_2).C(O.NO).NOEt$. [55°].—B'HCl.

NITRO-BENZENE $C_6H_5NO_2$. Mol. w. 123. [3°]. (209°) at 745 mm. (Brühl, *A.* 200, 188). S.G. $\frac{20}{4}$ 1·2039 (B.). S.V. 121·9 (Lossen, *A.* 254, 73); 121·5 (Ramsay). $\mu_\beta = 1{\cdot}5712$. $R_\infty = 52{\cdot}64$. *Dispersive power*: Barbier a. Roux, *C. R.* 108, 1249). Formed by nitration of benzene (Mitscherlich, *P.* 31, 625). The rate of nitration has been studied by Lothar Meyer (*B.* 22, 18). In small quantity by the action of ozonised air on a mixture of sulphuric acid and benzene (L. Maquenne, *Bl.* [2] 37, 298). Formed also by the action of ppd. Cu_2O (1 mol.) in the cold upon an aqueous solution of diazo-benzene nitrite (1 mol.), obtained by slowly adding a solution of 15 g. $NaNO_2$ in 50 c.c. of water to a mixture of 9 g. of aniline, 20 g. HNO_3 (1·4), and 50 c.c. of water. When the evolution of nitrogen has ceased the nitro-benzene is distilled off with steam; the yield is 42 p.c. of the theoretical (Sandmeyer, *B.* 20, 1494).

Preparation.—A mixture of nitric acid (100 pts.) and H_2SO_4 (115 pts.) is run into benzene. The product is washed with alkali and distilled.

Properties.—Oil, v. sol. alcohol and ether. Not attacked by chlorine or bromine in the cold.

Reactions.—1. For *bromination* the presence of carriers ($FeBr_3$ or $FeCl_3$) are necessary. Thus nitrobenzene (10 g.) heated with $FeBr_3$ (3 g.) and bromine (4·3 c.c.) in sealed tubes for 10 hours at 105° gives 65 p.c. of the theoretical amount of *m*-bromo-nitro-benzene. When the same mixture is heated for 30 hours at 120° the product is tetra-bromo-nitro-benzene (Scheufelen, *A.* 231, 158). Bromine at 250° forms $C_6H_2Br_4$ and a little C_6HBr_5 (Kekulé, *A.* 137, 169).—2. *Chlorine* in presence of $FeCl_3$ forms *m*-chloro-nitro-benzene and (5,2,1)-di-chloro-nitro-benzene. 3. Not attacked by boiling dilute potash or ammonia. Boiling alcoholic potash forms azoxybenzene.—4. Readily reduced to aniline.—5. *Chromic oxychloride* forms a powder $C_6H_5(NO_2)(CrO_2Cl)_2$, decomposed by water with reproduction of nitro-benzene (Henderson a. Campbell, *C. J.* 57, 253; *cf.* Étard, *A. Ch.* [5] 23, 272).—6. Exposed to *sunlight* in alcoholic solution it is reduced to aniline, aldehyde being formed (Ciamician a. Silber, *B.* 19, 2899; *G.* 16, 536).—7. Conc. HClAq at 245° forms di-chloro-aniline (Baumhauer, *A. Suppl.* 7, 204).—8. Reduced in alcoholic solution by *sodium-amalgam* to azo-benzene (Werigo, *A.* 135, 176; Alexijeff, *Bl.* [2] 1, 324).

o-**Di-nitro-benzene** $C_6H_4(NO_2)_2$ [1:2]. Mol. w. 168. [118°]. S. (alcohol) 3·8 at 24·8°; 33 at 78°. Formed in small quantity in the preparation of the *m*-isomeride, and purified by successive crystallisations from alcohol and HOAc (Rinne a. Zincke, *B.* 7, 869; Körner, *G.* 4, 354; Lobry, *R. T. C.* 2, 239). Long colourless needles (from hot water) or monoclinic tables (from alcohol) (Bodewig, *J.* 1884, 464). May be sublimed. Yields on reduction *o*-nitro-aniline [71°] and *o*-phenylene-diamine [99°].

m-**Di-nitro-benzene** $C_6H_4(NO_2)_2$ [1:3]. [90°] (Reissert, *B.* 23, 2243). (297° cor.) (Meyer a. Stadler, *B.* 17, 2649 note). S. (alcohol) 5·9 at 24·8°. The chief product of the action of boiling fuming HNO_3 on benzene or nitrobenzene (Deville, *A. Ch.* [3] 3, 187; Muspratt a. Hofmann, *A.* 57, 214). Formed also from (4,2,1)-di-nitro-aniline by elimination of NH_2 (Rudneff, *Z.* 1871, 203). Prepared by adding benzene to a mixture of equal volumes of H_2SO_4 and fuming HNO_3, and heating until a sample of the oily layer solidifies on cooling. The product is poured into water, and the solid crystallised from alcohol (Körner; Beilstein a. Kurbatoff, *A.* 176, 43).

Properties.—Colourless flexible needles, v. e. sol. boiling alcohol. Detonates when projected into a red-hot tube filled with nitrogen (Berthelot, *A. Ch.* [6] 16, 24). A mixture with $KClO_3$ is a powerful explosive (*rackarock*).

Reactions.—1. On *reduction* it yields *m*-nitro-aniline [114°] and *m*-phenylene-diamine (Hofmann, *Pr.* 11, 518).—2. Alcoholic KCy forms $C_6H_3(NO_2)(OEt).CN$ (Lobry de Bruyn, *R. T. C.* 2, 205).—3. Alkaline K_3FeCy_6 forms (4,2,1)- and (6,2,1)-di-nitro-phenols (Hepp, *B.* 13, 2347; *A.* 215, 355).

p-**Di-nitro-benzene** $C_6H_4(NO_2)_2$ [1:4]. [172°]. Deposited from the alcoholic mother-liquor from which the *m*-isomeride has crystallised (Körner). Flat monoclinic needles, sl. sol. cold alcohol. May be sublimed. Yields *p*-nitro-aniline [146°] and *p*-phenylene-diamine [140°] on reduction. Forms a sparingly soluble compound with naphthalene.

i-**Tri-nitro-benzene** $C_6H_3(NO_2)_3$ [1:2:4]. [57·5°]. S.G. $^{15\cdot5}$ 1·73. S. (alcohol) 5·4 at 15·5°; S. (benzene) 141 at 15·5°. Formed by heating *p*-di-nitro-benzene with a mixture of HNO_3 and H_2SO_4 (Hepp, *A.* 215, 362; Lobry de Bruyn, *R. T. C.* 9, 190). Yellow crystals. Forms with aniline a compound $C_6H_3(NO_2)_3C_6H_5NH_2$. [84°].

Reactions. — 1. NaOMe in HOMe forms $C_6H_3(NO_2)_2(OMe)$ [4:2:1] [88°].—2. NaOEt forms $C_6H_3(NO_2)_2(OEt)$ [4:2:1] [86°].—3. Boiling aqueous Na_2CO_3 forms (4,2,1)-di-nitro-phenol [112°]. 4. Alcoholic NH_3 forms di-nitro-aniline [175°].

s-**Tri-nitro-benzene** $C_6H_3(NO_2)_3$ [1:3:5]. [122°]. Prepared by heating *m*-di-nitro-benzene (40 g.) with HNO_3 (120 g.) and fuming H_2SO_4 (300 g.) for one day at 80° and then for two days at 120°, the yield being 50 p.c. (Hepp, *A.* 215, 347; Claus, *B.* 16, 1597). Trimetric plates; *a*:*b*:*c* = ·954:1: ·733, sl. sol. cold alcohol, v. e. sol. benzene (forming a compound with C_6H_6). Not volatile with steam. With aniline it forms $C_6H_3(NO_2)_3NH_2Ph$ crystallising from benzene in red plates [124°]. With naphthalene it forms

$C_6H_3(NO_2)_3C_{10}H_8$ [153°], and with di-methyl-aniline $C_6H_3(NO_2)_3NMe_2Ph$ [108°].

Reactions.—1. Alkaline K_3FeCy_6 oxidises it to picric acid.—2. NaOMe dissolved in HOMe forms, in the cold, $C_6H_3(NO_2)_2(OMe)$ [105°] (De Bruyn, *R. T. C.* 9, 208).—3. Reduced by tin and HClAq to tri-amido-benzene.

References.—Bromo-, Chloro-, Chloroiodo- and Iodo-nitro-benzene.

NITRO-BENZENE-AZO- compounds *v.* Azo-compounds and Disazo- compounds.

NITRO-BENZENE-AZOXY- compounds *v.* Azoxy- compounds.

DI-NITRO-BENZENE TETRA-CARBOXYLIC ACID $C_6(NO_2)_2(CO_2H)_4$ [1:4:2:3:5:6]. *Di-nitro-pyromellitic acid.* Formed by oxidising di-nitro-tri-methyl-benzoic acid with alkaline $KMnO_4$ (Nef, *A.* 237, 19). Silky needles (from ether).

Ethyl ether Et_4A^{iv}. [130°]. Needles.

NITRO-BENZENE PHOSPHONIC ACID $C_6H_4(NO_2)PO(OH)_2$. *Nitrophosphenylic acid.* [132°]. S. 98 at 22°; 92 at 98°. Obtained by nitrating benzene phosphonic acid (Michaelis a. Benziger, *B.* 8, 1310; *A.* 188, 275). Deliquescent crystals exploding above 200°.—BaA″ 2aq.—Ba(HA″)$_2$ 2aq.—CaA″ ½aq.—PbA″.—Ag$_2$A″.

***m*-NITRO-BENZENE-SULPHINIC ACID** $C_6H_4(NO_2)SO_2H$ [1:3]. [95°]. Formed, together with nitrobenzene and N_2, by boiling the compound $C_6H_4(NO_2).NH.NH.SO_2.C_6H_4(NO_2)$ with baryta-water. Long silky needles. V. e. sol. ether, sl. sol. alcohol.

Salts.—KA′: small e. sol. prisms.—AgA′: long silky needles, sl. sol. water.—BaA′$_2$ 1½aq: yellowish prisms (Limpricht, *B.* 20, 1240).

***p*-Nitro-benzene-sulphinic acid** $C_6H_4(NO_2).SO_2H$ [1:4]. [120°]. Formed in the same way as the preceding acid from the corresponding *p*- compound. Plates. Less soluble in ether than the *m*-isomeride.—BaA′$_2$aq: yellowish prisms (Limpricht, *B.* 20, 1241).

o-NITRO-BENZENE SULPHONIC ACID $C_6H_4(NO_2)SO_3H$ [1:2]. Formed in small quantity in the nitration of benzene sulphonic acid (Limpricht, *A.* 177, 60).—NH$_4$A′: long needles.—KA′: sl. sol. water.—BaA′$_2$ aq: v. e. sol. water.—PbA′$_2$ 3aq.

Chloride $C_6H_4(NO_2)SOCl$. [67°].

Amide $C_6H_4(NO_2)SO_2NH_2$. [186°]. Reduced by HI in HOAc it yields $C_6H_4\langle{}^{NH}_{SO_2}\rangle$ [193°] (Cleve, *B.* 20, 1534).

***m*-Nitro-benzene sulphonic acid** $C_6H_4(NO_2)(SO_3H)$ [1:3]. Formed by sulphonating nitro-benzene, or by nitrating benzene sulphonic acid (Schmidt, *A.* 120, 163; Meyer a. Stüber, *A.* 165, 164; Rose, *Z.* 1871, 224; Limpricht, *A.* 177, 60). Formed also by the action of $ClSO_3H$ on nitro-benzene in CS_2 (Armstrong, *Z.* 1871, 321; Limpricht, *B.* 18, 2175). Deliquescent laminæ.—NH$_4$A′. Prisms.—KA′. S. 1·7 to 1·9 at 7°.—NaA′.—BaA′$_2$ aq. S. (of BaA′$_2$) 4 at 21° (Goslich, *A.* 180, 104); 2 at 7° (L.).—CaA′$_2$ 2aq. S. (of CaA′$_2$) 6 at 6°.—MgA′$_2$ 4aq.—ZnA′$_2$ 3aq.—PbA′$_2$ 2aq. S. (of PbA′$_2$) 4 at 10°.

Chloride $C_6H_4(NO_2).SO_2Cl$. [61°].

Amide $C_6H_4(NO_2).SO_2NH_2$. [161°]. Reduced by HI and HOAc to $C_6H_4\langle{}^{NH}_{SO_2}\rangle$ [83°].

***p*-NITRO-BENZENE SULPHONIC ACID** $C_6H_4(NO_2)SO_3H$ [1:4]. Formed in small quantity in the nitration of benzoic acid (Limpricht).—NH$_4$A′. Plates. S. 8·5 at 7°.—KA′. Prisms. S. 3·7 at 7°.—BaA′$_2$ 3aq. S. (of BaA′$_2$) 4·6 at 6°.—CaA′$_2$ 2aq.—PbA′$_2$ 2aq. S. (of PbA′$_2$) 11·8 at 5·5°. [The solubilities of salts here given are the weights dissolved in 100 c.c. of the solution.]

Chloride $C_6H_4(NO_2).SO_2Cl$. Oil.

Amide $C_6H_4(NO_2).SO_2NH_2$. [131°].

(α)-Nitro-benzene *m*-disulphonic acid $C_6H_3(NO_2)(SO_3H)_2$. Formed, together with the (β)-isomeride, by nitration of benzene *m*-disulphonic acid (Heinzelmann, *A.* 188, 160; 190, 222). Slender deliquescent needles (containing *x*aq).—(NH$_4$)$_2$A″: flat prisms.—K$_2$A″.—BaA″4aq.—BaA″ 5aq.—BaA″ 6aq.—Ba$_2$A″(OH)$_2$ 15aq.—PbA″ 4aq.—Pb$_2$A″O 2½aq.—Ag$_2$A″.

Chloride $C_6H_3(NO_2)(SO_2Cl)_2$. [96°].

Amide $C_6H_3(NO_2)(SO_2NH_2)_2$. [242°].

(β)-Nitro-benzene *m*-disulphonic acid $C_6H_3(NO_2)(SO_3H)_2$ [4:1:3]. Formed as above. Very hygroscopic crystals. Its salts are more soluble than those of the (α)-isomeride.—(NH$_4$)$_2$A″.—K$_2$A″ ½aq (?).—BaA″ 5aq.—PbA″4aq.

Chloride $C_6H_3(NO_2)(SO_2Cl)_2$. Oil.

Nitro-benzene disulphonic acid $C_6H_3(NO_2)(SO_3H)_2$. Formed from nitro-amido-benzene disulphonic acid by the diazo- reaction (Limpricht, *B.* 8, 289).—PbA″ aq: needles.

Di-nitro-benzene sulphonic acid $C_6H_3(SO_3H)(NO_2)_2$[1:2:4]. [108°]. Formed from $(C_6H_3(NO_2)_2)_2S_2$, and fuming HNO_3 (Willgerodt a. P. Mohr, *J. pr.* [2] 34, 117). Very hygroscopic yellow prisms (containing 3aq), v. sol. water, sl. sol. ether, insol. benzene. Not attacked by fuming HNO_3 at 200°.

Reactions.—1. *Aniline* forms, on boiling, $C_6H_3(NO_2)_2(NPhH)$ [156°].—2. Boiling alcoholic *ammonia* forms $C_6H_3(NO_2)_2(NH_2)$ [178°].—3. KHS forms, in the cold, $C_6H_3(NO_2)_2SH$.—4. Rapidly decomposed by cold *potash*, becoming di-nitro-phenol [114°].

Salts.—KA′.—NaA′ aq.—BaA′$_2$ aq.—CaA′$_2$ 2aq.—ZnA′$_2$ 6aq.—PbA′$_2$ 3aq.

Chloride $C_6H_3(SO_2Cl)(NO_2)_2$. [102°].

Amide $C_6H_3(SO_2NH_2)(NO_2)_2$. [154°].

Di-nitro-benzene sulphonic acid $C_6H_3(NO_2)_2SO_3H$ [3:2:1]. Formed by warming nitro-benzene *m*-sulphonic acid with H_2SO_4 (1 vol.) and HNO_3 (3 vols.) (Limpricht, *B.* 9, 554; Sachse, *A.* 188, 143). Deliquescent crystals. NH$_4$A′.—KA′1½aq.—BaA′$_2$ 3aq.—PbA′$_2$3aq.

Chloride $C_6H_3(NO_2)_2SO_2Cl$. [89°].

Amide $C_6H_3(NO_2)_2SO_2NH_2$. [238°].

Di-nitro-benzene disulphonic acid $C_6H_2(NO_2)_2(SO_3H)_2$. Formed by boiling nitro-benzene *m*-sulphonic acid with H_2SO_4 (1 vol.) and fuming HNO_3 (6 vols.) (Limpricht, *B.* 8, 289). Crystalline mass. Its chloride and amide are crystalline and decompose without melting.—K$_2$A″ aq.—Na$_2$A″ 3aq.—BaA″ 2aq.—CaA″ aq.—PbA″ 3aq.—CuA″ 3aq.

Tri-nitro-benzene sulphonic acid $C_6H_2(NO_2)_3SO_3H$. [185°]. Prepared by boiling chloro-tri-nitro-phenol (picryl chloride) with alcohol and dry $NaHSO_3$ (Willgerodt, *J. pr.* [2] 32, 117). Large crystals (containing 2aq), melting at 100° when hydrated. Decomposed by alkalis in the cold into SO_2 and picric acid.—NaA′2aq.

NITRO-BENZENYL-AMIDO-OXIM *v.* Nitro-benzamidoxim.

NITRO-BENZIDINE *v.* NITRO-DI-*p*-AMIDO-DIPHENYL.

NITRO-BENZIL $C_{14}H_9(NO_2)O_2$. [142°]. Formed by nitration of benzoïn or benzil (Zinin, *A. Suppl.* 3, 153; Hausmann, *B.* 23, 531) Yellow crystals, sl. sol. alcohol.

(α)-*Dioxim* $C_{14}H_{11}N_3O_4$ [225°]. Formed by heating nitrobenzil with hydroxylamine hydrochloride at 100°. Crystalline body, v. sl. sol. alcohol.

(β)-*Dioxim.* [185°]. Formed by heating the (α)-isomeride with alcohol at 165° for several hours. White needles, v. sol. alcohol. Like the (α)-isomeride it is split up by conc. HClAq at 100° into hydroxylamine and nitro-benzil.

Di-nitro-benzil $C_{14}H_8(NO_2)_2O_2$. [131°]. S. (alcohol) ·73 in the cold; 2·4 at 78°. Formed, together with the following isomeride by boiling benzil with fuming HNO_3 (Zagumenny, *J. R.* 4, 278). Octahedra or moss-like forms.

Di-nitro-benzil [147°]. S. (alcohol) ·34 in the cold; 1·9 at 78°. Formed as above. Plates.

Iso-di-nitro-benzil $C_{14}H_8(NO_2)_2O_2$. [205°]. S. (95 p.c. alcohol) ·042 in the cold; ·9 on boiling. Formed by oxidation of (α)- or (γ)-di-nitro-deoxybenzoïn by CrO_3 in HOAc (Golubeff, *J. R.* 13, 29; *B.* 17, 581). Yellow needles.

o-NITRO-BENZOIC ACID $C_6H_4(NO_2).CO_2H$ [1:2]. Mol. w. 167. [147·7°] (Reissert, *B.* 23, 2244). S. ·61 at 16·5°. Formed in small quantity in the preparation of the *m*- isomeride by nitration of benzoic acid (Griess, *B.* 8, 526; *A.* 166, 129; L. Liebermann, *B.* 10, 862; Widnmann, *A.* 193, 204). Obtained also by saponifying its nitrile. Prepared by oxidising o-nitro-cinnamic acid with chromic acid mixture (Beilstein a. Kuhlberg, *A.* 163, 134; Widnmann, *B.* 8, 393) or, better, by oxidising o-nitro-toluene (Weith, *B.* 7, 1058; Widnmann, *A.* 193, 225; Noyes, *B.* 16, 53; Monnet, Reverdin, a. Nölting, *B.* 12, 443) or o-nitro-benzyl chloride (Nölting, *B.* 17, 385).

Properties.—Small triclinic needles (from water), v. sol. alcohol and ether, v. sl. sol. water. Has a sweet taste. Very slightly volatile with steam.

Salts.—BaA'_2 3aq. Triclinic crystals, v. sol. water.—CaA'_2 2aq: needles.—PbA'_2aq.—AgA'. Crystals, v. sol. hot water.

Ethyl ether EtA'. [30°]. Triclinic crystals.

Chloride $C_6H_4(NO_2)$.COCl. Oil.

Cyanide $C_6H_4(NO_2)$.CO.CN. [54°]. Formed from the chloride and AgCy at 100° (Claisen a. Shadwell, *B.* 12, 351). White prisms.

Anhydride $(C_6H_4(NO_2).CO)_2O$. [135°]. Needles (Bischoff a. Rach, *B.* 17, 2789).

Amide $C_6H_4(NO_2).CONH_2$. [176°] (Bischoff, *A.* 239, 109). With KOH and bromine it yields $C_6H_4(NO_2)$(CONHBr) converted by boiling potash into o-nitro-aniline (Hoogewerff a. Van Dorp, *R. T. C.* 8, 173).

Di-nitro-anilide $C_6H_4(NO_2).CO.NHC_6H_3(NO_2)_2$. [178°]. Formed by nitrating benzoyl-*m*-nitro-aniline (Schwartz, *B.* 10, 1708).

Nitrile $C_6H_4(NO_2)$.CN. *o-Nitro-benzonitrile.* Mol. w. 148. [110°]. Obtained by heating the amide with P_2O_5 at 100° (Hübner a. Bärtlein, *B.* 10, 1713). Formed also by the action of hot cuprous potassium cyanide on o-nitro-diazo-benzene chloride (Sandmeyer, *B.* 18, 1494) and by treating the oxim of o-nitro-benzoic aldehyde with Ac_2O (Gabriel a. Meyer, *B.* 14, 2338). Needles, v. sol. water and alcohol.

m-Nitro-benzoic acid $C_6H_4(NO_2).CO_2H$ [1:3]. [141°]. S. ·25 at 10°; 10 at 100° (Mulder); ·235 at 16·5° (Beilstein). Formed by nitration of benzoic acid (Mulder, *A.* 34, 297; Gerland, *A.* 91, 185; Hübner, *A.* 222, 72). Formed also by boiling nitro-hippuric acid with HClAq (Bertagnini, *A.* 78, 104; 79, 259) and by the oxidation of *m*-nitro-toluene (Beilstein, *A.* 132, 137; 155, 25; 163, 136). Obtained also by the action of hot cuprous potassium cyanide solution upon *m*-nitro-diazo-benzene chloride, and saponification of the crude nitrile; the yield being 72 p.c. (Sandmeyer, *B.* 18, 1494).

Properties.—Colourless laminæ (from water), v. e. sol. alcohol and ether. May be sublimed. Crystallises in three monoclinic modifications (Bodewig, *J.* 1879, 677). Yields amido-benzoic acid on reduction and azoxybenzoic acid on heating with alcoholic potash (Griess, *A.* 131, 92).

Salts.—$NH_4HA'_2$.— NaA' 3aq: colourless tables.—KA'aq. Needles. S. 14 in the cold; 200 at 100° (Sokoloff, *J.* 1864, 343).—MgA'_2 7aq.—CaA'_2 2aq. S. 3·3 in the cold; 5·5 at 100°.—Ca(OBz)A' 3aq (Salkowsky, *B.* 10, 1258).—SrA'_2 $2\frac{1}{2}$aq. — SrA'_2 4aq. — BaA'_2 4aq. Needles. S. ·38 in the cold, 5·3 at 100° (Sokoloff). S. (of BaA'_2) ·22 at 9° (Mills, *C. J.* 19, 363).—ZnA'_2 5aq. —ZnA'_2 4aq. S. 1·6 in the cold 7·7 at 100°.—CdA'_2 4aq (Schiff, *A.* 104, 326).—PbA'_2.—MnA'_2 4aq.—FeA'_3.—CuA'_2 aq.—AgA'.

Methyl ether MeA'. [70°]. (279°). Prisms (Chancel, *Compt. Chim.* 1849, 179; *A.* 72, 275).

Ethyl ether EtA'. [43°] (Tafel a. Enoch, *B.* 23, 1551). (296°). Monoclinic prisms. Decomposed by bromine at 170°–200° into nitro-benzoic acid and ethylene bromide (Naumann, *A.* 133, 202).

s-Tri-chloro-phenyl ether $C_6H_2Cl_3A'$. [132°]. Formed by nitrating the benzoyl derivative of (6,4,2,1)-tri-chloro-phenol (Daccomo, *B.* 18, 1165).

Di-bromo-phenyl ether $C_6H_3Br_2A'$ *v.* vol. i. p. 607.

Nitro-phenyl ethers v. Nitro-benzoyl derivatives of NITRO-PHENOLS.

Chloride $C_6H_4(NO_2)$.COCl. [34°]. (184° at 50 mm.); (275°–278°). Prisms (Cahours, *A. Ch.* [3] 23, 339; Hugh, *B.* 7, 1267; Claisen a. Thompson, *B.* 12, 1942).

Cyanide $C_6H_4(NO_2)$.CO.CN. (231° at 145 mm.). Formed from the chloride and AgCy (C. a. T.). Heavy oil.

Anhydride $(C_6H_4(NO_2).CO)_2O$. Solid (Gerhardt, *A.* 87, 158).

Acetic-m-nitro-benzoic anhydride $C_6H_4(NO_2)$.CO.OAc. [45°]. Formed from the Ag salt and AcCl (L. Liebermann, *B.* 10, 863; Beilstein, *Bn.* 2, 786; Greene, *Am.* 11, 414).

Benzoic-m-nitro-benzoic anhydride $C_6H_4(NO_2)$.CO.OBz. Crystalline (Gerhardt).

Amide $C_6H_4(NO_2).CONH_2$. [142°]. Needles (Field, *A.* 65, 45; Chancel, *Compt. Chim.* 1849, 180; Beilstein, *A.* 132, 137; Schiff, *A.* 218, 185). Its alcoholic solution mixed with $AgNO_3$ and NaOH gives a gelatinous pp. of $C_6H_4(NO_2)$.CO.NHAg (Tafel a. Enoch, *B.* 23, 1550). With bromine and potash it gives *m*-nitro-aniline (Hoogewerff a. Van Dorp, *R. T. C.*

8, 173). With *m*-nitro-benzoyl chloride it is converted into its *m*-nitro-benzoyl derivative [195°] (W. Schulze, *A.* 251, 158).

Anilide $C_6H_4(NO_2).CONHPh$. [144°]. Plates (Engler a. Volkshausen, *B.* 8, 34; Hübner, *B.* 9, 774).

m-Nitro-anilide $C_6H_4(NO_2).CO.NHC_6H_4NO_2$. [187°]. Needles (from amyl alcohol) (McHugh, *B.* 7, 1268).

Di-nitro-anilide $C_6H_4(NO_2)CO.NHC_6H_3(NO_2)_2$ [1:2:4]. [165°]. Formed by nitration of the benzoyl derivatives of o- and *p*-nitro-aniline (Schwartz, *B.* 10, 1708.

p-Toluide $C_6H_4(NO_2).CO.NHC_6H_4Me$. [162°]. Needles (from alcohol) (Hübner, *A.* 210, 335).

Nitro-p-toluide $C_6H_4(NO_2).CO.NH.C_6H_3Me.NO_2$ [1:4:2]. [188·5°]. Yellow silky needles (from alcohol). Formed by nitrating the *p*-toluide.

Mesidide $C_6H_4(NO_2).CO.NHC_6H_2Me_3$. [205°].

Nitro-mesidide $C_6H_4(NO_2).CO.NHC_6H(NO_2)Me_3$. [207°]. Formed, together with the following, by nitrating the mesidide (Schack, *B.* 10, 1711).

Di-nitro-mesidide $C_6H_4(NO_2).CO.NHC_6Me_3(NO_2)_2$. [307°]. Needles.

Nitrile $C_6H_4(NO_2).CN$. [117°]. Formed by nitrating benzonitrile, or by dehydrating *m*-nitro-benzoic amide (Beilstein a. Kuhlberg, *A.* 146, 336; Engler, *Z.* [2] 4, 613; *A.* 149, 297; Fricke, *B.* 7, 1321). Formed also by the action of hot cuprous potassium cyanide solution upon *m*-nitro-diazo-benzene chloride (Sandmeyer, *B.* 18, 1494). Prepared by adding benzonitrile (10 mols.) to KNO_3 (11 mols.) dissolved in H_2SO_4 below 25° (Schöpff, *B.* 18, 1063). Needles (from water), sl. sol. water, v. sol. alcohol and ether.

p-Nitro-benzoic acid $C_6H_4(NO_2).CO_2H$ [1:4]. [238°]. S. ·075 at 16°. Formed by the action of fuming HNO_3 on toluene (Glenard a. Boudault, *A.* 48, 344; G. Fischer, *A.* 127, 137; 130, 128; Beilstein a. Wilbrand, *A.* 126, 255; 128, 257), and by oxidising *p*-nitro-toluene with chromic acid (Beilstein a. Geitner, *A.* 139, 335; Körner, *Z.* [2] 5, 636; Rosenstiehl, *Z.* [2] 5, 701). Produced also by the oxidation of *p*-nitro-cinnamic acid, and, in small quantity, by the nitration of benzoic acid (Griess, *B.* 8, 528; Ladenburg, *B.* 8, 536). Obtained also by the action of a hot cuprous potassium cyanide solution upon *p*-nitro-diazo-benzene chloride, and saponification of the crude nitrile thus got (Sandmeyer, *B.* 18, 1492). Prepared by oxidising *p*-nitro-toluene (50 g.) with CrO_3 (250 g.) and H_2SO_4 (110 g.) diluted with water (450 g.) (Schlosser a. Skraup, *M.* 2, 519; *cf.* Michael a. Norton, *B.* 10, 580).

Properties.—Yellowish laminæ (from water) or needles (by sublimation), v. sol. alcohol and ether. Less soluble in water than the *m*- and o- isomerides. Reduced by tin and HCl to *p*-amido-benzoic acid, and by sodium-amalgam to *p*-azo-benzoic acid.

Salts.—NH_4A' 2aq: efflorescent laminæ.—NaA′ 3aq: triclinic crystals (Bilfinger, *A.* 135, 154).—KA′ 2aq. S. 33 in the cold; 200 at 100° (Sokoloff, *J.* 1864, 343).—BaA'_2 5aq: monoclinic crystals (Bücking a. Haushofer, *A.* 193, 212). S. ·4 in the cold; 12·5 at 100°.—BaA′(OBz) (Salkowsky, *B.* 9, 24).—CaA'_2 8aq: efflorescent tables. S. 3 in the cold; 8·3 at 100°.—CaA'_2 9aq. —CaA′(OBz) 3aq (Salkowski, *B.* 10, 1258).—SrA′(OBz) aq.—ZnA'_2 2aq. S. (of ZnA'_2) ·7 at 17° (Mills, *C. J.* 19, 363); 1·25 at 100°.—PbA'_2.

Methyl ether MeA′. [96°].

Ethyl ether EtA′. [57°].

Chloride $C_6H_4(NO_2).COCl$. [75°]. (c. 204° at 105 mm.). Slender needles (from ligroïn) (Gevekoht, *A.* 221, 335).

Amide $C_6H_4(NO_2).CONH_2$. [198°]. Needles. (Beilstein a. Reichenbach, *A.* 132, 143). Treatment with bromine and KOHAq converts it into *p*-nitro-aniline.

Anilide $C_6H_4(NO_2).CONHPh$. [204°] (Leo, *K.* 3, 552).

Nitrile $C_6H_4(NO_2).CN$. [147°]. Formed from the amide and P_2O_5 (Engler, *A.* 149, 298; Fricke, *B.* 7, 1321), or by the action of hot cuprous potassium cyanide solution on *p*-nitro-diazo-benzene chloride (Sandmeyer, *B.* 18, 1492). Laminæ (from alcohol), v. sol. hot alcohol.

Fourth and fifth nitro-benzoic acids have been described by Fittica (*B.* 8, 252, 710, 741; 9, 788; 10, 481; *J. pr.* [2] 17, 188), but their existence has been contested by other chemists (Leo Liebermann, *B.* 10, 1038; Widmann, *B.* 10, 1159; Claus, *B.* 13, 891).

(4,3,1)-Di-nitro-benzoic acid $C_7H_4N_2O_6$ *i.e.* $C_6H_3(NO_2)_2CO_2H$ [4:3:1]. [161°]. S. ·673 at 25°. Prepared by heating *p*-nitro-benzoic acid with nitric and sulphuric acids in sealed tubes, and separated from the (4,2,1) isomeride, simultaneously formed, by the greater solubility of the latter in water (Claus a. Halberstadt, *B.* 13, 815). Colourless crystals. Sol. alcohol, ether, and hot water, sl. sol. cold water. Very bitter taste. Sublimes undecomposed.

Salts. — A'_2Ba 4aq: white crystals. — A'_2Ca 3aq: plates. The potassium, sodium, and ammonium salts are easily soluble.

Di-nitro-benzoic acid $C_6H_3(NO_2)_2(CO_2H)$ [5:2:1]. [177°]. Formed, together with the (4,2,1)- and (6,2,1)-isomerides by boiling o-nitro-benzoic acid with a mixture of fuming HNO_3 (1 pt.) and H_2SO_4 (1 pt.) for 15 minutes (Griess, *B.* 7, 1223). Needles or prisms, sl. sol. cold water, m. sol. hot water. The di-amido-benzoic acid, obtained by reduction, yields *p*-phenylene-diamine on distillation.—BaA'_2 4aq: six-sided plates, sl. sol. hot water.

Di-nitro-benzoic acid $C_6H_3(NO_2)_2CO_2H$ [4:2:1]. [179°]. S. 1·849 at 25°. Formed in the prepation of each of the two preceding acids (Griess, *B.* 7, 1225; Claus a. Halberstadt, *B.* 13, 816; Hübner a. Stromeyer, *B.* 13, 461; *A.* 222, 79). Obtained also by heating di-nitro-toluene with fuming HNO_3 at 100° for a fortnight (Tiemann a. Judson, *B.* 3, 223). White needles or tables. May be sublimed. Tastes bitter. On reduction with tin and HClAq it at once yields *m*-phenylene-diamine.—BaA'_2 3aq: m. sol. cold water.—CaA'_2 2aq.—MgA'_2 9aq.

Di-nitro-benzoic acid $C_6H_3(NO_2)_2CO_2H$ [6:2:1]. [202°]. Formed, together with styphnic acid $C_6H(NO_2)_3(OH)_2$ and the (4,2,1)- and (5,2,1)-di-nitro-benzoic acids, by heating *o*-nitro-benzoic acid with HNO_3 and H_2SO_4 (Griess). Felted needles (from boiling water), v. sol. boiling water. Tastes intensely bitter. Split up on distillation into CO_2 and *m*-di-nitro-benzene. On treatment with tin and HClAq it yields *m*-phenylene-diamine. BaA'_2 2aq: v. e. sol. cold water.

Di-nitro-benzoic acid $C_6H_3(NO_2)_2CO_2H$ [5:3:1]. [204°]. S. 1·9 at 100°. Formed by nitration of benzoic acid or of *m*-nitro-benzoic acid with a mixture of HNO_3 and H_2SO_4 (Cahours, *A. Ch.* [3] 25, 30; Voit, *A.* 99, 100; Tiemann a. Judson, *B.* 3, 223; Muretoff, *Z.* [2] 6, 641; Michler, *A.* 175, 152). Obtained also by heating di-nitro-toluene [93°] with fuming HNO_3 at 150°, or by oxidising it with chromic acid mixture (Staedel, *B.* 14, 902; *A.* 217, 194; Hubner, *A.* 222, 73), and in small quantity by the oxidation of 'β'-di-nitro-naphthalene with dilute HNO_3 (S.G. 1·15) at 150° (Beilstein a. Kurbatow, *B.* 13, 355).

Preparation.—1. By heating benzoic acid (20 g.) with H_2SO_4 (180 g.) and fuming HNO_3 (50 g.) for 4 hours nearly to boiling (Hübner).—2. By heating *m*-nitro-benzoic acid (100 g.) with fuming nitric acid (500 g.) and H_2SO_4 (600 g.) for 12 hours (H.).

Properties.—Thin tables (from dilute HNO_3) or monoclinic crystals (Henniges, *J.* 1882, 902), v. sl. sol. cold water, sl. sol. dilute HNO_3, v. sol. alcohol and HOAc. Reduced by tin and HCl to di-amido-benzoic acid, which yields *m*-phenylene-diamine on distillation with baryta.

Salts.—NaA′.—KA′.—BaA'_2aq (Hübner): m. sol. hot water.—$BaA'_2$5aq (Muretoff).—CaA'_2aq.—$MgA'_2$8aq.—MnA'_2 2aq.—PbA'_2aq.—AgA′: needles (from hot water).

Ethyl ether EtA′. [94°] (H.); [91°] (B. a. K.). S. (90 p.c. alcohol) ·562 at 13°.

Amide $C_6H_3(NO_2)_2CONH_2$. [183°] (Voit, *A.* 99, 105); [177°] (M.). Plates (from water).

Tri-nitro-benzoic acid $C_6H_2(NO_2)_3CO_2H$. [190°]. Obtained by heating tri-nitro-toluene with fuming HNO_3 for a fortnight at 100° (T. a. J.). Trimetric crystals; $a:b:c$ = ·887:1: ·572 (Friedländer, *Z. K.* 1, 623). May be sublimed.—AgA′: plates, sl. sol. water.

References.—Bromo-, Chloro-, and Iodo-, Nitrobenzoic acids.

o-NITRO-BENZOIC ALDEHYDE

$C_6H_4(NO_2)$.CHO. Mol. w. 151. [44°] (G. a. M.); [46°] (F. a. H.).

Formation.—1. In small quantity, together with the *m*-isomeride, by adding benzoic aldehyde to a mixture of HNO_3 and H_2SO_4 (Rudolph, *B.* 13, 310; *cf.* Fittica, *B.* 10, 1630).—2. By treatment of its oxim with chromic acid mixture (Gabriel a. Meyer, *B.* 14, 829).—3. By oxidising o-nitro-cinnamic acid with dilute $KMnO_4$ (Friedländer a. Henriques, *B.* 14, 2801).—4. By adding $NaNO_2$ to a cold solution of o-nitro-cinnamic ether in fuming nitric acid (F. a. H.).—5. In small quantity by the action of water on the compound of o-nitro-toluene with CrO_2Cl_2 (Richter, *B.* 19, 1062).

Preparation.—50 grms. of crude *o*-nitro-cinnamic acid are suspended in $2\frac{1}{2}$ litres of water, neutralised with Na_2CO_3 and filtered. The clear solution is put into a large stoppered bottle, 1 litre of benzene added, and kept cold during the reaction by the addition of ice. 1225 c.c. of a 6 p.c. solution of $KMnO_4$ is added by degrees, shaking continuously, in order that the nitro-benzaldehyde, as it is formed, may be removed by the benzene from the action of the oxidising agent. The emulsion which is produced is now treated with a warm solution of 150 grms. of sodium sulphite and HCl added, which dissolves the MnO_2. The benzene layer, which contains the whole of the nitrobenzaldehyde is removed, and the latter obtained by distilling off the benzene. The yield is 50 p.c. to 60 p.c. of the theoretical (Einhorn, *B.* 17, 119).

Properties.—Long yellow needles (from water), sl. sol. water, v. sol. alcohol and ether. May be distilled. Volatile with steam. With $NaHSO_3$ it forms a compound crystallising in plates.

Reactions.—1. On *reduction* with tin and HOAc it yields anthranil $C_6H_4<\begin{smallmatrix}CO\\NH\end{smallmatrix}>$, the lactam of o-amido-benzoic acid (Friedländer a. Henriques, *B.* 15, 2105; *cf.* Rudolph, *B.* 13, 310). Reduced by $FeSO_4$ and NH_3 to amido-benzoic aldehyde (Friedländer, *B.* 15, 2572; 17, 456).—2. Yields *o*-nitro-benzoic acid on *oxidation* with dilute aqueous $KMnO_4$. It also undergoes this oxidation when administered to dogs (Sieber a. Smirnoff, *M.* 8, 88).—3. Conc. NaOHAq converts it into o-nitro-benzoic acid and *o*-nitro-benzyl alcohol.—4. NaOAc and Ac_2O yield *o*-nitro-cinnamic acid by Perkin's reaction.—5. On warming with a dilute alcoholic solution of *urea* a compound $C_6H_4(NO_2)$.CH(NH.CO.$NH_2)_2$ [200°] is formed (Lüdy, *M.* 10, 295). When a few drops of H_2SO_4 are added to an alcoholic solution of o-nitro-benzoic aldehyde and urea there is formed a different compound $C_{19}N_4H_{22}O_7$ [170°].—6. With *di-methyl-aniline* it forms nitro-tetra-methyl-di-amido-tri-phenyl-methane $C_6H_4(NO_2)$.CH($C_6H_4NMe_2)_2$.—7. *Aceto-acetic ether* (2 mols.) and NH_3 form *o*-nitro-phenyl-di-methyl-pyridine dihydride dicarboxylic ether [120°] and a compound $C_{19}H_{20}N_4O_5$ [189°], forming a salt B′HCl, converted by nitrous acid into an indifferent isomeride [192°] (Lepetit, *B.* 20, 1338).—8. Boiling conc. aqueous KCy forms o-azoxy-benzoic acid.—9. *Aldehyde* and a little baryta-water forms $C_9H_9NO_4$ [120°], converted by further treatment with baryta-water into $C_6H_4(NO_2)$.CH(OH).CH_2.CH_2OH [109°], and by NaOHAq into indigo (Baeyer a. Drewson, *B.* 15, 2861).—10. *Acetone* and NaOH forms o-nitro-styryl methyl ketone, which on warming with more alkali yields indigo.

Oxim $C_6H_4(NO_2)$.CH:NOH. *o-Nitro-ω-nitroso-toluene.* [96°]. Formed by the action of hydroxylamine on the aldehyde in alcoholic solution, or by treating (2,4,1)-nitro-amido-phenyl-acetic acid with nitrous acid (Gabriel a. Meyer, *B.* 14, 826; 15, 3057; 16, 520). Slender needles (from hot water), v. sol. alcohol and ether. Tastes sweet. Dissolves in alkalis. Conc. HClAq at 160° decomposes it into o-nitro-benzoic acid and NH_3. Boiling with Ac_2O and NaOAc forms the nitrile of o-nitro-benzoic acid.

Methyl derivative of the oxim $C_6H_4(NO_2)$.CH:NOMe. [58°].

Phenyl hydrazide $C_6H_4(NO_2)$CH:N_2HPh. [153°] (P.); [148°] (L.). Formed by adding phenyl-hydrazine to an alcoholic solution of the base (Pickel, *A.* 232, 232; Lüdy, *M.* 10, 314). Scarlet needles, sl. sol. hot water, forming a dark-blue solution in conc. H_2SO_4.

***m*-Nitro-benzoic aldehyde** $C_6H_4(NO_2)$.CHO. [3:1]. [58°]. Obtained by dissolving benzoic aldehyde (1 vol.) in a mixture of fuming HNO_3 (1 vol.) and H_2SO_4 (10 vols.) in the cold (Bertagnini, *A.* 79, 259; 86, 190; Lippmann a. Hawliczek, *B.* 9, 146; Friedländer a. Henriques,

B. 14, 2802; Ehrlich, *B.* 15, 2010). Needles (from water), m. sol. hot water, v. sol. alcohol.

Reactions.—1. *Chromic acid* oxidises it to *m*-nitro-benzoic acid.—2. *Tin* and HOAc reduce it to *m*-amido-benzoic aldehyde.—3. *Ammonia* forms $(C_6H_4(NO_2)CH)_3N_2$, which on heating with aqueous KOH forms tri-nitro-amarin $C_{21}H_{15}N_5O_6$. 4. *Ammonia* and *acetoacetic ether* form $C_6H_4(NO_2).C_5NH_2Me_2(CO_2Et)_2$ [65°] (Lepetit, *B.* 20, 1338, 2397).—5. *Sodium succinate* and acetic anhydride form nitro-phenyl-paraconic acid $C_6H_4(NO_2).CH.CH(CO_2H).CH_2.CO.O$ (Salomonson, *R. T. C.* 6, 1).—6. When its benzene solution is shaken with H_2SO_4 there is formed $C_6H_4(NO_2).CHPh_2$ [90°]; while toluene, by similar condensation, yields $C_6H_4(NO_2).CH(C_7H_7)_2$ [85°] (Tschacher, *B.* 21, 188).—7. *Phenyl-acetonitrile* and alcoholic NaOEt yields the nitrile of nitro-α-phenyl-cinnamic acid (Frost, *A.* 250, 156).—8. After administration to a dog it is excreted as *m*-nitro-hippuric acid (Sieber, *M.* 8, 88).

Combinations. — $(C_7H_5NO_3)NH_4SO_3H$ $\frac{1}{2}$aq: colourless prisms. — $(C_7H_5NO_3)NaSO_3H$ 5aq: yellowish crystalline scales (from hot water).—$(C_7H_5NO_3)NPhH_2SO_3H_2$: needles (Schiff, *A.* 195, 301).—$(C_7H_5NO_3)_4PH_3$: powder, insol. alcohol. Formed from the aldehyde, PH_3, and HCl (Messinger a. Engels, *B.* 21, 333).

Oxim $C_6H_4(NO_2).CH:NOH$. [119°]. Needles (from water) (Gabriel, *B.* 15, 3060). PCl_5 yields *m*-nitro-benzonitrile (Gabriel, *B.* 16, 520).

Iso-oxim. [118°]. Formed by passing HCl into an ethereal solution of the oxim, and decomposing the hydrochloride by Na_2CO_3. Needles (from ether). Combines with phenyl cyanate in ethereal solution with formation of $C_6H_4(NO_2).CH.NO.CONPhH$ [75°], which readily changes into an isomeride [105°]. By treatment with NaOMe and MeI it is converted into a mixture of two isomeric methyl derivatives $C_6H_4(NO_2).CH:NOMe$, melting at 69° and at 117° (Goldschmidt a. Ernst, *B.* 23, 2170). MeI acting on its silver salt gives the methyl ether, melting at 69°. NaOEt and benzyl chloride yield a benzyl ether [148°]. Phenyl cyanate in ethereal solution yields $C_6H_4(NO_2).CH:NO.CO.NHPh$ [105°], crystallising in yellow needles.

Phenyl-hydrazide $C_6H_4(NO_2).CH:N_2HPh$. [121°] (Pickel, *A.* 232, 232; Lüdy, *M.* 10, 315). Orange tables. Yields an acetyl derivative $C_{13}H_{10}(NO_2)N_2Ac$ [170°] (Schroeder, *B.* 17, 2097). Nitrous acid converts it into $(C_6H_4(NO_2).CH:N.NPh)_2NOH$, which crystallises in needles, forming a deep-blue pp. in H_2SO_4.

p-Nitro-benzoic aldehyde $C_6H_4(NO_2).CHO$ [4:1]. [106°].

Formation.—1. By boiling *p*-nitro-benzyl chloride (10 pts.) with $Pb(NO_3)_2$ (14 pts.), water (60 pts.), and HNO_3 (S.G. 1·3) (Fischer a. Greiff, *B.* 13, 670).—2. By oxidising *p*-nitro-cinnamic ether (Friedländer a. Henriques, *B.* 14, 2803) or *op*-di-nitro-cinnamic ether (Friedländer a. Maly, *A.* 229, 212; *cf.* Baeyer, *B.* 14, 2317).

Preparation.—1. By adding KNO_3 to a cooled solution of *p*-nitro-cinnamic acid, or its methyl or ethyl ether, in strong H_2SO_4; the yield is 60 p.c. to 95 p.c. (Basler, *B.* 16, 2714).—2. 45 pts. of chromyl chloride (CrO_2Cl_2) are slowly added to 20 pts. *p*-nitro-toluene, dissolved in 80 to 100 pts. of CS_2. After standing for two days, the pp. $(C_6H_4(NO_2)CH_3,Cr_2O_4Cl_4)$ is separated, washed with CS_2, and treated with water. The CS_2 is driven off with steam, and the product recrystallised from water; yield, 60 p.c. to 70 p.c. of the nitro-toluene (Richter, *B.* 19, 1060).

Properties.—Long colourless prisms (from hot water), sl. sol. water and ether, m. sol. alcohol. May be sublimed. Volatile with steam. Forms with $NaHSO_3$ a compound crystallising in plates.

Reactions.—1. *Chromic acid mixture* oxidises it to *p*-nitro-benzoic acid.—2. *Aniline* forms $C_6H_4(NO_2).CH:NPh$ [93°].—3. *Dimethylaniline* condenses with it to *p*-nitro-tetra-methyl-di-*p*-amido-tri-phenyl-methane. — 4. When administered to dogs it is excreted as *p*-nitro-hippuric acid.—5. With *p-toluidine* and conc. HClAq it forms $C_6H_4(NO_2).CH(C_6H_3Me.NH_2)_2$ [172°] (Bischler, *B.* 20, 3302).—6. *Ammonia* and *acetoacetic ether* form the compound $C_6H_4(NO_2).C_5NH_2Me_2(CO_2Et)_2$ [118°–122°]. — 7. *Indoxyl* with HClAq and HOAc forms the indogenide $C_6H_4<^{CO}_{NH}>C:CH.C_6H_4NO_2$, crystallising in red needles [273°].

Oxim $C_6H_4(NO_2)CH:NOH$. [129°]. Reddish-yellow scales (Gabriel a. Herzberg, *B.* 16, 2000).

Iso-oxim [175°] (Behrend, *A.* 263, 349).

Benzyl ether of the iso-oxim $C_6H_4(NO_2).CH<^{N(C_7H_7)}_{O}$. [118°]. Formed by oxidising (β)-benzyl-*p*-nitro-benzyl-hydroxylamine with K_3FeCy_6 (Behrend a. König, *B.* 23, 2750). Needles (from alcohol), split up by hot HClAq into *p*-nitro-benzoic aldehyde and (β)-benzyl-hydroxylamine.

Phenyl-hydrazide $C_6H_4(NO_2)CH:N_2HPh$. [125°]. Red needles (Pickel, *A.* 232, 232). Forms a red solution in conc. H_2SO_4 (Lüdy, *M.* 10, 315).

NITROBENZOIC ANHYDRIDE *v. Anhydride* of NITROBENZOIC ACID.

m-**NITRO-BENZOIC IMIDO-ETHYL ETHER** $C_9H_{10}N_2O_3$ *i.e.* $C_6H_4(NO_2).C(NH).OEt$. Formed by treatment of $C_6H_4(NO_2).CONHAg$ with EtI, followed by ethereal HCl (Tafel a. Enoch, *B.* 23, 1550). Yellow oil.—B'HCl. White mass, v. sol. water and alcohol; converted by hot water into *m*-nitro-benzoic ether.—$B'H_2C_2O_4$. [132°].

NITRO-BENZONITRILE *v. Nitrile* of NITROBENZOIC ACID.

o-**NITRO-BENZOPHENONE** $C_{13}H_9NO_3$ *i.e.* $C_6H_5.CO.C_6H_4(NO_2)$. *o-Nitro-di-phenyl-ketone* [105°]. Formed by oxidation of *o*-nitro-di-phenyl-methane with CrO_3 in acetic acid (Geigy a. Koenigs, *B.* 18, 2403). Colourless crystals.

m-Nitro-benzophenone $C_6H_5.CO.C_6H_4.NO_2$ [95°]. Formed by the action of *m*-nitro-benzoyl chloride upon benzene in presence of Al_2Cl_6 (Geigy a. Koenigs, *B.* 18, 2401; *cf.* Becker, *B.* 15, 2090). Yellowish needles.

p-Nitro-benzophenone $C_6H_4(NO_2).CO.C_6H_5$ [138°]. Formed by oxidation of *p*-nitro-di-phenyl-methane with CrO_3 in acetic acid (Basler, *B.* 16, 2717). Small white plates or needles. Sol. benzene, hot alcohol, and hot water, sl. sol. cold water, cold alcohol, ligroïn, and CS_2.

(α)-Di-nitro-benzophenone $(C_6H_4(NO_2))_2CO$. [190°]. Formed, together with a larger quantity of the (β)-isomeride, by heating benzophenone with fuming HNO_3 at 60° (Prätorius, *B.* 10,

1855; 11, 744; Staedel, *A.* 194, 349; 218, 344). Formed also by oxidation of the corresponding di-nitro-di-phenyl-methane [183°] by CrO_3 in HOAc (Staedel a. Sauer, *B.* 11, 1747). Long needles (from HOAc). Yields on reduction di-amido-benzophenone [172°].

(β)-**Di-nitro-benzophenone** $C_{13}H_8N_2O_5$. [149°]. Formed as above. Laminæ (from benzene or HOAc). Yields on reduction di-amido-benzophenone [165°].

Oxim $(C_6H_4.NO_2)_2C:NOH$: [207°]; small yellow needles (from hot alcohol).

Phenyl hydrazide $(C_6H_4.NO_2)_2C:N_2HC_6H_5$; [220°]; red powder; sol. acetic acid, sl. sol. alcohol, insol. water (Münchmeyer, *B.* 20, 510).

(γ)-**Di-nitro-benzophenone** $C_{13}H_8N_2O_5$. [190°]. Formed by oxidation of the di-nitro-di-phenyl-methane [118°]. Crystals. Yields on reduction di-amido-benzophenone [131°].

Tetra-nitro-benzophenone $C_{13}H_6(NO_2)_4O$. [225°]. Formed by oxidising tetra-nitro-di-phenyl-methane (Staedel, *A.* 218, 341). Needles (from HOAc).

p-**NITRO-BENZOYL-ACETIC ACID** $C_9H_7NO_5$ *i.e.* $C_6H_4(NO_2).CO.CH_2.CO_2H$. *Nitro-phenyl methyl ketone carboxylic acid.* [135°]. Formed by digesting *p*-nitro-phenyl-propiolic ether with H_2SO_4 (85 p.c.) at 35° till it is completely soluble in aqueous NaOH (Perkin a. Bellenot, *B.* 17, 326; 18, 952; *C. J.* 49, 444). Needles, v. sol. alcohol and ether, sol. water. $FeCl_3$ colours its alcoholic or hot aqueous solution reddish-brown. On heating by itself or with dilute acids or alkalis it splits up into CO_2 and *p*-nitro-acetophenone.

Methyl ether MeA′. [107°]. Monoclinic crystals; v. sol. hot alcohol. NaOMe forms yellow crystals of $C_6H_4(NO_2).CO.CHNa.CO_2Me$, a body from which benzyl chloride produces $C_6H_4(NO_2).CO.CH(C_7H_7).CO_2Me$ [57°].

Ethyl ether EtA′. [76°]. Monoclinic crystals; $a:b:c = \cdot358:1:1\cdot238$; $\beta = 72° \ 22'$. Its alcoholic solution is coloured brownish-violet by $FeCl_3$. Nitrous acid acting on its ethereal solution forms $C_6H_4(NO_2).CO.C(NOH).CO_2Et$ [220°]. Yields $C_6H_4(NO_2).CO.CHNa.CO_2Et$, crystallising in orange needles, whence aqueous $AgNO_3$ forms an explosive amorphous Ag salt. The sodium salt is converted by ethyl iodide into the ether $C_6H_4(NO_2).CO.CHEt.CO_2Et$ [40°].

NITRO-BENZOYL-ACETOACETIC ETHER *v.* ACETOACETIC ETHER.

o-**NITRO-BENZOYL-ACETONE** $C_{10}H_9NO_4$ *i.e.* $NO_2.C_6H_4.CO.CH_2.CO.CH_3$ [55°]. Got by boiling *o*-nitro-benzoyl-aceto-acetic ether with H_2SO_4 (1 pt.) and water (2 pts.) for 4 hours (Gevekoht, *A.* 221, 332). Crystallised from benzoline. Insol. water, v. sol. alcohol and ether. Gives with phenyl-hydrazine a compound melting at 120°, crystallising from alcohol in slender needles, possibly nitro-di-phenyl-methyl-pyrazole (Fischer a. Bülow, *B.* 18, 2136).

p-**NITRO-BENZOYL-ANGELIC ETHER** $C_6H_4(NO_2).CO.CH(C_3H_5).CO_2Et$. [46°]. Formed by the action of allyl iodide upon the sodio-derivative of *p*-nitro-benzoyl-acetic ether (Perkin a. Bellinot, *B.* 18, 957). Colourless plates.

(α)-**DI-NITRO-BENZOYL-BENZOIC ACID** $C_{14}H_8(NO_2)_2O_3$. [240°]. Formed from benzoyl-benzoic acid, HNO_3, and H_2SO_4 (Plaskuda, *B.* 7, 988). Plates.—BaA'_2 aq.—CaA'_2 2aq.

(β)-**Di-nitro-benzoyl-benzoic acid** $C_6H_4(NO_2).CO.C_6H_3(NO_2).CO_2H$. [212°]. Formed by boiling di-nitro-phenyl-*p*-tolyl ketone with CrO_3 and HOAc (Plaskuda a. Zincke, *B.* 7, 984). Plates (from hot water).

o-**NITRO-BENZOYL-BENZYL-MALONIC ETHER** $C_6H_4(NO_2).O.C(CH_2Ph)(CO_2Et)_2$. [94°]. Formed from sodium benzyl-malonic ether and o-nitro-benzoyl chloride, or from benzyl chloride and sodium o-nitro-benzoyl-malonic ether (Bischoff a. Siebert, *A.* 239, 103). Prisms (from dilute alcohol). V. sol. ether and hot alcohol, sl. sol. ligroïn. Gives no colour with $FeCl_3$. Alcoholic KOH produces benzyl-malonic acid and o-nitro-benzoic acid. Ammonia forms o-nitro-benzamide and benzyl-malonic ether.

NITRO-BENZOYL CHLORIDE *v. Chloride* of NITRO-BENZOIC ACID.

NITRO-BENZOYL CYANIDE *v. Cyanide* of NITRO-BENZOIC ACID.

NITRO-BENZOYL-FORMIC ACID *v.* NITRO-PHENYL-GLYOXYLIC ACID.

o-**NITRO-BENZOYL-MALONIC ETHER** $C_6H_4(NO_2).CO.CH(CO_2Et)_2$. [54°]. The sodium-derivative $C_6H_4(NO_2).CO.CNa(CO_2Et)_2$ is formed by the action of NaOEt on di-nitro-di-benzoyl-malonic ether, or of o-nitro-benzoyl chloride (1 mol.) on di-sodio-malonic ether (1 mol.) (Bischoff, *B.* 16, 1044; 17, 2791; 22, 387). Needles or prisms (from alcohol). $FeCl_3$ colours its alcoholic solution dark-red. Bromine acting on its sodium derivative forms the bromo-derivative $C_6H_4(NO_2).CO.CBr(CO_2Et)_2$ [72°]. On reduction by zinc-dust and HCl it yields (*Py.* 1,3)-di-oxy-quinoline (*Py.* 2)-carboxylic acid, and other bodies.

o-Di-nitro-di-benzoyl-malonic ether $(C_6H_4(NO_2).CO)_2C(CO_2Et)_2$. [93°]. Colourless tables or prisms. Obtained by the action of o-nitro-benzoyl chloride (2 mols.) on di-sodio-malonic ether (1 mol.) in alcoholic solution. By treatment with sodium ethylate one of the nitro-benzoyl groups is removed with formation of sodio-nitro-benzoyl-malonic ether and nitro-benzoic ether. By alcoholic NH_3 both benzoyl groups are removed with production of malonic ether and nitro-benzamide (2 mols.) (Bischoff a. Rach, *B.* 17, 2789).

m-**NITRO-BENZOYL PEROXIDE** $(C_6H_4(NO_2).CO)_2O_2$. Oil, ppd. by adding water to a solution of benzoyl peroxide in fuming HNO_3 (Brodie, *Pr.* 12, 655).

DI-*p*-NITRO-DI-BENZOYL-SUCCINIC ETHER $C_6H_4(NO_2).CO.CH(CO_2Et).CH(CO_2Et).CO.C_6H_4(NO_2)$. [180°]. Formed by the action of iodine on an ethereal solution of the sodium derivative of *p*-nitro-benzoyl-acetic ether (Perkin a. Bellenot, *C. J.* 49, 452; *B.* 18, 953). Needles. Forms an amorphous di-sodium derivative.

o-**NITRO-BENZYL ALCOHOL** $C_7H_7NO_3$ *i.e.* $C_6H_4(NO_2).CH_2OH$. [74°]. Prepared by the action of aqueous NaOH on o-nitrobenzoic aldehyde (Friedländer a. Henriques, *B.* 14, 2804; Gabriel a. Borgmann, *B.* 16, 2065; Geigy a. Koenigs, *B.* 18, 2403). Yellow needles, sl. sol. water. Yields on reduction by zinc and HCl o-amido-benzyl alcohol [82°]. Chromic acid oxidises it to o-nitro-benzoic acid.

m-Nitro-benzyl alcohol $C_6H_4(NO_2).CH_2OH$. (175°–180° at 3 mm.). Formed by heating *m*-nitro-benzoic aldehyde with alcoholic potash, and ppg. by water (Grimaux, *Bl.* [2] 8, 433).

Preparation.—2 pts. of *m*-nitro-benzaldehyde are mixed with a cooled solution of 1 pt. of KOH in 6 pts. of water. After standing overnight the product is extracted with ether; the yield is nearly the theoretical (Becker, *B.* 15, 2091).

Oil, decomposed by distillation under atmospheric pressure.

p-Nitro-benzyl alcohol $C_6H_4(NO_2).CH_2OH$. [92°]. Formed by heating its acetyl derivative with aqueous NH_3 at 100° (Beilstein a. Kuhlberg, *Z.* [2] 3, 467; *A.* 147, 343). Formed also, together with di-nitro-*p*-toluidine, by warming the *p*-nitro-benzyl ether of di-nitro-*o*-cresol with alcoholic NH_3 (Staedel, *A.* 217, 183).

Preparation.—1. Finely powdered *p*-nitro-benzaldehyde (1 pt.) is added to 5 or 6 pts. of 15 p.c. aqueous NaOH, and allowed to stand for 12 hours; it is then diluted with a little water and extracted with ether; the yield is 80 p.c. to 90 p.c. of the theoretical.—2. 20 pts. of *p*-nitro-benzyl-acetate (obtained by nitration of benzyl acetate) in 40 pts. of boiling alcohol is treated with 35 pts. of 15 p.c. aqueous NaOH, quickly cooled and poured into 200 pts. of iced water, and the pp. collected; the yield is about 75 p.c. (Basler, *B.* 16, 2715).

Properties.—Yellowish needles. Yields *p*-nitro-benzoic acid on oxidation. Concentrated nitric acid converts it into the nitrate $C_6H_4(NO_2).CH_2.O.NO_2$ [71°] (Staedel, *B.* 14, 90).

Acetyl derivative $C_6H_4(NO_2).CH_2OAc$. [78°]. Formed by dropping benzyl acetate into fuming HNO_3. Pale-yellow needles.

o-NITRO-BENZYLAMINE $C_7H_8N_2O_2$ *i.e.* $C_6H_4(NO_2).CH_2NH_2$. Formed by heating o-nitro-benzyl-phthalimide with HClAq at 200° (Gabriel, *B.* 20, 2228). Liquid, v. sol. water.—B'HCl. Needles, v. sol. water.—$B'_2H_2PtCl_6$ 2aq.

Formyl derivative $C_7H_7AcN_2O_2$. [90°]. Formed by heating the hydrochloride with dry sodium formate and formic acid (Gabriel a. Jansen, *B.* 23, 2813). Crystals. Yields quinazoline dihydride on reduction by zinc and HCl.

Acetyl derivative. [99°]. Needles. Yields on reduction $C_6H_4(NH_2).CH_2NHAc$ [113·5°].

Benzoyl derivative [112°]. Needles (from hot alcohol). Yields on reduction $C_6H_4(NH_2).CH_2NHBz$ [109°].

m-Nitro-benzyl-amine $C_6H_4(NO_2).CH_2NH_2$. Formed by heating *m*-nitro-benzyl-phthalimide with HClAq (Gabriel a. Hendess, *B.* 20, 2869). Formed also from *m*-nitro-benzyl chloride and alcoholic NH_3 (Borgmann, *C. C.* 1885, 456). Needles.—$B'_2H_2PtCl_6$: plates.

Acetyl derivative $C_6H_4(NO_2).CH_2NHAc$. [91°]. Needles, sol. hot water.

p-Nitro-benzyl-amine $C_6H_4(NO_2).CH_2NH_2$. Prepared from *p*-nitro-benzyl chloride by treatment with potassium phthalimide and decomposition of the *p*-nitro-benzyl-phthalimide (Hafner, *B.* 23, 337). Strongly alkaline oil, absorbing CO_2 from the air. Converted by nitrous acid into *p*-nitro-benzyl alcohol. CS_2 forms $C_6H_4(NO_2).CH_2NH.CS.NH_3.CH_2.C_6H_4NO_2$ [193°].—B'HCl: plates, m. sol. water.—$B_2'H_2PtCl_6$.—$B'HNO_3$: needles, sl. sol. water.

Acetyl derivative $C_6H_4(NO_2).CH_2NHAc$. [133°]. Needles, sol. water. Formed by heating the base with Ac_2O and NaOAc, or by nitration of the acetyl derivative of benzylamine (Amsel a. Hofmann, *B.* 19, 1286).

Benzoyl derivative [156°]. Needles.

Di-*p*-nitro-di-benzyl-amine $C_{14}H_{13}N_3O_4$ *i.e.* $(C_6H_4(NO_2).CH_2)_2NH$. [93°]. Obtained, together with the following isomeride and tri-nitro-tri-benzylamine, by heating nitro-benzyl chloride with aqueous NH_3 at 100° (Strakosch, *B.* 6, 1056). Yellow plates (from alcohol).—B'HCl. [212°].—$B'_2H_2PtCl_6$.

Di-nitro-di-benzyl-amine. [above 100°]. Formed as above.—B'HCl. [173°].

Tri-*o*-nitro-tri-benzyl-amine $(C_6H_4(NO_2).CH_2)_3N$. [157°]. Formed almost exclusively by heating o-nitro-benzyl chloride with aqueous NH_3. Long yellowish needles. Sol. benzene, sl. sol. alcohol. Its salts are decomposed by water (Lellmann a. Stickel, *B.* 19, 1605).

Tri-*p*-nitro-tri-benzyl-amine $(C_6H_4(NO_2).CH_2)_3N$. [163°]. Formed by heating *p*-nitro-benzyl chloride with aqueous NH_3 (Strakosch). Needles (from HOAc).

Tri-nitro-benzyl-amine $N(CH_2.C_6H_4.NO_2)_3$. [159°]. Formed by nitration of tri-benzyl-amine with a mixture of conc. HNO_3 and conc. H_2SO_4. Colourless crystals. Sol. hot acetic acid, insol. alcohol and ether (Marquardt, *B.* 19, 1030).

***o*-NITRO-BENZYL-ANILINE** $C_6H_4(NO_2).CH_2.NHC_6H_5$. Prepared by heating 2 mols. of aniline with 1 mol. of o-nitro-benzyl chloride in alcoholic solution for 2 hours on the water-bath. It crystallises in two allotropic forms, of which the unstable form changes into the stable by fusion or by long keeping. The unstable form crystallises in reddish-yellow monoclinic needles, $a:b:c$ = ·8585:1:1·1587, $\beta = 87° 42' 52''$; and melts at [44°]. The stable form crystallises in glistening brown triclinic prisms, $a:b:c$ = 1·6764:1:?, $\alpha = 117°$, $\beta = 137° 40' 6''$, $\gamma = 69° 38' 44''$; it melts at [57°]. V. sol. alcohol, ether, and benzene, sparingly in petroleum-ether. Reduced by tin and HCl to $C_{13}H_{10}N_2$ [83°].—B'HCl 3aq: white needles, basified by much water.

Acetyl derivative $C_6H_4(NO_2).CH_2.NPhAc$. [75°] (Paal a. Krecke, *B.* 23, 2637).

Benzoyl derivative $C_6H_4(NO_2)CH_2.NPhBz$. [101°]. Well-formed crystals; sol. alcohol, ether, and acetic acid, v. sol. chloroform, sl. sol. petroleum-ether. By reduction with tin and HCl it is converted into $C_6H_4(NH_2).CH_2NPhBz$ [115°] (Lellmann a. Stickel, *B.* 19, 1605; 24, 718; Söderbaum a. Widman, *B.* 23, 2193).

Formyl derivative $C_6H_4(NO_2).CH_2.NC_7H_7.CHO$. [77°]. Yellow monoclinic plates; $a:b:c$ = ·548:1:1·085; $\beta = 69° 7'$. Yields phenyl-quinazoline dihydride on reduction (Paal a. Busch, *B.* 22, 2683).

m-**Nitro-benzyl-aniline** $C_6H_4(NO_2)CH_2.NHC_6H_5$. [86°]. From *m*-nitro-benzyl chloride and aniline (Borgmann, *C. C.* 1885, 456). Orange-red needles.—B'HCl: plates.

p-**Nitro-benzyl-aniline** $C_6H_4(NO_2)CH_2.NHC_6H_5$. [68°]. Formed from *p*-nitro-benzyl chloride and aniline (Strakosch,

B. 6, 1062). Golden-yellow needles, sol. hot alcohol.—B'HCl. Plates.

Di-nitro-di-benzyl-aniline $(C_6H_4(NO_2).CH_2)_2NC_6H_5$. [206°]. Formed in small quantity as a by-product of the action of o-nitro-benzyl chloride upon aniline. Greenish-yellow needles. Sparingly soluble in acetic acid (Lellmann a. Stickel, *B.* 19, 1608).

m-**Nitro-benzyl-aniline** $C_6H_4(NO_2).NH.C_7H_7$. [107°]. From *m*-diazo-nitro-benzene *m*-nitro-benzyl-anilide by heating with conc. HCl at 100° (Meldola a. Streatfeild, *C. J.* 51, 114).

The *Nitrosamine* is an oil.

p-**Nitro-benzyl-aniline** $C_6H_4(NO_2).NH.C_7H_7$, [143°]. From *p*-diazo-nitro-benzene *p*-nitro-benzyl-anilide by heating with conc. HCl at 100° (Meldola a. Streatfeild, *C. J.* 51, 113; Meldola a. Salmon, *C. J.* 53, 779). Golden scales.

Nitrosamine $C_6H_4(NO_2).N(NO).C_7H_7$. [108°].

Acetyl derivative [109°].

Benzoyl derivative $C_6H_4(NO_2).NBz.CH_2Ph$. [194°]. Needles.

p-**Nitro-di-benzyl-aniline** $C_6H_4(NO_2).N(CH_2.C_6H_5)_2$. [130°]. Formed by nitration of di-benzyl-aniline dissolved in acetic acid. Yellow needles. Sol. hot alcohol and acetic acid, sl. sol. cold alcohol, v. sol. ether and benzene (Matzudaira, *B.* 20, 1613).

NITRO-BENZYL-BENZENE *v.* NITRO-DI-PHENYL-METHANE.

Di-*m*-nitro-di-benzyl-benzene $C_{20}H_{16}N_2O_4$ *i.e.* $C_6H_4(CH_2.C_6H_4NO_2)_2$. [165°]. Formed by the action of H_2SO_4 on a mixture of *m*-nitro-di-phenyl-methane and *m*-nitro-benzyl alcohol (Becker, *B.* 15, 2091).

Di-*p*-nitro-di-benzyl-benzene $C_6H_4(NO_2).CH_2.C_6H_4.CH_2.C_6H_4(NO_2)$. [c. 146°]. Formed as a by-product in the preparation of *p*-nitro-di-phenyl-methane by the action of H_2SO_4 on a mixture of *p*-nitro-benzyl alcohol and benzene (Basler, *B.* 16, 2716). Small white concentric needles. Sol. benzene and hot acetic acid, v. sl. sol. other solvents.

m-**NITRO-BENZYL BROMIDE** $C_7H_6Br.NO_2$ *i.e.* $C_6H_4(NO_2).CH_2Br$. [58°]. Formed by heating *m*-nitro-toluene with bromine at 130° (Wachendorff, *A.* 185, 266).

p-**Nitro-benzyl bromide** [100°]. Formed from *p*-nitro-toluene and Br (W.). Needles.

p-**NITRO-BENZYL-CARBAMIC ETHER** $C_6H_4(NO_2).CH_2.NH.CO_2Et$. [117°]. Formed from *p*-nitro-benzylamine and $ClCO_2Et$ (Hafner, *B.* 23, 340). Silky needles, v. sol. ether.

o-**NITRO-BENZYL CHLORIDE** $C_7H_6ClNO_2$ *i.e.* $C_6H_4(NO_2).CH_2Cl$. [49°]. Formed, together with the *p*-isomeride, by nitration of benzyl chloride in the cold (Beilstein a. Geitner, *A.* 139, 337; Abelli, *G.* 13, 97; Nölting, *B.* 17, 385; Kumpf (*A.* 224, 100). Formed also by treating *o*-nitro-benzyl alcohol with PCl_5 in the cold (Gabriel a. Borgmann, *B.* 16, 2066; Geigy a. Königs, *B.* 18, 2401). Thick crystals. Reduced by $SnCl_2$ to *o*-'benzylene-imide' C_7H_7N, an amorphous base (Lellmann a. Stickel, *B.* 19, 1611). Aniline yields oily $C_6H_4(NO_2).CH_2NHPh$ reduced by zinc-dust in HOAc to the amido-compound $C_6H_4(NH_2).CH_2.NHPh$ [82°] (Söderbaum a. Widman, *B.* 23, 2193).

m-**Nitro-benzyl-chloride** $C_6H_4(NO_2).CH_2Cl$. [47°]. (c. 178° at 35 mm.). Long yellow needles. V. sol. alcohol, ether, and benzene. Formed by the action of PCl_5 on the alcohol (Gabriel a. Borgmann, *B.* 16, 2064).

p-**Nitro-benzyl chloride** [4:1] $C_6H_4(NO_2).CH_2Cl$. [71°]. Formed by treating benzyl chloride with HNO_3 (S.G. 1·48) at −10° (Elbs a. Bauer, *J. pr.* [2] 34, 343; *cf.* Beilstein a. Geitner, *A.* 139, 337; Strakosch, *B.* 6, 1056; Grimaux, *Bl.* [2] 8, 433). Formed also by passing chlorine into *p*-nitro-toluene at 190° (Wachendorff, *B.* 8, 1101; *A.* 185, 271). Crystals.

Reactions.—1. *Ammonium sulphide* gives *p*-nitro-benzyl mercaptan (Strakosch, *B.* 5, 697). 2. *Alcoholic potash* gives an azo- derivative of di-nitro-stilbene.—3. An alkaline solution of SnO forms *p*-dinitro-dibenzyl (W. Roser, *A.* 238, 363).—4. *Chromic acid mixture* oxidises it to *p*-nitro-benzoic acid.—5. A solution of $SnCl_2$ in HClAq reduces it to *p*-'benzylene-imide' C_7H_7N, an amorphous base (L. a. S.).

NITRO-BENZYL CYANIDE *v.* *Nitrile* of NITRO-PHENYL-ACETIC ACID.

o-NITRO-BENZYL-ETHYL-MALONIC ETHER $C_{16}H_{21}NO_6$ *i.e.* $C_6H_4(NO_2).CH_2.CEt(CO_2Et)_2$. Formed from ethyl-malonic ether, NaOEt, and *o*-nitro-benzyl chloride (Lellmann a. Schleich, *B.* 20, 440). Reduced by zinc and HOAc to $C_{14}H_{17}NO_3$ [114°].

p-**Nitro-benzyl-ethyl-malonic ether** [52°]. Formed in like manner. Needles.

o-NITRO-BENZYL ETHYL OXIDE $C_6H_4(NO_2).O.C_2H_5$. Formed by heating o-nitro-benzyl chloride with alcohol in a boiling brine-bath (Errera, *G.* 18, 232). Oil.

m-**Nitro-benzyl ethyl oxide.** Prepared by heating *m*-nitro-benzyl chloride with alcoholic potash (E.). Oil, solidifying in a freezing mixture.

p-**Nitro-benzyl ethyl oxide** [24°]. Prepared by heating *p*-nitro-benzyl chloride with alcohol (E.). Trimetric crystals.

NITRO-BENZYLIDENE-ACETONE *v.* NITRO-STYRYL METHYL KETONE.

NITRO-BENZYLIDENE-ACETONAMINE *v.* ACETONAMINE.

m-**DI-NITRO-DI-BENZYLIDENE-DI-AMIDO-DIPHENYL** $C_6H_4(NO_2).CH:N.C_6H_4.C_6H_4.N:CH.C_6H_4(NO_2)$. Formed by heating *op*-di-amido-diphenyl with *m*-nitro-benzoic aldehyde and alcohol at 100° (Reuland, *B.* 22, 3011). Yellow crystalline powder, m. sol. alcohol. The isomeric compound from *p*-nitro-benzoic aldehyde and *op*-di-amido-diphenyl melts at 208°, while that from di-*p*-amido-diphenyl and *m*-nitro-benzoic aldehyde melts at 234° (Schiff a. Vanni, *A.* 258, 375).

m-**NITRO-BENZYLIDENE-ANILINE** $C_{13}H_{10}N_2O_2$ *i.e.* [3:1]$C_6H_4(NO_2).CH:NPh$. [61°]. Formed from *m*-nitro-benzoic aldehyde and aniline (Lazorenko, *J.* 1870, 760). Needles.

p-**Nitro-benzylidene-aniline** [4:1]$C_6H_4(NO_2).CH:NPh$. [93°]. Formed by heating aniline with *p*-nitro-benzoic aldehyde at 100° (Fischer, *B.* 14, 2524).

Di-*m*-nitro-benzylidene-aniline [3:1]$C_6H_4(NO_2).CH:N.C_6H_4(NO_2)$ [1:3]. [153°]. Formed by warming the alcoholic solution of *m*-nitro-benzoic aldehyde with *m*-nitro-aniline (Hantzsch, *B.* 23, 2775).

m-**NITRO-BENZYLIDENE BROMIDE** $C_6H_4(NO_2).CHBr_2$[1:3]. [102°]. Formed by

heating *m*-nitro-toluene (1 mol.) with bromine (2 mols.) at 140° (Wachendorff, *A.* 185, 278). Minute needles (from alcohol).

p-Nitro-benzylidene bromide $C_6H_4(NO_2).CHBr_2$[1:4]. [82°]. Formed by heating *p*-nitro-toluene (1 mol.) with bromine (2 mols.) at 140° (W.). Needles or rectangular plates (from alcohol). By heating with aniline it yields *p*-rosaniline (Zimmermann a. Müller, *B.* 17, 2936).

***m*-NITRO-BENZYLIDENE CHLORIDE** $C_6H_4(NO_2).CHCl_2$. [65°]. Formed from *m*-nitro-benzoic aldehyde and PCl_5 (Widmann, *B.* 13, 676; Erlich, *B.* 15, 2010). Thin monoclinic plates or needles (from alcohol); v. sol. ether.

p-Nitro-benzylidene chloride $C_6H_4(NO_2).CHCl_2$. [46°]. Formed from *p*-nitro-benzoic aldehyde and PCl_5 (Zimmermann a. Müller, *B.* 17, 2937; 18, 997), and by nitration of benzylidene chloride (Hübner a. Beute, *B.* 6, 803). Prisms (from alcohol). Yields *p*-rosaniline on heating with aniline.

***o*-NITRO-BENZYLIDENE-HYDRAZINE** $(C_6H_4(NO_2).CH)_2N_2$. [181°]. Formed from *o*-nitrobenzoic aldehyde and hydrazine salts (Curtius a. Jay, *J. pr.* [2] 39, 43). Yellow needles.

***p*-NITRO-BENZYLIDENE-INDOXYL** *v. Indogenide* of *p*-NITRO-BENZOIC ALDEHYDE.

***o*-NITRO-BENZYLIDENE MALONIC ACID** $C_{10}H_7NO_6$ *i.e.* [2:1]$C_6H_4(NO_2).CH:C(CO_2H)_2$. [161°]. Formed by heating *o*-nitro-benzoic aldehyde with malonic acid and HOAc at 60° (Stuart, *C. J.* 47, 158; 49, 365). Needles (from water), v. sol. ether, v. e. sol. ether, sl. sol. $CHCl_3$. With HBr it yields a yellow compound melting at 227°. Boiling water decomposes it slowly, forming *o*-nitro-benzoic aldehyde, malonic acid, and a little *o*-nitro-cinnamic acid. — BaA″ $2\frac{1}{2}$aq: feathery tufts, converted by warm water into insoluble BaA″aq.—Ag_2A″.

Ethyl ether Et_2A″. [53°].

m-Nitro-benzylidene-malonic acid [3:1]$C_6H_4(NO_2).CH:C(CO_2H)_2$. [205°]. Formed from *m*-nitro-benzoic aldehyde, malonic acid, and HOAc (Stuart, *C. J.* 47, 155; 49, 361). Crystals, sl. sol. cold water and ether. Partially decomposed by hot water into *m*-nitro-benzoic aldehyde and malonic acid. Split up on fusion into CO_2 and *m*-nitro-cinnamic acid [196°]. HBr forms $C_6H_4(NO_2).CHBr.CH(CO_2H)_2$. Bromine combines with it, yielding the dibromide $C_6H_4(NO_2).CHBr.CBr(CO_2H)_2$.

Ethyl ether Et_2A″. [73°].

p-Nitro-benzylidene-malonic acid $C_6H_4(NO_2).CH:C(CO_2H)_2$. [227°]. Formed from *p*-nitro-benzoic aldehyde, malonic acid, and HOAc at 60° (Stuart, *C. J.* 43, 408). Formed also, together with a small quantity of the *ortho*-acid from benzylidene-malonic ether by nitration and saponification (Stuart, *C. J.* 47, 155). Crystals, split up on fusion into CO_2 and *p*-nitro-cinnamic acid. Decomposed by hot water into *p*-nitro-benzoic aldehyde and malonic acid. Bromine forms $C_6H_4(NO_2).CHBr.CBr(CO_2H)_2$ which gives off HBr at 100°, leaving a residue [188°], and is decomposed by water yielding $C_6H_4(NO_2)CH:CBr.CO_2H$ [208°].

Ethyl ether Et_2A″. [93°]. Prisms. Converted by HBr into $C_6H_4(NO_2)CHBr.CH(CO_2H)_2$ [89°] (Stuart, *C. J.* 49, 362).

***m*-NITRO-BENZYLIDENE DI-METHYL DISULPHONE** $C_9H_{11}NS_2O_6$ *i.e.* [1:3]$C_6H_4(NO_2).CH(SO_2CH_3)_2$. [179°]. Formed by oxidising *m*-nitro-benzylidene-di-thio-di-glycollic acid (Bongartz, *B.* 21, 487). Slender needles (from dilute HOAc).

p-Nitro-benzylidene di-methyl disulphone [1:4]$C_6H_4(NO_2).CH(SO_2CH_3)_2$. [248°]. Formed by oxidising *p*-nitro-benzylidene-di-thio-di-glycollic acid with $KMnO_4$ (B.). Yellowish needles (from hot water).

NITRO-BENZYLIDENE-PHTHALIDE

$$C_{15}H_9NO_4 \textit{ i.e. } C_6H_4\begin{cases} C\!:\!C(NO_2).C_6H_5 \\ CO.O \end{cases}$$

Preparation.—10 pts. of crude di-nitro-benzyl-phthalide are dissolved in 20 pts. of hot alcohol, diluted with 10 pts. of hot water, and heated for half an hour on the water-bath; the yield is 46 p.c. of theoretical, but when pure di-nitro- compound is used, nearly 100 p.c. (Gabriel, *B.* 18, 1251, 3471).

Properties.—Glistening crystals. Split up on dry distillation into phenyl cyanate and phthalic anhydride. Alcoholic NaOH converts it into the salt $C_{15}H_9NO_5Na_2 2\frac{1}{2}$aq which crystallises in colourless prisms and is decomposed by acids into ω-nitro-toluene $C_6H_5.CH_2(NO_2)$ and phthalic anhydride. Reduced by HI and P to isobenzylidene-phthalide $C_6H_4\begin{cases} CH:CPh \\ CO.O \end{cases}$ [91°] and a compound $C_{15}H_{11}NO_2$ [257°] whence KOH and MeI yield two isomeric bodies $C_{16}H_{13}NO_2$ melting at 237° and 121° (Gabriel, *B.* 20, 2863).

NITRO-BENZYLIDENE-PHTHALIMIDINE

$$C_{15}H_{10}N_2O_3 \textit{ i.e. } C_6H_4\begin{cases} C{=}C(NO_2).C_6H_5 \\ CO \end{cases}\!\!>NH$$

Phthalimidyl-nitro-benzyl. Formed together with oxy-nitro-benzyl-phthalimidine by leading N_2O_3 or N_2O_4 into a benzene solution of benzal-phthalimidine or of deoxybenzoïn-*o*-carboxyl-amide $C_6H_4(CO.NH_2).CO.CH_2.C_6H_5$ (Gabriel, *B.* 18, 2439).

Nitro-benzylidene-phthalimidic acid $C_{15}H_{12}N_2O_4$ *i.e.* $C_6H_4(CO_2H).C(NH_2):C(NO_2).C_6H_5$ [145°–150°]. Formed by dissolving nitro-benzyl-idene-phthalimidine in hot dilute NaOH and precipitating with an acid (Gabriel, *B.* 18, 2440). Acetyl chloride reconverts it into the anhydride. Nitrous acid passed into the solution in benzene converts it into nitro-benzylidene-phthalide.

Salts.—A′Ag: microcrystalline powder.—A′$_2$Ba 7aq: long yellow needles or short prisms.

Ethyl ether A′Et: [155°]; yellow crystals.

Nitro-iso-benzylidene-phthalimidine *v.* (*Py.* 1:4:2)-NITRO-OXY-PHENYL-ISOQUINOLINE.

NITRO-BENZYLIDENE-DI-THIO-DI-GLYCOLLIC ACID $C_{11}H_{11}NS_2O_6$ *i.e.* $C_6H_4(NO_2).CH(S.CH_2.CO_2H)_2$. The *o*-, *m*-, and *p*- varieties of this acid are formed by the action of thioglycollic acid on the three nitro-benzoic aldehydes (Bongartz, *B.* 21, 479).

o-Acid [123°]. Needles (from HOAc).

m-Acid [130°]. Needles (from dil. HOAc).

p-Acid [162°]. Needles (from dil. HOAc).

***o*-NITRO-BENZYLIDENE-DI-UREA** $C_9H_{11}N_5O_4$ *i.e.* $C_6H_4(NO_2).CH(NH.CO.NH_2)_2$. [200°]. Formed by warming an alcoholic solution of urea with *o*-nitro-benzoic aldehyde (Schiff,

A. 251, 186; Lüdy, *M.* 10, 304). Needles (containing aq), sl. sol. water and alcohol.

o-NITRO-BENZYL IODIDE $C_6H_4(NO_2).CH_2I$ [75°]. Formed from o-nitro-benzyl chloride, KI, and alcohol (Kumpf, *A.* 224, 103). Plates.

p-Nitro-benzyliodide $C_6H_4(NO_2).CH_2I$. [127°]. Formed in like manner. Needles.

***p*-NITRO-BENZYL-MALONIC ACID** $C_6H_4(NO_2).CH_2.CH(CO_2H)_2$. Formed by saponification of the ether which is obtained in small quantity, together with di-nitro-di-benzyl-malonic ether, by the action of *p*-nitro-benzyl chloride upon sodio-malonic ether (Lellmann a. Schleich, *B.* 20, 434). Yellow powder. Carbonises at 240° without melting. CaA″ and BaA″: yellow pps.

Ethyl ether Et_2A'': [63°]; yellowish prisms; sol. ordinary solvents.

Di-o-nitro-di-benzyl-malonic ether $(C_6H_4(NO_2).CH_2)_2:C(CO_2Et)_2$. [97°]. Obtained by the action of o-nitro-benzyl chloride upon sodio-malonic ether. Yellow crystals. Sol. alcohol and ether (Lellmann a. Schleich, *B.* 20, 438).

Di-*p*-nitro-di-benzyl-malonic ether $(C_6H_4(NO_2).CH_2)_2:C(CO_2Et)_2$. [170°]. Formed by the action of *p*-nitro-benzyl chloride upon sodio-malonic ether. Colourless silky needles. Sol. acetic acid, sl. sol. alcohol, and chloroform.

***p*-NITRO-BENZYL MERCAPTAN** $C_7H_7NSO_2$ *i.e.* $C_6H_4(NO_2).CH_2SH$. [140°]. Formed from *p*-nitro-benzyl chloride and alcoholic ammonium sulphide (Strakosch, *B.* 5, 698). Laminæ.

TRI-NITRO-BENZYL-MESITYLENE $C_{16}H_{15}(NO_2)_3$. [185°]. Formed by nitration of benzyl-mesitylene at 0° (Louise, *A. Ch.* [6] 6, 182). Prisms (from alcohol-chloroform).

TRI-NITRO-BENZYL METHYL KETONE $C_6H_2(NO_2)_3CH_2.CO.CH_3$. [89°]. Obtained by boiling tri-nitro-phenyl-acetoacetic ether (10 g.) dissolved in HOAc (100 g.) with H_2SO_4 (20 g.) and water (30 g.) for 8 hours (Dittrich, *B.* 23, 2723). Long yellowish-white needles, sol. alkalis.

Phenyl-hydrazide $C_{15}H_{13}N_5O_6$. [125°].

NITRO-*p*-BENZYL-PHENOL $C_{13}H_{11}NO_3$ *i.e.* $Ph.CH_2.C_6H_3(NO_2)OH$ [1:3:4]. [75°]. From benzyl-phenol and HNO_3 (S.G. 1·4). Prisms. Volatile with steam.—KA′: brick-red needles (Rennie, *C. J.* 41, 221).

Di-nitro-*p*-benzyl-phenol $Ph.CH_2.C_6H_2(NO_2)_2OH$ [1:3:5?:4]. [88°]. From the above, HOAc, and HNO_3. Formed also by the action of HNO_3 on *p*-benzyl-phenol sulphonic acid (Rennie, *C. J.* 49, 408). Oxidised by CrO_3 it gives benzoic acid.—KA′; orange needles.—BaA'_2.

Di-nitro-o-benzyl-phenol [82°]. Obtained by warming o-benzyl-phenol sulphonic acid with dilute HNO_3 (Rennie).—KA′aq.—BaA'_2.

Tri-nitro-benzyl-phenol $C_{13}H_8(NO_2)_3OH$. [148°]. Got by dissolving potassic benzyl-phenol sulphonic acid in HNO_3 (S.G. 1·4) and evaporating (Rennie, *C. J.* 41, 36, 223). Silky pale-yellow needles. Yields *p*-nitro-benzoic acid on oxidation with chromic acid mixture.—$C_{13}H_8(NO_2)_3OK$.

NITRO-*p*-BENZYL-PHENOL SULPHONIC ACID ×$C_7H_7.C_6H_2(OH)(NO_2)SO_3H$.—KA′. Formed by action of HNO_3 (S.G. 1·2) and potassic benzyl-phenol sulphonate (Rennie, *C. J.* 41, 35).

Nitro-o-benzyl-phenol sulphonic acid. Formed in like manner.—KA: yellow scales.

DI-NITRO BENZYL-PHTHALIDE $C_{15}H_{10}N_2O_6$ *i.e.* $C_6H_4\begin{cases}C(NO_2).CH(NO_2).C_6H_5 \\ CO.O\end{cases}$ (?). [113°]. Formed by passing nitrous acid gas into a solution of benzylidene-phthalide in benzene (Gabriel, *B.* 18, 1251). Colourless crystals. Readily converted into nitro-benzylidene-phthalide (*q.v.*).

o-NITRO-BENZYL-PHTHALIMIDE $C_6H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>N.CH_2.C_6H_4(NO_2)$ [1:2]. [219°]. Formed from potassium phthalimide and o-nitro-benzyl chloride at 100°–130° (Gabriel, *B.* 20, 2227). Prisms.

m-Nitro-benzyl-phthalimide. [155°]. Formed in like manner. Needles.

p-Nitro-benzyl-phthalimide. [175°] (S.); [172°] (Hafner, *C. C.* 1889, 671). Prisms (from HOAc) (Salkowski, *B.* 22, 2142).

***p*-NITRO-BENZYL-PIPERIDEÏN** $C_6H_4(NO_2).CH_2.NC_5H_8$. [35°–40°]. Formed by dissolving its polymeride in HClAq and ppg. by ammonia (Lellmann a. Schwaderer, *B.* 22, 1333). Readily polymerises to $(C_6H_4(NO_2).CH_2.NC_5H_8)_2$ [120·5°], which is also obtained by treating di-piperideïn with *p*-nitro-benzyl chloride and NaOHAq.

NITRO-BENZYL-PIPERIDINE $C_6H_4(NO_2).CH_2NC_5H_{10}$. The o-, *m*-, and *p*-isomerides are formed by the action of o-, *m*-, and *p*- nitro-benzyl chloride on piperidine in hot alcoholic solution (Lellmann a. Pekrun, *A.* 259, 40).

o-Isomeride. Oil. Reduced by $SnCl_2$ to o-amido-benzyl-piperidine [82·5°]. — B′HCl. — $B'_2H_2PtCl_6$.

m-Isomeride. Oil. Reduced by $SnCl_2$ to *m*-amido-benzyl-piperidine [112°].—B′HCl.

p-Isomeride. [34°]. B′HCl.—$B'_2H_2PtCl_6$.

NITRO-BENZYL-QUINOLINE TETRA-HYDRIDE $C_6H_4(NO_2).CH_2NC_9H_{10}$. The three isomerides are formed by heating o-, *m*-, and *p*-nitro-benzyl chloride (1 mol.) with quinoline tetrahydride (2 mols.) in hot alcoholic solution (Lellmann a. Pekrun, *A.* 259, 50).

o-Isomeride. [111°]. Brownish-red tables.—$B'_2H_2PtCl_6$: yellow amorphous pp.

m-Isomeride. [99°]. Red prisms; reduced by $SnCl_2$ to *m*-amido-benzyl-quinoline tetrahydride [82°].

p-Isomeride. [102°]. Red prisms. — $B'_2H_2PtCl_6$.

NITRO-BENZYL SELENOCYANIDE $C_8H_6N_2SeO_2$ *i.e.* $C_6H_4(NO_2).CH_2SeCN$. [122·5°]. Formed by nitration of benzyl selenocyanide at −4° (C. L. Jackson, *B.* 8, 321; *A.* 179, 16). Needles (from alcohol).

o-NITRO-BENZYL SULPHIDE $(C_6H_4(NO_2).CH_2)_2S$. [124°]. Formed, together with a little of the disulphide, by passing NH_3 and H_2S into an alcoholic solution of o-nitro-benzyl chloride (Jahoda, *M.* 10, 880). White plates. Yields on oxidation by HNO_3 the sulphoxide $(C_6H_4(NO_2).CH_2)_2SO$ [163°] and the sulphone $(C_6H_4(NO_2).CH_2)_2SO_2$ [200°].

o-Nitro-benzyl disulphide $(C_6H_4(NO_2).CH_2)_2S_2$. [47°]. Formed as above (J.).

p-Nitro-benzyl disulphide [89°]. Yellow crystals (Strakosch, *B.* 5, 698).

***p*-NITRO-BENZYL SULPHOCYANIDE** $C_6H_4(NO_2).CH_2.SCN$. Formed from *p*-nitro-

benzyl chloride and alcoholic potassium sulpho-cyanide (Henry, *B.* 2, 638). Small needles.

p-NITRO-BENZYL-DI-THIO-CARBAMIC ACID $NO_2.C_6H_4.CH_2.NH.CS.SH$. The *p*-nitro-benzyl-ammonium salt [193°] of this acid is formed by treating *p*-nitro-benzylamine with CS_2 in ether (Hafner, *B.* 23, 339).

DI-*p*-NITRO-DI-BENZYL-THIO-UREA $CS(NH.CH_2.C_6H_4.NO_2)_2$. [202°]. Formed by boiling *p*-nitro-benzyl-ammonium *p*-nitro-benzyl-di-thio-carbamate with HgO and alcohol (Hafner, *B.* 23, 340). Needles, sl. sol. alcohol.

o-NITRO-BENZYL-*p*-TOLUIDINE $C_6H_4(NO_2).CH_2.NH.C_6H_4Me$. [72°]. Obtained by heating 4 pts. of *p*-toluidine with 1 pt. of o-nitro-benzyl chloride for ½ hr. on the water-bath. Yellow crystals. V. sol. most ordinary solvents.

Salts. — B'HCl: colourless needles. — $B'_2H_2PtCl_6{}^{x}$: sparingly soluble pp.—$B'_2H_2SO_4{}^{x}$: thin glistening plates.

Acetyl derivative $C_6H_4(NO_2).CH_2.NAcC_6H_4Me$: [65°]; stout crystals; on reduction with tin and HCl it is converted into o-amido-benzyl-toluidine. [79°]. (Lellmann a. Stickel, *B.* 19, 1609; 24, 718).

Formyl derivative [79°]. Formed by heating a solution of formyl-*p*-toluidine in benzene with sodium till dissolved, and then adding *p*-nitro-benzyl chloride (Paal a. Busch, *B.* 22, 2695). Needles.

o-Nitro-benzyl-o-toluidine. *Formyl derivative* $C_6H_4(NO_2).CH_2.N(C_7H_7).CHO$. [76°]. Formed from *o*-nitro-benzyl chloride and sodium formyl-o-toluidine (Paal a. Busch, *B.* 22, 2701). Yellow needles grouped in spherules.

p-NITRO-BENZYL-UREA $C_8H_9N_3O_3$ *i.e.* $NH_2.CO.NH.CH_2.C_6H_4NO_2$. [197°]. Formed by heating *p*-nitro-benzylamine hydrochloride with silver cyanate at 100° (Hafner, *B.* 23, 339). Pale-yellow needles, v. sol. HOAc and alcohol.

DI-*p*-NITRO-DI-BENZYL-UREA $CO(NH.CH_2.C_6H_4NO_2)_2$. [234°]. Formed by boiling the corresponding thio-urea with HgO; or by adding a solution of $COCl_2$ in benzene to one of *p*-nitro-benzylamine in ether (Hafner, *B.* 23, 340). Silvery needles (from HOAc).

NITRO-BROMO- compounds *v.* BROMO-NITRO-COMPOUNDS.

NITRO-BRUCINE *v.* BRUCINE.

ω-NITRO-*n*-BUTANE $C_4H_9NO_2$ *i.e.* $CH_3.CH_2.CH_2.CH_2.NO_2$. (152° cor.). S.G. $\frac{0}{}$ ·9945. Formed from *n*-butyl iodide and $AgNO_2$ (Züblin, *B.* 10, 2083; Pribram a. Handl, *M.* 2, 656). Reduced by tin and HCl to butylamine. HClAq at 140° forms hydroxylamine and *n*-butyric acid.

β-Nitro-butane $CH_3.CH_2.CH(NO_2).CH_3$. (138°). Formed from *sec*-butyl iodide (120 pts.) and silver nitrite (150 pts.) (V. Meyer a. Locher, *B.* 7, 1506; *A.* 180, 134). Formed also from $CH_3.CHBrNO_2$ and $ZnEt_2$ (Bevad, *J. R.* 20, 125).

ω-Nitro-isobutane $(CH_3)_2CH.CH_2NO_2$. (137°–144°). S.G. $\frac{0}{}$ 1·0083. Formed from *sec*-isobutyl iodide and $AgNO_2$ (Demole, *B.* 7, 709, 790; *A.* 175, 142; P. a. H.). Unlike ω-nitro-*n*-butane, it does not give a crystalline pp. with NaOEt, although it dissolves in alkalis.

Nitro-*tert*-butane $(CH_3)_3CNO_2$. (110°–130°). Formed, in small quantity, together with *tert*-butyl nitrite, by the action of $AgNO_2$ on *tert*-butyl iodide (Tscherniak, *A.* 180, 155). Oil, smelling like peppermint. Does not dissolve in alkalis. May be reduced to *tert*-butylamine (*cf.* V. Meyer, *A.* 244, 222).

Di-nitro-butane $C_4H_8N_2O_4$. Formed from bromo-ω-nitro-*n*-butane, aqueous KNO_2 and dilute H_2SO_4 (Züblin, *B.* 10, 2085). Oil, decomposed at 190° by distillation. — $KC_4H_7N_2O_4$: golden scales, sol. water and alcohol. — $AgC_4H_7N_2O_4$: yellow scales with blue reflex.

Di-nitro-butane $C_4H_8(NO_2)_2$. (197°). S.G. $\frac{15}{0}$ 1·205. Formed by the action of HNO_3 on di-isoamyl ketone or on propyl-acetoacetic ether (Chancel, *C. R.* 94, 399; 96, 1466). Heavy oil, forming crystalline K and Ag salts. Decomposed on distillation.

Di-(β)-nitro-butane $CH_3.CH_2.C(NO_2)_2.CH_3$. (199° cor.). Formed by oxidising butyl-ψ-nitrole with nitric acid (V. Meyer, *B.* 9, 701), or by boiling isovaleric acid with HNO_3 (Bredt, *B.* 15, 2324). Oil, not soluble in alkalis. Tin and HCl convert it into hydroxylamine and methyl ethyl ketone.

Di-nitro-isobutane $(CH_3)_2CH.CH(NO_2)_2$. Formed from bromo-nitro-isobutane, KNO_2, and dilute H_2SO_4 (Z.). Oil. — $KC_4H_7(NO_2)_2$. — $AgC_4H_7(NO_2)_2$ ½aq.

DI-NITRO-ISOBUTYL-ANILINE $C_{10}H_{13}N_3O_4$ *i.e.* $C_4H_9NH.C_6H_3(NO_2)_2$. [80°]. Formed from bromo-*m*-di-nitro-benzene and isobutylamine (Romburgh, *R. T. C.* 4, 192). Yellow needles.

Tri-nitro-isobutyl-aniline $C_6H_2(NO_2)_3NHC_4H_9$. [95°]. Formed from chloro-tri-nitro-benzene (picryl chloride) and isobutylamine (R.). Converted by fuming HNO_3 into the nitramine $C_6H_2(NO_2)_3N(NO_2)C_4H_9$ [110°].

m-NITRO-ISOBUTYL-BENZENE $C_{10}H_{13}NO_2$ *i.e.* $C_6H_4(NO_2).C_4H_9$. (251°) at 740 mm. Formed from nitro-amido-isobutyl-benzene by elimination of NH_2 (Gelzer, *B.* 21, 2941). Oil. Yields *m*-nitro-benzoic acid on oxidation.

o-Nitro-*tert*-butyl-benzene $C_6H_4(NO_2).CMe_3$ [1:2]. (249°). S.G. $\frac{15}{}$ 1·074. Formed from *tert*-butyl-benzene and fuming HNO_3 (Senkowsky, *B.* 23, 2416). Yellow oil, Smelling like cymene. Reduced by tin and HCl to $C_6H_4(NH_2).CMe_3$, (c. 235°), S.G. $\frac{15}{}$ ·977, which yields an acetyl derivative [159°].

p-Nitro-*tert*-butyl-benzene $C_6H_4(NO_2).CMe_3$ [1:4]. [30°]. (276°). Formed at the same time as the preceding (S.). Yellow needles (from alcohol). Yields, on reduction, $C_6H_4(NH_2).CMe_3$ S.G. $\frac{15}{}$ ·953.

NITRO-*m*-ISOBUTYL-BENZOIC ACID $C_6H_3(C_4H_9)(NO_2)CO_2H$. [140°]. Formed by nitration of *m*-isobutyl-benzoic acid (Kelbe a. Pfeiffer, *B.* 19, 1727). Small needles (from petroleum-ether).—AgA': somewhat soluble pp.—MeA': liquid.

Nitro-*p*-isobutyl-benzoic acid $C_6H_3(C_4H_9)(NO_2)CO_2H$. [161°]. Long fine needles (from water). Formed by nitration of *p*-isobutyl-benzoic acid.—AgA': white pp.

Methyl ether MeA': fluid (Kelbe a. Pfeiffer, *B.* 19, 1726).

NITRO-BUTYLENE $C_4H_7NO_2$. (154°–158°). Formed by allowing HNO_3 (S.G. 1·52) to drop into *tert*-butyl alcohol (Haitinger, *Sitz. W.* 77 [2] 428; *A.* 193, 366; *M.* 2, 286). Formed also in small quantity by saturating HNO_3 with isobutylene (H.). Pale-yellow oil, heavier than water. Dissolves in alkalis, and is reppd. by acids. Excess of water at 100° splits it up into

acetono and nitro-methane. Br unites, forming oily $C_4H_7Br_2NO_2$.—$NaC_4H_6NO_2$: powder, v. sol. water.

NITRO-ISOBUTYL-PHENOL $C_4H_9.C_6H_3(NO_2)(OH)$ [1:3:4]. [95°]. (290°) at 711 mm. Formed by boiling nitro-amido-isobutyl-benzene with dilute potash (Gelzer, *B.* 21, 2947). Red needles (from alcohol), v. sol. hot water.

Di-nitro-isobutyl-phenol $C_4H_9.C_6H_2(NO_2)_2OH$. [93°]. Formed from isobutyl-phenol [99°], HOAc, and HNO_3 (Studer, *A.* 211, 244; *B.* 14, 1474; Liebmann, *B.* 14, 1842). Sulphur-yellow needles (from alcohol). Yields di-nitro-amido-isobutyl-benzene on heating with NH_3Aq.

TRI-NITRO-ISOBUTYL-TOLUENE $C_6HMe(C_4H_9)(NO_2)_3$. *Artificial musk.* [97°]. Formed by heating isobutyl-toluene with HNO_3 and H_2SO_4 for 24 hours on a water-bath (Baur, *C. R.* 111, 238). White needles, sol. alcohol and ether. Its solutions smell like musk. Forms a crystalline compound with naphthalene [90°].

TRI-NITRO-ISOBUTYL-XYLENE $C_6Me_2(C_4H_9)(NO_2)_3$. [110°]. Formed by nitration of isobutyl-xylene (Baur, *C. R.* 111, 238). White needles. Its alcoholic solution smells like musk.

NITRO-CAMPHOLENIC ACID *v.* CAMPHOLENIC ACID.

NITRO-CAMPHOR *v.* CAMPHOR.

TETRA-NITRO-CARBAZOLE $C_{12}H_5(NO_2)_4NH$. Formed by nitrating carbazole (Graebe, *A.* 202, 26). Lemon-yellow crystals (from HOAc), insoluble in alcohol and ether.—$C_{12}H_5(NO_2)_4NK$: insol. water.

Four tetra-nitro-carbazoles have been described by Ciamician and Silber (*G.* 12, 277) as formed by the nitration of carbazole. The melting-points of three of them are 308°, above 320°, and about 285°, while the fourth decomposes before melting.

NITRO-CARBOXY-CINNAMIC ACID $C_6H_3(CH:CH.CO_2H)(NO_2)(CO_2H)$[1:2:4]. [287°] (Löw, *A.* 231, 371). Formed by nitrating carboxy-cinnamic acid. Hemispherical aggregates or regular tablets (from water). That the NO_2 is in the o- position is shown by the fact that, by Baeyer's synthesis, it gives rise to indigo di-carboxylic acid. Heated with conc. H_2SO_4 it does not turn blue. It yields a dibromido, which is converted by aqueous NaOH into nitro-carboxy-phenyl-propiolic acid.

NITRO-CARBOXY-PHENYL-PROPIONIC ACID $C_6H_3(NO_2)(CO_2H)CH:CH.CO_2H$ [3:1:4]? [192°]. Got by nitration (Widman, *B.* 22, 2273).

NITRO-CARVACROL $C_{10}H_{13}NO_3$ *i.e.* $C_6H_2(C_3H_7)Me(NO_2)(OH)$. [78°]. Formed from nitroso-carvacrol, KOH, and K_3FeCy_6 (Paterno a. Canzoneri, *G.* 10, 233). Needles, almost insol. water.

NITRO-CHLORO-derivatives *v.* CHLORO-NITRO-derivatives.

NITRO-CHLOROFORM *v.* TRI-CHLORO-NITRO-METHANE.

DI-NITRO-CHOLESTERIN $C_{26}H_{42}(NO_2)_2O$. [121°]. Obtained by nitration of cholesterin (Preis a. Raymann, *B.* 12, 224). Colourless needles, sl. sol. cold alcohol. By boiling a hot saturated solution of cholesterin in HOAc with HNO_3 (S.G. 1·54), Reinitzer (*M.* 9, 440) obtained a nitro- compound melting at 94°. By adding cholesterin (1 pt.) to a mixture of HOAc (10 pts.) and fuming HNO_3 (3 pts.), Latschinoff (*J. R.* 10, 360) obtained a compound crystallising in plates, decomposing at 180° without melting.

NITRO-CHOLESTERYL-CHLORIDE $C_{26}H_{42}(NO_2)Cl$. [148°–149°]. Colourless needles. Prepared by nitration of cholesteryl chloride (Preis a. Raymann, *B.* 12, 225).

NITRO-CHRYSENE *v.* CHRYSENE.

NITRO-CHRYSOQUINONE *v.* CHRYSOQUINONE.

NITRO-CINCHONAMINE *v.* CINCHONA BASES.

o-NITRO-CINNAMIC ACID $C_9H_7NO_4$ *i.e.* [2:1]$C_6H_4(NO_2)$.CH:CH.CO_2H. Mol. w. 193. [232°] (M.); [237°] (T. a. O.); [240°] (Baeyer, *B.* 13, 2257). Formed, together with the *p*-isomeride, by nitrating cinnamic acid (Beilstein a. Kuhlberg, *A.* 163, 126; Müller, *A.* 212, 124). Formed also from o-nitro-benzoic aldehyde, Ac_2O, and NaOAc (Gabriel a. Meyer, *B.* 14, 830).

Preparation.—1. Cinnamic acid (1 pt.) is dissolved in nitric acid (5 pts.); the mixture is poured upon snow, and the ppd. acids separated by means of alcohol (B. a. K.).—2. Cinnamic ether (10 g.) is dropped into fuming HNO_3 at 0°. The solution is poured at once into water at 0°. The *solid* pp. is washed with water, and treated with alcohol, which dissolves the *o*-, leaving the *p*- compound (Stuart, *C. J.* 43, 408). Fair yield (4 g.).—3. The product of nitration of cinnamic acid is etherified, and the o-nitro-cinnamic ether is separated from the *p*-isomeride by means of its greater solubility in ether (Tiemann a. Opermann, *B.* 13, 2060). The acid may then be obtained from its ether by hydrolysis with H_2SO_4 (Fischer a. Kuzel, *A.* 221, 265).

Properties.—Needles, insol. water, sl. sol. cold alcohol. Yields o-nitro-benzoic acid on oxidation by chromic acid mixture. Its solution in H_2SO_4 becomes blue on warming or on standing.

Salts. — CaA'_2 2aq: yellow needles. — BaA'_2 4aq: minute yellow needles.

Methyl ether MeA'. [73°].

Ethyl ether EtA'. [42°] (M.); [44°] (B.). Trimetric crystals, $a:b:c$ = ·927:1: ·517. Readily combines with bromine. Reduced by aqueous ammonium sulphide to carbostyril. In hot alcoholic solution tin and HCl reduce it to *o*-amido-cinnamic ether.

Chloride $C_6H_4(NO_2)$.CH:CH.COCl. [65°]. Crystalline solid (Fischer a. Kuzel, *B.* 16, 34).

m-Nitro-cinnamic acid [3:1]$C_6H_4(NO_2)$.CH:CH.CO_2H. [197°]. Prepared by heating *m*-nitro-benzoic aldehyde with Ac_2O and NaOAc (Schiff, *B.* 11, 1783; Tiemann a. Opermann, *B.* 13, 2060). Yellow needles. Yields *m*-nitro-benzoic acid on oxidation. A mixture of HNO_3 (2 pts. of S.G. 1·5) and conc. H_2SO_4 (5 pts.) converts it at 0° into ωm-di-nitro-styrene (Friedländer a. Lazarus, *A.* 229, 233). Reduced by tin and HCl to *m*-amido-cinnamic acid.—AgA': insoluble pp.

Ethyl ether EtA'. [79°].

p-Nitro-cinnamic acid [4:1] $C_6H_4(NO_2)$.CH:CH.CO_2H. [286°] (T. a. O.); [288°] (D.). Formed by nitration of cinnamic acid (Mitscherlich, *A. Ch.* [3] 4, 73; E. Kopp, *C. R.* 53, 634; Tiemann a. Opermann, *B.* 13, 2059).

Preparation.—From cinnamic acid (1 pt.) and cold HNO_3 (5 pts.). The acids produced are etherified, the *p*-ether, [139°], crystallising from

alcohol. It is saponified by H_2SO_4 (1 pt.), HOAc (1 pt.), and water (1 pt.) (Drewson, *A.* 212, 150).

Properties.—Prisms, v. sl. sol. boiling alcohol. Yields *p*-oxy-benzoic acid on oxidation.

Salts.—KA': very soluble crystals.—CaA'_2 3aq.—CaA'_2 2aq.—SrA'_2 5aq.—BaA'_2 3aq: minnte needles.—$MgA'_2$6aq: nodules.—HgA'_2.—$Hg_3A'_4Cl_2$ 3aq.—AgA': insoluble pp.

Methyl ether MeA'. [161°]. (286°).

Ethyl ether EtA'. [139°] (B. a. K.); [137°] (Müller, *A.* 212, 125). Combines with bromine forming a dibromide whence alcoholic potash produces two bromo-nitro-cinnamic ethers, melting at 63° and 93°. Reduced by tin and HCl to *p*-amido-cinnamic acid and *p*-amido-styrene (Bender, *B.* 14, 2359).

Anhydride $(C_6H_4(NO_2).CH:CH.CO)_2O$. Formed from the K salt and $POCl_3$ (Chiozza, *A. Ch.* [2] 39, 231). Melts under boiling water.

Amide $C_6H_4(NO_2).CH:CH.CONH_2$. [155°–160°] (Cahours, *A. Ch.* [3] 27, 452).

α-*m*-Di-nitro-cinnamic ether $C_6H_4(NO_2).CH:C(NO_2).CO_2Et$. Formed from *m*-nitro-cinnamic ether, HNO_3 (1 pt.) and H_2SO_4 (2 pts.) below 20° (Friedländer a. Lazarus, *A.* 229, 235). Thick plates (from ether). Insol. water and light petroleum.

Reactions.—1. With alcohol, on warming, it forms $C_6H_4(NO_2).CH(OEt).CH(NO_2).CO_2Et$, a colourless oil. When this is dissolved in ether and ammonia is passed in, a pp. of $C_6H_4(NO_2).CH(OEt).C(NH_4)(NO_2).CO_2Et$ is formed. This is soluble in water and gives pps. with many metallic salts. The compound $C_6H_4(NO_2).CH(OEt).CH(NO_2).CO_2Et$ is converted by the simultaneous action of bromine and NaOH into the ethyl derivative of di-bromo-di-nitro-α-phenyl-methyl-carbinol.—2. Boiled with water it forms alcohol, nitro-methane, CO_2, and *m*-nitro-benzoic aldehyde.

α*p*-Di-nitro-cinnamic acid [4:1] $C_6H_4(NO_2).CH:C(NO_2).CO_2H$. Formed from *p*-nitro-cinnamic acid, HNO_3, and H_2SO_4 at −10° to −20°. White plates. At 0° it decomposes into CO_2 and α*p*-di-nitro-styrene.

Methyl ether MeA'. [127°].

Ethyl ether EtA'. [110°]. Formed from *p*-nitro-cinnamic ether (1 pt.), HNO_3 (2 pts. of S.G. 1·5), and H_2SO_4 (4 pts.) (Friedländer a. Mähly, *A.* 229, 210). Thin plates (from benzene-ligroïn), v. sol. benzene, nearly insol. ligroïn.

Reactions.—1. CrO_3 in HOAc oxidises it to *p*-nitro-benzoic acid.—2. $K_2Cr_2O_7$ and HOAc forms *p*-nitro-benzoic aldehyde.—3. Boiling water decomposes it into alcohol, CO_2, *p*-nitro-benzoic aldehyde, and nitro-methane. Boiling dilute acids behave in the same way, only the nitro-methane appears as hydroxylamine.—4. A solution in conc. H_2SO_4 at 100° poured into water gives a pp. of *p*-nitro-benzaldoxim.—5. Boiling dilute (5 p.c.) Na_2CO_3 forms bright-yellow plates of $C_{14}H_{10}N_2O_3$ [188°], insol. water, dilute acids, and alkalis.—6. *Alcohol* unites forming $C_6H_4(NO_2).CH(OEt).CH(NO_2)CO_2Et$ [52°], whence the alcohol cannot be removed by heating at 110°, or even with dilute HCl at 90°. Methyl alcohol forms the corresponding $C_6H_4(NO_2).CH(OMe).CH(NO_2).CO_2Et$ [77°].—7. Tin and HCl reduce it to α*p*-diamido-phenyl-propionic ether and *p*-amido-phenyl-acetonitrile.

o-NITRO-CINNAMIC ALDEHYDE $C_9H_7NO_3$ *i.e.* [2:1] $C_6H_4(NO_2).CH:CH.CHO$. [127°]. Formed by boiling o-nitro-oxy-phenyl-propionic aldehyde with Ac_2O (Baeyer a. Drewson, *B.* 16, 2207). Formed also by condensation of o-nitro-benzoic aldehyde with aldehyde by means of dilute NaOH, the yield being 40 p.c. of the theoretical (Diehl a. Einhorn, *B.* 20, 2335).

Preparation.—25 g. of cinnamic aldehyde are slowly added to 500 g. of conc. H_2SO_4 containing 20 g. of KNO_3. The solution is precipitated in water, and the mixture of o- and *p*-nitro-cinnamic aldehydes is crystallised from alcohol with animal-charcoal. The product is dissolved in absolute alcohol and the boiling solution mixed with an equal volume of sodium bisulphite solution; the solution is quickly cooled and separates the greater part of the bisulphite compound of the *p*-isomeride, the remaining portion being salted out by the addition of NaCl; the filtrate contains the bisulphite of the o-isomeride. The two isomerides are obtained from their bisulphites by decomposing the latter in aqueous solution with H_2SO_4 (Diehl a. Einhorn).

Properties.—Colourless needles, v. sol. boiling water and $CHCl_3$, sl. sol. alcohol and ether. Combines with bisulphites. Yields quinoline on reduction. On heating with malonic acid in HOAc it yields $C_6H_4(NO_2).CH:CH.CH(OH).CH(CO_2H)_2$ [269°] and o-nitro-phenyl-butinene dicarboxylic acid $C_{12}H_9NO_6$ [213°] (Einhorn a. Gehrenbeck, *A.* 253, 374).

Phenyl-hydrazide $C_6H_4(NO_2).CH:CH.CH.N_2HPh$. [158°]. Needles.

Di-phenyl-hydrazide $C_6H_4(NO_2).CH:CH.CH.N_2Ph_2$. [69°]. Yellow crystals (Cornelius a. Homolka, *B.* 19, 2240).

***m*-Nitro-cinnamic aldehyde** $C_6H_4(NO_2).CH:CH.COH$. [116°]. Formed by eliminating H_2O from *m*-nitro-β-oxy-β-phenyl-propionic aldehyde (Göhring, *B.* 18, 720). Prepared by dissolving 100 pts. of *m*-nitro-benzaldehyde in 2,000 pts. of alcohol, diluting with 4,000 pts. of water, and adding at once to the milky liquid 35 pts. of coml. acetic aldehyde and 70 pts. of 10 p.c. aqueous NaOH. After 12 hours' standing the pp. is separated, pressed, washed, and crystallised; the yield is 50 p.c. of the theoretical (Kinkelin, *B.* 18, 483). Long thin prisms, v. sol. benzene and acetic acid, sl. sol. cold alcohol, ether, and hot water. Unites with Br forming $C_6H_4(NO_2).CHBr.CHBr.CHO$ [c. 90°].

Phenyl-hydrazide $C_6H_4(NO_2).C_2H_2.CH.N_2HPh$: [160°]; red tables.

***p*-Nitro-cinnamic aldehyde** [4:1] $C_6H_4(NO_2).CH:CH.CHO$. [142°]. Formed from *p*-nitro-benzoic aldehyde, aldehyde, and dilute NaOH, the resulting *p*-nitro-β-oxy-β-phenyl-propionic acid being boiled with HOAc (Göhring, *B.* 18, 372; Einhorn, *A.* 253, 348). Formed also, together with the o-isomeride, by nitration of cinnamic aldehyde (*v. supra*). Colourless needles. Combines with bisulphites. Condenses with acetone in presence of NaOH to $(C_6H_4(NO_2).CH:CH.CH:CH)_2CO$ [218°] and $C_6H_4(NO_2).CH:CH.CH:CH.CO.CH_3$ [132°], the last compound forming a phenyl-hydrazide melting at 210°.

Oxim $C_6H_4(NO_2).CH:CH.CH(NOH)$. [179°].

Phenyl-hydrazide $C_6H_4(NO_2).C_2H_2.CH:N_2HPh$. [181°]. Orange

red crystals, forming a red solution in conc. H_2SO_4.

Anilide $C_6H_4(NO_2).C_3H_3$:NPh. [133°].

o-**NITRO-CINNAMOYL-ACETO-ACETIC ETHER** $C_{15}H_{15}NO_6$ *i.e.* $C_6H_4(NO_2)$.CH:CH.CO.CHAc.CO_2Et. [120°]. Prepared by the action of o-nitro-cinnamoyl chloride on sodio-acetacetic ether (Fischer a. Kuzel, *B.* 16, 34). Yellow prisms. Sol. chloroform, sl. sol. alcohol and ether. It forms stable salts with alkalis, soluble in water with a reddish-yellow colour. Gives a dark-red colouration in alcoholic solution with Fe_2Cl_6. Boiled with 30 p.c. dilute H_2SO_4 it gives nitro-cinnamoyl-acetone.

o-**NITRO-CINNAMOYL-ACETONE** $C_6H_4(NO_2)$.CH:CH.CO.CH_2.CO.CH_3. [113°]. Prepared by boiling o-nitro-cinnamoyl-aceto-acetic ether with dilute H_2SO_4(30 p.c.). By longer boiling with dilute H_2SO_4 it is converted into o-nitro-styryl-methyl-ketone (o-nitro-benzylidene-acetone) (Fischer a. Kuzel, *B.* 16, 35). Fine yellow prisms. Sol. hot alcohol, sl. sol. cold alcohol, ether and CS_2. Gives a red colouration with Fe_2Cl_6. Dissolves in alkalis with a yellow colour.

NITRO-COCCUSIC ACID *v.* Tri-nitro-oxy-*m*-toluic acid.

NITRO-CODEÏNE *v.* Codeïne.

NITRO-COMENIC ACID *v.* Comenic acid.

NITRO-COMPOUNDS. Compounds containing the group nitroxyl (NO_2) directly united, by means of its nitrogen, to carbon. Their most general characteristic is that they yield amido-compounds on reduction (*v.* Amines and Amido-acids).

Formation.—1. Fatty nitro- compounds are formed by the action of silver nitrite on alkyl iodides. The isomeric nitrites are also formed in this reaction.—2. Aromatic nitro- compounds are formed by the direct action of nitric acid. The nitric acid must usually be concentrated, and its action is intensified by mixture with H_2SO_4. Phenols and oxy-acids may be nitrated by dilute nitric acid. Various anilides, boiled with dilute nitric acid (S.G. 1·029), are converted into di-nitro- derivatives of the base. Thus acetyl-methyl-aniline becomes di-nitro-methyl-aniline (Norton a. Allen, *B.* 18, 1995).—3. Aromatic amido- compounds may be converted into the corresponding nitro- compounds by the cuprous reaction (Sandmeyer, *B.* 20, 1495). For this purpose cupric sulphate (50 g.) is dissolved, together with glucose (15 g.), in boiling water (100 c.c.), and at once treated with soda (20 g.) dissolved in water (60 c.c.). After cooling, the mixture is neutralised with acetic acid. To this mixture the nitrate of the diazotised base (prepared from the base, HNO_3, and $NaNO_2$) is added in the cold.—4. Fatty compounds of the form X.CHBr.NO_2 are converted by KNO_2 in alkaline solution into salts of di-nitro- compounds of the form X.CK$(NO_2)_2$.

Reactions.—1. Acid reducing agents yield amido-compounds directly, but alkaline reducing agents (*e.g.* sodium-amalgam; zinc-dust and NaOH) acting upon aromatic nitro- compounds yield in the first place intermediate bodies, *v.* Azo- and Azoxy- compounds. In some cases where reduction is effected by tin and HClAq chlorination may take place; thus *m*-nitro-toluene gives a chloro-toluidine. The best general reducing agent is a solution of $SnCl_2$ in HClAq.—2. In the groups $CH_2.NO_2$ and $CH.NO_2$ hydrogen is displaceable by metals, and hence bodies containing these groups dissolve in alkalis. Such solutions yield, on addition of bromine, compounds containing the groups CHBr.NO_2 and CBrNO_2. The compounds X.CHBrNO_2 can further give rise to X.CNaBrNO_2 and X.CBr_2NO_2.—3. Primary fatty nitro- compounds yield hydroxylamine on heating with HClAq at 140°, *e.g.* $CH_3.CH_2NO_2 + H_2O = CH_3.CO.OH + H_2NOH$ (V. Meyer a. Locker, *A.* 180, 163).—4. *Nitrous acid* converts primary fatty nitro- compounds into nitrolic acids, containing the group CH(NO)(NO_2) or C(NOH).NO_2, which form red solutions with alkalis. Nitrous acid converts secondary fatty nitro- compounds into nitroles, containing the group C(NO)(NO_2), which are blue when in the liquid state or in solution.—5. Aromatic nitro- compounds may be reduced by heating with halogen acids. Thus nitro-benzene is reduced to aniline by heating with HIAq at 104°, by HBrAq at 185°, and by HClAq at 245° (Baumhauer, *A. Suppl.* 7, 212).—6. Boiling aqueous alkalis can in some cases displace NO_2 by hydroxyl. In this way o-di-nitro-benzene is converted into o-nitro-phenol.—7. When aromatic compounds containing two or more nitroxyls in one benzene nucleus are treated with alcoholic NH_3 and H_2S it is usual for one nitroxyl only to be reduced to amidogen.—8. Aromatic di- and tri- nitro- compounds frequently form molecular compounds with one another and with aromatic hydrocarbons.—9. The acetyl derivatives of nitrated aromatic amines, in which the NO_2 group is in the o- or *p*- position to the NHAc group (*e.g.* acetyl-o- and *p*- nitro-aniline, di-acetyl-nitro-*p*-phenylene diamine, diacetyl-nitro-*p*-naphthylene diamine, acetyl-o-nitro-β-naphthylamine, &c.), are readily soluble in cold aqueous KOH(1:2) with a deep-yellow colour. On standing saponification takes place, and the nitro- compound crystallises out. When the NO_2 group is in the *m*-position to the NHAc group, *e.g.* acetyl-*m*-nitraniline, acetyl-*m*-nitro-*p*-toluidine, &c., the substance is not soluble in aqueous KOH (Kleemann, *B.* 19, 336).

NITRO-o-COUMARIC ACID. *Methyl derivative* $C_{10}H_9NO_5$ *i.e.* [5:2:1] $C_6H_3(NO_2)$(OMe).CH:CH.CO_2H. [238°]. Formed by heating $C_6H_3(NO_2)$(OMe).CHO with NaOAc and Ac_2O (Schnell, *B.* 17, 1383). White needles, sl. sol. cold water, v. sol. alcohol and ether.—CaA'_2.—BaA'_2.—AgA'.

Anhydride $C_6H_3(NO_2)\Big<\begin{matrix}CH{:}CH\\ O\ \ .CO\end{matrix}$. *Nitro-coumarin.* [183°]. Formed by dissolving coumarin in cold fuming HNO_3 (Delalande, *A. Ch.* [3] 6, 343; Bleibtreu, *A.* 59, 191). Formed also by heating nitro-salicylic aldehyde [125°] with Ac_2O and NaOAc (Taege, *B.* 20, 2110). Needles. Oxidised by $KMnO_4$ to nitro-o-oxy-benzoic acid [228°]. Reduced by $FeSO_4$ and NH_3 to amido-coumarin [161°]. Bromine vapour gives a di-bromide [271°].

Nitro-o-coumaric acid $C_9H_7NO_5$ *i.e.* [3:2:1] $C_6H_3(NO_2)$(OH).CH:CH.CO_2H. [242°]. Formed by heating its methyl derivative with NaOHAq. Yellow crystals (from alcohol). Not converted into nitro-coumarin by boiling water or by HBrAq.

Methyl derivative $C_6H_3(NO_2)(OMe).CH:CH.CO_2H$. [193°]. Formed from the methyl derivative of (3,2,1)-nitro-salicylic aldehyde by Perkin's reaction (Miller a. Kinkelin, *B.* 22, 1709). Prisms (from alcohol). With methyl iodide it gives the ether $C_6H_3(NO_2)(OMe).CH:CH.CO_2Me$ [89°].

Nitro-o-coumarinic acid [3:2:1] $C_6H_3(NO_2)(OH).CH:CH.CO_2H$. [150°]. Formed by dissolving nitro-coumarin in boiling aqueous alkalis, and ppg. the cold solution by HCl (Miller a. Kinkelin, *B.* 22, 1706). Yellow prisms (from warm alcohol). On warming with water or alcohol it changes to its anhydride, nitro-coumarin. Its salts are explosive.—$Na_2C_9H_5NO_5$.—$BaC_9H_5NO_5$ $3\frac{1}{2}$aq.—$Ag_2C_9H_5NO_5$.

Methyl derivative $C_6H_4(NO_2)(OMe).CH:CH.CO_2H$. [136°]. Tables.

Methyl derivative of the methyl ether $Me_2C_9H_5NO_5$. [69°]. Formed from the Ag salt and MeI. Prisms. Readily reconverted into the acid, even by aqueous Na_2CO_3.

Anhydride $C_6H_3(NO_2)<\begin{matrix}CH:CH\\O.CO\end{matrix}$. *Nitro-coumarin.* [191°]. Formed from (3,2,1)-nitro-salicylic aldehyde (60 g.), NaOAc (90 g.), and Ac_2O (130 g.). Prisms (from benzene), or needles (from alcohol).

Nitro-*m*-coumaric acid [2:3:1] $C_6H_3(NO_2)(OH).CH:CH.CO_2H$. [218°]. Formed from *m*-amido-cinnamic acid by nitration and displacement of NH_2 by OH through the diazo-reaction (Luff, *B.* 22, 293). Needles (from water or alcohol).

Nitro-*m*-coumaric acid [4:3:1] $C_6H_3(NO_2)(OH).CH:CH.CO_2H$. [248°]. Formed by nitrating *m*-coumaric acid (Luff, *B.* 22, 296). Golden-yellow needles (from alcohol).

Methyl derivative $C_6H_3(NO_2)(OMe).CH:CH.CO_2H$. [218°]. Formed from [4,3,1] $C_6H_3(NO_2)(OMe).CHO$ by Perkin's reaction (Landsberg, *D. P. J.* 262, 139).

Methyl ether of the methyl derivative $C_6H_3(NO_2)(OMe).CH:CH.CO_2Me$. [143°]. Plates (Rieche, *B.* 22, 2359). Formed by nitration of $C_6H_4(OMe).CH:CH.CO_2Me$.

Ethyl ether of the methyl derivative $C_6H_3(NO_2)(OMe).CH:CH.CO_2Et$. [163°]. Needles (from alcohol) (Ulrich, *B.* 18, 2572).

***s*-Nitro-*m*-coumaric acid** [5:3:1] $C_6H_3(NO_2)(OH).CH:CH.CO_2H$. Accompanies the (2,3,1)-acid (*v. supra*). Crystals.

Nitro-*m*-coumaric acid [6:3:1] $C_6H_3(NO_2)(OH).CH:CH.CO_2H$. [216°]. Formed from acetyl-*m*-amido-cinnamic acid by nitration and displacement of NHAc by hydroxyl (Luff, *B.* 22, 292). Yellow powder.

Nitro-*p*-coumaric acid [3:4:1] $C_6H_3(NO_2)(OH).CH:CH.CO_2H$. [198°]. Formed from its methyl derivative by heating with HOAc saturated with HBr (Einhorn a. Grabfield, *A.* 243, 374). Yellow needles (from alcohol). Forms a dibromide [72°].

Ethyl ether EtA′. [109°].

Methyl derivative $C_6H_3(NO_2)(OMe).CH:CH.CO_2H$. [140°]. Formed from [3:4:1] $C_6H_3(NO_2)(OMe).CHO$, NaOAc, and Ac_2O. White needles. Yields a dibromide [178°], from which alkalis form the acid $C_6H_3(NO_2)(OMe).C_2HBr.CO_2H$ [205°].

Methyl ether of the methyl derivative $C_6H_3(NO_2)(OMe).CH:CH.CO_2Me$. [125°].

Ethyl ether of the methyl derivative $C_6H_3(NO_2)(OMe).CH:CH.CO_2Et$. [100°].

Di-nitro-o-coumaric acid. *Methyl derivative* $C_6H_2(NO_2)_2(OMe).CH:CH.CO_2H$. [193°]. Formed by nitrating the methyl derivative of o-coumaric acid (Perkin, *C. J.* 39, 416). Orange-brown needles (from alcohol).

Di-nitro-*m*-coumaric acid. *Methyl derivative of the methyl ether* $C_6H_2(NO_2)_2(OMe).CH:CH.CO_2Me$. [178°]. Formed by nitration (Rieche, *B.* 22, 2358). Yellowish needles (from alcohol). Yields on saponification $C_6H_2(NO_2)_2(OMe).CH:CH.CO_2H$, which decomposes at 215°.

NITRO-o-COUMARIC ALDEHYDE $C_6H_3(NO_2)(OH).CH:CH.CHO$. [200°]. Formed from $C_6H_3(NO_2)(OH).CHO$ [126°], aldehyde, and aqueous NaOH (Von Miller a. Kinkelin, *B.* 20, 1931; 22, 1716). Yellow needles. Forms a sodium derivative, crystallising in red tables, and a phenyl-hydrazide [235°].

Nitro-o-coumaric aldehyde [3:2:1] $C_6H_3(NO_2)(OH).CH:CH.CHO$. [133°]. Formed in the same way from the aldehyde $C_6H_3(NO_2)(OH).CHO$ [109°] (M. a. K.). Golden needles, v. sol. alcohol. Forms a sodium derivative, crystallising in red needles, a phenyl-hydrazide [157°], and a methyl derivative [115°].

NITRO-COUMARIN *v. Anhydride* of NITRO-COUMARIC ACID.

NITRO-o-CRESOL $C_7H_7NO_3$ *i.e.* $C_6H_3Me(OH)(NO_2)$ [1:2:3]. [70°]. Obtained, together with the (1,2,5)-isomeride, by nitrating o-cresol (Hofmann a. Miller, *B.* 14, 567; Staedel, *A.* 217, 50, 203; Rapp, *A.* 224, 175; Hirsch, *B.* 18, 1512). Formed also by boiling a dilute acid solution of o-diazotoluene sulphate (1 mol.) with HNO_3 (1 mol.) (Nölting a. Wild, *B.* 18, 1339; Deninger, *J. pr.* [2] 40, 299). Yellow prisms (from dilute alcohol), insol. water, v. sol. alcohol and ether; volatile with steam.—$KC_7H_6NO_3$: garnet-red trimetric tables.—AgA′: red needles.

Methyl ether MeA′. Oil.

Ethyl ether EtA′. Oil.

Nitro-o-cresol $C_6H_3Me(OH)(NO_2)$ [1:2:4]. [108°]. Formed by boiling diazotised nitro-o-toluidine [107°] with water (Nölting a. Collin, *B.* 17, 269). Yellow needles (from ligroïn). Its K, Ag, and NH_4 salts form yellow crystals.

Methyl ether. [74°] (Witt, *B.* 23, 3638).

Nitro-o-cresol $C_6H_3Me(OH)(NO_2)$ [1:2:5]. [95°] (N. a. W.); [80°–85°] (H.). Formed from nitro-o-toluidine [128°] by the diazo- reaction, or by merely boiling with conc. NaOHAq (Nevile a. Winther, *C. J.* 41, 423). Formed also by nitrating o-cresol (Hirsch, *B.* 18, 1512). Needles (from water), not volatile with steam. When crystallised from water it melts at 30°–34°, but it melts at 95° after crystallisation from ether.

Ethyl ether EtA′. [71°]. Formed by nitrating the ethyl derivative of o-cresol (Staedel, *A.* 217, 155, 203; Kayser, *B.* 15, 1133). Needles.

Nitro-o-cresol $C_6H_3Me(OH)(NO_2)$ [1:2:6]. [143°]. Formed from nitro-o-toluidine [92°] by the diazo- reaction (Ullmann, *B.* 17, 1961). Yellow needles (from water). Has an intensely sweet taste.

***c*-Nitro-*m*-cresol** $C_6H_3Me(OH)(NO_2)$ [1:3:4]. [56°]. Formed, together with the (1,3,6)-iso-

meride from *m*-cresol, HOAc, and HNO_3 (Staedel, *A.* 217, 51; *A.* 259, 223; Claus, *J. pr.* [2] 39, 63). Yellow monoclinic plates (from benzene), volatile with steam. Gives di-bromo-nitro-cresol [93°]. Its K salt forms red plates.

Ethyl ether EtA'. [51°]. White needles (from dilute alcohol).

s-Nitro-*m*-cresol $C_6H_3Me(OH)(NO_2)$ [1:3:5]. [91°]. Formed from nitro-*m*-toluidine by the diazo- reaction (Nevile a. Winther, *C. J.* 41, 417). Yellow crystals, not volatile with steam. Crystallises from water in a hydrated condition, and then melts at 62°.

Nitro-*m*-cresol $C_6H_3Me(OH)(NO_2)$ [1:3:6]. [129°]. Formed, together with the (1,3,4)-isomeride from *m*-cresol, HNO_3, and HOAc below 0° (Staedel, *A.* 259, 210; Claus, *J. pr.* [2] 39, 63). Formed also by oxidising nitroso-*m*-cresol with alkaline K_3FeCy_6 (Bertoni, *G.* 12, 304). Colourless crystals, not volatile with steam. Gives di-bromo-nitro-cresol [143°]. Reduces to amido-cresol [174°].—KA' 2aq: yellow plates.—NaA' 2aq.

Ethyl ether EtA'. [54°].

Nitro-*p*-cresol $C_6H_3Me(OH)(NO_2)$ [1:4:3]. [34°]. Formed from acetyl-*p*-toluidine by nitrating and boiling the product with conc. NaOHAq (Wagner, *B.* 7, 537; Nevile a. Winther, *C. J.* 41, 426), by the action of nascent nitrous acid on *p*-toluidine (Deninger, *J. pr.* [2] 40, 299), or by boiling *p*-diazotoluene sulphate (1 mol.) with HNO_3 (1 mol.) (Nölting a. Wild, *B.* 18, 1339). Formed also by nitrating *p*-cresol (Armstrong a. Thorpe, *B. A.* 1875, 112; Hofmann a. Miller, *B.* 14, 572; Staedel, *A.* 217, 54). Yellow crystals (from benzene), volatile with steam.—NaA'.—AgA'.

Methyl ether MeA'. (274°).

Ethyl ether EtA'. (275°–285°).

Benzyl ether C_7H_7A'. [54°]. Formed from benzyl chloride and the Ag salt (Frische, *A.* 224, 142).

o-*Nitro-benzyl ether* [163°].

Nitro-*p*-cresol $C_6H_3Me(OH)(NO_2)$ [1:4:2]. [77°]. Formed from the corresponding nitro-*p*-toluidine by the diazo- reaction (Nevile a. Winther, *C. J.* 41, 422; Knecht, *A.* 215, 87). Yellow needles (from ligroïn).

Methyl ether MeA'. (267°). Oil.

Di-nitro-*o*-cresol $C_6H_2Me(OH)(NO_2)_2$[1:2:3:5]. [86°]. S. (alcohol). 7·8 at 15°. Formed by heating (1,2,5)-*o*-cresol sulphonic acid with dilute HNO_3 (Nevile a. Winther, *C. J.* 37, 631; 41, 422). Formed also by boiling o-diazo-toluene disulphonic acid with dilute HNO_3 (N. a. W.), or from o-diazo-toluene nitrate and HNO_3 (Nölting a. De Salis, *B.* 14, 987; *A. Ch.* [6] 4, 105). Obtained also from the corresponding di-nitro-toluidine (N. a. S.), and by nitrating *o*-cresol and the (3,1,2)- and (5,1,2)-nitro-o-cresols (Hirsch, *B.* 18, 1512; Barr, *B.* 21, 1543). Formed also from $C_6H_2Me(OH)Br_2$ and fuming HNO_3 (Claus, *J. pr.* [2] 38, 327). Yellow needles, slightly volatile with steam. Yellow dye.—KA'*x*aq: yellow crystals.

Salts.—BaA'$_2$.—BaA'$_2$3½aq.—AgA'.

Ethyl ether EtA'. [51°]. Obtained by nitrating $C_6H_4Me(OEt)$[1:2] (Staedel, *B.* 14, 899; *A.* 217, 153; 259, 219), or from the Ag salt and EtBr (N. a. S.). Yields di-nitro-*o*-toluidine [210°] on heating with alcoholic NH_3 at 130° (Van Romburgh, *R. T. C.* 3, 397).

p-Nitro-benzyl ether $C_6H_4(NO_2).CH_2A'$. [145°]. Obtained by nitrating the benzyl ether of *o*-cresol (Staedel). Needles.

Di-nitro-*m*-cresol $C_6H_2Me(OH)(NO_2)_2$[1:3:4:5or2]. [99°]. Formed from di-nitro-amido-cresol by elimination of NH_2 (Nietzki a. Ruppert, *B.* 23, 3479). Needles.

Ethyl ether EtA'. [22°].

Di-nitro-*m*-cresol $C_6H_2Me(OH)(NO_2)_2$[1:3:4:6].

Ethyl ether EtA'. [97°]. Formed by nitrating ethyl-nitro-cresol [51°] (Staedel, *A.* 259, 226).

Di-nitro-*p*-cresol $C_6H_2Me(OH)(NO_2)_2$[1:4:3:5]. [85°]. A product of the action of nitrous acid on *p*-toluidine nitrate, on amido-toluic acid [167°], and on *p*-toluidine disulphonic acid (Beilstein a. Kreusler, *A.* 144, 183; Martius a. Wichelhaus, *Z.* [2] 5, 440; *B.* 2, 207; Richter, *A.* 230, 323). Formed also by boiling di-nitro-*p*-toluidine with aqueous NaOH (Wagner, *B.* 7, 536); by nitrating *p*-cresol and (3,1,4)-nitro-*p*-cresol (Armstrong a. Field, *B.* 6, 974; Frische, *A.* 224, 139); or boiling diazo-*p*-toluene sulphonate with dilute HNO_3 (Nevile a. Winther, *C. J.* 37, 631). Yellow needles (from dilute alcohol).—NaA': red needles. S. 2·3 at 17°.—KA'. S. 1·5 at 16° (M. a. W.); ·99 at 17° (Staedel). Used as a dye (gold-yellow). A sample of 'Victoria yellow' was found by Martius and Wichelhaus to consist of a salt of a dinitrocresol [110°]. Victoria-yellow is poisonous (Weyl, *B.* 20, 2835).—BaA'$_2$.—AgA'. S. ·29 at 17°.

Methyl ether MeA'. [122°].

Ethyl ether EtA'. [73°]. Formed by nitrating ethyl-*p*-cresol (Staedel, *A.* 217, 161). When heated with alcoholic NH_3 it yields di-nitro-*p*-toluidine [168°] (Romburgh, *R. T. C.* 3, 405).

Benzoyl ether C_7H_7A'. [109°].

p-Nitro-benzyl ether [186°].

Di-nitro-*p*-cresol $C_6H_2Me(OH)(NO_2)_2$. Obtained by the action of excess of nitrous acid on $C_6H_3Me(OH)(NO_2)$[1:4:2] (Knecht, *A.* 215, 90). Yellow needles (from water). Does not melt when heated but forms a violet sublimate

Tri-nitro-o-cresol $C_6HMe(OH)(NO_2)_3$. [102°] Formed by heating nitro-o-diazo-toluene nitrate with nitric acid (S.G. 1·33) (Nölting a. Collin, *B.* 17, 270). Orange prisms (from acetone). Yields $NaNO_2$ when heated with NaOHAq. With naphthalene it forms $(C_7H_5N_3O_7)C_{10}H_8$ [106°].

Tri-nitro-*m*-cresol $C_6HMe(OH)(NO_2)_3$[1:3:2:4:6]. [106°]. S. 2·2 at 20°; ·8 at 100° (Duclos). Formed by nitration of *m*-cresol or its sulphonic acid (Duclos, *A.* 109, 141; Nölting a. De Salis, *B.* 14, 987; 15, 1861; *A. Ch.* [6] 4, 118; Beilstein a. Kellner, *A.* 128, 165). Formed also by the action of HNO_3 on nitroso-*m*-cresol (Wurster a. Riedel, *B.* 12, 1799); by heating nitro-coccusic acid with water at 180° (Liebermann a. Dorp, *A.* 163, 101; Kostanecki a. Niementowski, *B.* 18, 251); and by the action of cold conc. HNO_3 on (2,6,3,4,1)-di-iodo-toluquinone (Kehrmann, *J. pr.* [2] 39, 392). Yellow needles (from water). Forms with naphthalene a compound $(C_7H_5N_3O_7)C_{10}H_8$ [127°].—NH_4A'. Converted by warm aqueous KCy into

purple crystals of potassium 'cresyl-purpurate' $KC_9H_6N_5O_6$ (Sommaruga, *Z.* 1870, 657).—KA': yellow needles.—Pb(OH)A'.—AgA': prisms.

Ethyl ether EtA'. [72°] (N. a. S.); [75°] (Staedel, *A.* 259, 221, 227). Converted by cold alcoholic NH_3 into tri-nitro-toluidine [126°].

NITRO-o-CRESOL SULPHONIC ACID $C_7H_7NSO_6$ *i.e.* $C_6H_2Me(OH)(NO_2)SO_3H$. Formed from (1,2,5)-*o*-toluidine sulphonic acid by dissolving in fuming HNO_3 and boiling the resulting nitro-diazo-toluene sulphonic anhydride with water (Hayduck, *A.* 172, 218). Deliquescent. —$BaC_7H_5NSO_6$ $3\frac{1}{2}$aq.—$Ba(C_7H_6NSO_6)_2$ 5aq.

Nitro-*p*-cresol sulphonic acid. *Ethyl derivative* $C_6H_2Me(OH)(NO_2).SO_3H$[1:4:2:5]. Formed by heating nitro-diazo-toluene sulphonic acid with NaOEt (Foth, *A.* 230, 306). Needles. —BaA'_2 4aq: yellow plates.

NITRO-CRYPTOPINE *v.* CRYPTOPINE.

NITRO-CUMENE $C_9H_{11}NO_2$ *i.e.* $C_6H_4Pr(NO_2)$. [−35°]. Formed from cumene and fuming HNO_3 at 0° (Pospekhoff, *J. R.* 18, 52; *Bl.* [2] 45, 178; *cf.* Cahours, *C. R.* 25, 552; 26, 315; Nicholson, *C. J.* 1, 2; Ritthausen, *J. pr.* 61, 79). Oil, volatile with steam.

Nitro-ψ-cumene $C_6H_2Me_3(NO_2)$[1:3:4:5]. [20°]. Formed by eliminating NH_2 from nitro-ψ-cumidine (Edler, *B.* 18, 629). Large thick prisms, volatile with steam.

Nitro-ψ-cumene $C_6H_2Me_3(NO_2)$. [71°]. (265°). Formed from ψ-cumene and cold fuming HNO_3 (Schaper, *Z.* [2] 3, 12; Fittig a. Laubinger, *Z.* [2] 4, 577). Colourless needles (from alcohol), volatile with steam. Yields on oxidation $C_6H_2Me_2(NO_2)CO_2H$ [195°].

Tri-nitro-cumene $C_9H_9N_3O_6$ *i.e.* $C_6H_2Pr(NO_2)_3$ [1:2:4:6]. [109°]. Formed from cumene, HNO_3, and H_2SO_4 (Fittig, *A.* 149, 328). Needles, sl. sol. cold alcohol.

Tri-nitro-ψ-cumene $C_6Me_3(NO_2)_3$. [185°]. Formed by nitrating ψ-cumene (Fittig a. Laubinger, *A.* 151, 261). Prisms (from benzene), almost insol. boiling alcohol. By passing hydrogen sulphide into its boiling ammoniacal alcoholic solution, nitro-ψ-cumidine-sulphonic acid $C_6Me_3(NO_2)(NH_2)SO_3H$ [1:3:4:2:6:5] is formed (Mayer, *B.* 19, 2312; 20, 966).

NITRO-ψ-CUMENOL $C_6HMe_3(OH)(NO_2)$ [1:3:4:6:2]. [48°]. Obtained by evaporating an alcoholic solution of the nitrate to dryness, and distilling the residue with steam (Auwers, *B.* 17, 2979; 18, 2658). Long reddish-yellow crystals (from alcohol), m. sol. hot water. Reconverted into the nitrate by warming with dilute HNO_3.

Nitrate $C_6HMe_3(NO_2).O.NO_2$. [84°]. Formed from ψ-cumenol and cold fuming HNO_3. Trimetric tables or prisms, insol. water, sl. sol. cold alcohol.

Methyl ether $C_6HMe_3(NO_2)OMe$. [42°].

Nitro-cumenol $C_6H_3Pr(NO_2)(OH)$. Oil, formed, together with an isomeride [86°], by nitrating $C_6H_4Pr(OH)$[1:2] (Fileti, *G.* 16, 120).

Di-nitro-ψ-cumenol $C_6Me_3(OH)(NO_2)_2$ [1:3:4:6:2:5]. [112°]. Formed by passing NH_3 into an alcoholic solution of the nitrate of nitro-ψ-cumenol [84°]. Yellow crystals, insol. water. Forms a red solution in alkalis.

NITRO-CUMIDINE $C_9H_{12}N_2O_2$ *i.e.* $C_6H_3(C_3H_7)(NO_2)(NH_2)$. [below 100°]. Formed by reducing di-nitro-cumene with alcoholic ammonium sulphide (Cahours, *C. R.* 24, 557; 26, 315). Yellow scales. Forms a crystalline benzoyl derivative.—B'HCl aq.—$B'_2H_2SO_4$aq: needles.

Nitro-ψ-cumidine $C_6HMe_3(NO_2)(NH_2)$ [1:3:4:5:6]. [47°]. Formed from acetyl-ψ-cumidine by nitration and saponification (Edler, *B.* 18, 629). Red needles (from dilute alcohol).

Acetyl derivative [194°] (E.); [204°] (Auwers, *B.* 18, 2661). Prisms (from alcohol).

Nitro-ψ-cumidine $C_6HMe_3(NO_2)(NH_2)$. [137°]. Formed by treating tri-nitro-ψ-cumene with alcoholic ammonium sulphide (Fittig a. Laubinger, *A.* 151, 262). Yellow needles.—B'HCl.—$B'_2H_2SO_4$ aq.

Nitro-ψ-cumidine *Acetyl derivative* $C_6HMe_3(NO_2)NHAc$. [131°]. Formed by nitration of acetyl-ψ-cumidine [112°] (Engel, *B.* 18, 2231). Yellow needles.

Di-nitro-ψ-cumidine $C_6Me_3(NO_2)_2(NH_2)$. [78°]. Formed from acetyl-ψ-cumidine [112°] by nitration and saponification (Engel, *B.* 18, 2232). Yellow needles.

Acetyl derivative. [204°]. Needles.

Di-nitro-ψ-cumidine $C_6Me_3(NO_2)_2(NH_2)$ [1:3:4:2:5:6]. [183°]. Obtained from acetyl-ψ-cumidine [164°] by nitration and saponification (Auwers, *B.* 18, 2661). Orange needles (from alcohol).

Acetyl derivative. [280°]. Sl. sol. alcohol.

NITRO-ψ-CUMIDINE SULPHONIC ACID $C_9H_{12}N_2SO_5$ *i.e.* $C_6Me_3(NO_2)(NH_2)(SO_3H)$ [1:3:4:2:6:5]. Formed by passing H_2S into a boiling solution of tri-nitro-ψ-cumene in alcoholic NH_3, and also by heating nitro-ψ-cumidine with $ClSO_3H$ at 165° (Mayer, *B.* 19, 2312; 20, 966). Colourless plates. Melts, with decomposition at 240°-260°. Forms an amorphous acetyl derivative $C_9H_{11}AcN_2SO_5$ [c. 230°].

NITRO-CUMINIC ACID $C_{10}H_{11}NO_4$ *i.e.* $C_6H_3Pr(NO_2).CO_2H$ [4:2:1]. [99°]. Formed by boiling nitro-isopropyl-cinnamic acid with CrO_3 in HOAc (Widman, *B.* 19, 269). Tables or monoclinic prisms.

Nitro-cuminic acid $C_6H_3Pr(NO_2).CO_2H$ [4:3:1]. [159°]. Obtained by nitration of cuminic acid (Gerhardt a. Cahours, *A. Ch.* [3] 1, 73; 25, 36; Fileti, *G.* 11, 15; Alexejeff, *J. R.* 17, 112; *Bl.* [3] 2, 727). Formed also by oxidation of its aldehyde (nitro-cuminol) [54°] (Lippmann a. Strecker, *B.* 12, 77; Widman, *B.* 15, 2547) and of nitro-cumyl methyl ketone (Widman, *B.* 21, 2232). Yellowish scales (from alcohol), turned red by sunlight, especially when dissolved in benzene (Alexejeff, *Bl.* [2] 45, 178).—CaA'_2.—PbA'_2.—AgA'.

Ethyl ether EtA'. (290°). Oil.

Nitrile $C_6H_3Pr(NO_2).CN$. [71°]. Formed by nitrating cumonitrile (Czumpelik, *B.* 2, 183).

Nitro-*n*-cuminic acid $C_6H_3Pr(NO_2).CO_2H$ [4:3:1]. [113°]. Formed by oxidation of nitro-*n*-cumyl methyl ketone by $KMnO_4$ (Widman, *B.* 21, 2231). Formed also by nitration of *n*-cuminic acid (Körner, *A.* 216, 230). Colourless needles (from hot water), turned brown by light.—BaA'_2 4aq.—SrA'_2 5aq.

Methyl ether MeA'. [64°]. Crystals from alcohol) (Abenius, *J. pr.* [2] 40, 438).

Nitro-n-cuminic acid $C_6H_3Pr(NO_2).CO_2H$ [4:2:1]. [157°]. Formed by oxidation of nitro-propyl-cinnamic acid (Widman, *B.* 19, 276). Tables (from dilute alcohol), sl. sol. water.

Di-nitro-cuminic acid $C_6H_2Pr(NO_2)_2.CO_2H$. [221°]. Formed by nitration of cuminic acid (Cahours, *A.* 69, 243; Lippmann a. Strecker, *B.* 12, 78). Reddish crystals.—BaA'_2.—CaA'_2.—AgA' aq (Kraut, *C. C.* 1859, 85).

Ethyl ether EtA'. [77·5°].

Amide $C_9H_9(NO_2)_2.CONH_2$. Crystals.

Di-nitro-ψ-cuminic acid $C_6Me_3(NO_2)_2.CO_2H$ [1:3:4:2:5:6]. [205°]. *Di-nitro-durylic acid.* Formed by nitrating ψ-cuminic acid (Gissmann, *A.* 216, 207; Nef, *A.* 237, 8). Prisms (from dilute alcohol).—CaA'_2 3aq.—BaA'_2 3aq.

NITRO-CUMINIC ALDEHYDE $C_{10}H_{11}NO_3$ *i.e.* $C_6H_3Pr(NO_2).CHO$ [4:2:1]. *Nitro - cuminol.* Formed by oxidising nitro-isopropyl-cinnamic acid with $KMnO_4$ (Einhorn a. Hess, *B.* 17, 2019). Oil, volatile with steam. With acetone and NaOHAq it produces di-isopropyl-indigo.

Nitro-cuminic aldehyde $C_6H_3Pr(NO_2)CHO$ [4:3:1]. [54°]. Formed by nitration of cuminic aldehyde (Lippmann a. Strecker, *B.* 12, 76; Widman, *B.* 15, 166). Triclinic prisms. Combines with bisulphites.

NITRO-ψ-CUMOQUINONE $C_9H_9NO_4$ *i.e.* $C_6Me_3O_2(NO_2)$ [1:3:4:2:5:6]. [113°]. Formed by heating ψ-cumoquinone carboxylic acid with HNO_3 (S.G. 1·4) at 100° for half an hour (Nef, *C. J.* 53, 428; *A.* 237, 17). Yellow plates, which may be sublimed. Heated with alcoholic SO_2 in sealed tubes it yields $C_6Me_3(OH)_2(NO_2)$ [106°].

NITRO-CUMYL-ACRYLIC ACID *v.* NITRO-PROPYL-CINNAMIC ACID.

NITRO-CUMYL METHYL KETONE $C_{11}H_{13}NO_2$ *i.e.* [1:2:4] $C_6H_3Pr(NO_2).CO.CH_3$. *Nitro-aceto-cumene.* [49°]. Formed by nitrating cumyl methyl ketone in the cold (Widman, *B.* 21, 2227). Prisms, v. sol. benzene, sl. sol. ligroïn.

Oxim $C_6H_3Pr(NO_2).C(NOH).CH_3$. [117°].

Phenyl-hydrazide [138°].

Nitro-n-cumyl methyl ketone [1:2:4] $C_6H_3Pr(NO_2).CO.CH_3$. Formed by nitrating n-cumyl methyl ketone (W.). Oil.

Oxim $C_9H_{10}(NO_2).C(NOH).CH_3$. [86°].

Phenyl hydrazide [139°].

NITRO-n-CUMYL-PROPIONIC ACID $C_6H_3Pr(NO_2).CH_2.CH_2.CO_2H$[4:3:1]. [99°]. Formed by nitration (Widman, *B.* 19, 2776). Crystals (from dilute HOAc).

NITRO-CYMENE $C_{10}H_{13}NO_2$ *i.e.* $C_6H_3MePr(NO_2)$ [1:4:2]. S.G. $\frac{15}{}$ 1·085. Formed by nitrating cymene (Barlow, *A.* 98, 245; Landolph, *B.* 6, 937; Fittica, *A.* 172, 314; Widman, *B.* 19, 584; Söderbaum a. Widman, *B.* 21, 2126). Yellow oil. Oxidised by $KMnO_4$ to nitro-oxy-isopropyl-benzoic acid and terephthalic acid.

Nitro-isocymene $C_6H_3MePr(NO_2)$ [1:3:x]. Formed from m-isocymene and fuming HNO_3 (Kelbe a. Warth, *A.* 221, 161). Oil, volatile with steam, but decomposed on distillation. Yields nitro-toluic acid [214°] on oxidation.

Di-nitro-cymene $C_6H_2MePr(NO_2)_2$. [54°]. Formed by nitrating cymene (Kraut, *A.* 92, 70). Got also from di-nitro-amido-cymene (Mazzara, *G.* 19, 160). Iridescent tablets (from alcohol).

Di-nitro-cymene [78°]. Formed from di-nitroso-cymene [72°] and HNO_3 (S.G. 1·35) (Kehrmann a. Messinger, *B.* 23, 3562). Crystals, v. sol. alcohol.

Di-nitro-cymene $C_{10}H_{12}(NO_2)_2$. S.G. $\frac{18}{}$ 1·206. Formed by nitrating cymene from ptychotis oil (Landolph). Oil, volatile with steam.

Di-nitro-cymene $C_{10}H_{12}(NO_2)_2$. [250°]. Got from a coal-tar cymene (Rommier, *Bl.* [2] 19, 434).

Tri-nitro-cymene $C_6HMePr(NO_2)_3$. [119°]. Formed by nitrating cymene (from camphor) (Fittig, *A.* 145, 142). Thin plates.

Tri-nitro-isocymene $C_6HMePr(NO_2)_3$. [73°]. Formed by nitration of m-isocymene (Kelbe, *A.* 210, 54). Yellow leaflets, smelling like musk.

NITRO-CYMENE SULPHONIC ACID $C_6H_2MePr(NO_2)SO_3H$[1:4:6:2]. Formed from cymene by sulphonation and nitration (Errera, *G.* 19, 533).—BaA'_2 aq.—MgA'_2 5aq.

Amide [139°]. Scales.

Nitro-cymene disulphonic acid $C_{10}H_{13}NS_2O_8$ *i.e.* $C_6HMePr(NO_2)(SO_3H)_2$. Formed from nitro-cymene and $ClSO_3H$ (Leone, *G.* 11, 512). Not obtained pure.—BaA'' 3½aq.—PbA'' 4½aq: needles.

NITRO-ISOCYMIDINE $C_{10}H_{14}N_2O_2$ *i.e.* $C_6H_2Me(C_3H_7)(NO_2)(NH_2)$. Formed by heating its phthalyl derivative with conc. HClAq at 180° (Kelbe a. Warth, *A.* 221, 176). Oil, volatile with steam.

Benzoyl derivative [177°]. Formed by nitrating benzoyl-isocymidine (K. a. W.). Needles (from alcohol).

Phthalyl derivative $C_{10}H_{12}(NO_2).N:C_2O_2:C_6H_4$. [167°]. Formed by nitrating phthalyl-isocymidine. Needles.

NITRODECOIC ACID $C_9H_{18}(NO_2).CO_2H$. A product of the action of boiling HNO_3 on the acids of cocoanut oil (Wirz, *A.* 104, 291).

NITRO-DRACYLIC ACID is p-NITRO-BENZOIC ACID.

NITRO-DULCITE *v.* DULCITE.

NITRO-c-DURENE $C_{10}H_{13}NO_2$ *i.e.* $C_6HMe_4(NO_2)$ [1:2:3:4:5]. *Nitro-prehnitene.* [61°]. (295° i.V.). Formed by the action of HNO_3 on c-durene (Töhl, *B.* 21, 905). Needles. Yields on reduction c-duridine [70°].

Di-nitro-c-durene $C_6Me_4(NO_2)_2$ [1:2:3:4:5:6]. [178°]. Formed from c-durene, HNO_3, and H_2SO_4 in the cold (Jacobsen, *B.* 19, 1214) and also from penta-methyl-benzene and fuming HNO_3 (Gottschalk, *B.* 20, 3287). Yellowish needles or prisms (from alcohol).

Di-nitro-durene $C_6Me_4(NO_2)_2$ [1:2:4:5:3:6]. [205°]. Formed from durene and conc. HNO_3 at 0° (Fittig a. Jannasch, *Z.* 1870, 162; Nef, *A.* 237, 3; *C. J.* 53, 428). Colourless prisms, sl. sol. alcohol.

Di-nitro-isodurene $C_6Me_4(NO_2)_2$ [1:2:3:5:4:6]. [156°]. Prepared from isodurene, HNO_3, and H_2SO_4 (Jacobsen, *B.* 15, 1853). Prisms, sl. sol. cold alcohol.

NITRO-DURENOL $C_6Me_4(NO_2)OH$. [130°]. Formed by nitration of durenol with ordinary HNO_3 at 0°. Yellow crystals. V. e. sol. alcohol, nearly insol. water. Dissolves in alkalis with a dark-yellow colour (Jacobsen a. Schnapauff, *B.* 18, 2844).

NITRO-c-DURIDINE $C_6Me_4(NO_2)(NH_2)$ [1:2:3:4:5:6]. [131°]. Formed by reducing di-nitro-c-durene with alcoholic ammonium sulphide (Töhl, *B.* 21, 904). Red

needles, sol. alcohol. Yields, on reduction, $C_6Me_4(NH_2)_2$ [140°].

NITRO-ERYTHRITE *v.* ERYTHRITE TETRA-NITRATE.

NITRO-ETHANE $C_2H_5NO_2$ *i.e.* $CH_3.CH_2.NO_2$. Mol. w. 75. (114°). S.G. $\frac{15}{15}$ 1·0561; $\frac{25}{25}$ 1·0461 (Perkin, *C. J.* 55, 689). M.M. 2·837. S.V. 80·3 (Schiff; Lossen, *A.* 254, 73). H.F.p. 26,880. H.F.v. 25,140 (Thomsen, *Th.*). Formed by adding EtI to cold silver nitrite and subsequently distilling from a water-bath (V. Meyer, *B.* 5, 399; *A.* 171, 1; 175, 88; Götting, *A.* 243, 115; Kissel, *J. R.* 1882, 226). Formed also by distilling $KEtSO_4$ with $NaNO_2$, the yield being 6 p.c. of the theoretical (Lauterbach, *B.* 11, 1225), and by the action of $AgNO_2$ on potassium chloro-propionate (Kolotoff, *Bl.* [2] 47, 169). Oil, with pleasant odour. With alcoholic soda it gives an amorphous pp. of C_2H_5ONa, a salt which is very soluble in water, forming a solution in which $HgCl_2$ ppts. crystalline $C_2H_4(NO_2)HgCl$. The solution of sodium nitro-ethane gives with $FeCl_3$ a blood-red colour, with $CuSO_4$ a green solution, and with $AgNO_3$ a white pp. rapidly turning black.

Reactions.—1. *Iron* and *acetic acid* reduce it to ethylamine.—2. When mixed with potash and KNO_2, and H_2SO_4 is slowly added, there is formed ethyl-nitrolic acid $CH_3.C(NOH).NO_2$, [81°], the alkaline salts of which form deep-red solutions (V. Meyer, *B.* 7, 425).—3. Fuming H_2SO_4 yields ethane *s*-di-sulphonic acid.—4. HClAq (S.G. 1·14) at 140° splits it up into hydroxylamine and HOAc (Meyer a. Locher, *A.* 180, 163).—5. NaOEt and EtI form oily C_5H_7NO (168°) (Götting). NaOMe and MeI form C_4H_5NO (c. 155°). According to Socoloff (*J. R.* 20, 579) alcoholic soda forms C_6H_9NO (175°) and the presence of alkyl iodides does not affect the product.—6. $ZnEt_2$ followed by water forms di-ethyl-hydroxylamine and other products (Kissel, *J. R.* 1887, 109).—7. *Benzoyl chloride* forms di-benzoyl-hydroxylamine and di-acetyl-hydroxylamine (Kissel, *J. R.* 1882, 40).

Constitution.—The constitution of nitro-ethane has been discussed by Victor Meyer (*B.* 5, 404; 8, 30; *A.* 244, 222); Geuther (*B.* 7, 1620); Alexejeff (*Bl.* [2] 46, 266); Socoloff (*Bl.* [2] 47, 166); Bevad (*J. R.* 20, 125), and others.

Di-nitro-methane $CH_3.CH(NO_2)_2$. (186° cor.). S.G. $\frac{23·5}{}$ 1·3503. Formed by the action of KNO_2 and alcoholic potash on bromo-nitro-ethane (Ter Meer, *A.* 181, 1). Formed also by the action of conc. HNO_3 on di-ethyl ketone and on methyl-acetoacetic ether (Chancel, *Bl.* [2] 31, 504; *C. R.* 96, 1466). Oil, with sweet taste. Reduced by tin and HClAq to hydroxylamine, NH_3, and HOAc. Reduced by sodium-amalgam to ethyl-azaurolic acid.—$CH_3.CK(NO_2)_2$: yellow monoclinic crystals, m. sol. cold water, insol. alcohol. Explodes when struck. Its aqueous solution gives a reddish-brown pp. with $FeCl_3$, a pale-blue pp. with $CuSO_4$, and a light-brown pp. with $HgCl_2$.—AgA′: lustrous yellow plates.

Tri - nitro - ethane (?) $CH_3.C(NO_2)_3$. [55°]. Formed from methyl-malonic acid and HNO_3 (Franchimont, *R. T. C.* 5, 281). Crystals.

Tetra-nitro-ethane (?). *Potassium derivative* $C_2K_2(NO_2)_4$. Formed from di-bromo-tetra-nitro-ethane, potash, and ammonium sulphide (Villiers, *C. R.* 97, 258; 98, 431). Crystals, which decrepitate below 100° and detonate at 200°, or even when treated with dilute acids.

NITRO - ETHENYL - TRI - AMIDO-BENZENE $C_8H_8N_2O_4$ *i.e.*
[1:2:3:4] $C_6H_2(NO_2)(NH_2)\lessdot{}^{NH}_{N}\gtrdot C.CH_3$. [295°–300°]. Formed by heating di-acetyl-di-nitro-*p*-phenylene-diamine with alcoholic NH_3 at 150° (Nietzki a. Hagenbach, *B.* 20, 331; *cf.* Biedermann a. Ledoux, *B.* 7, 1532). Red needles.

Nitro - di - ethenyl - tetra - amido - benzene $C_{10}H_9O_2N_5$ *i.e.*
[5:1:2:3:4] $C_6H(NO_2)\left(\lessdot{}^{NH}_{N}\gtrdot CMe\right)_2$. [276°].
Formed by nitration of di-ethenyl-tetra-amido-benzene (Nietzki a. Hagenbach, *B.* 20, 331). Orange-red needles (containing aq). By reduction it is reconverted into di-ethenyl-tetra-amido-benzene.—$B''H_2Cl_2PtCl_4\,\frac{1}{2}aq$: long golden-yellow needles.

DI - NITRO - DI - ETHENYL - TETRA-AMIDO-DITOLYL
$CMe\lessdot{}^{NH}_{N}\gtrdot C_6HMe(NO_2).C_6HMe(NO_2)\lessdot{}^{NH}_{N}\gtrdot CMe\left[1:3:{}^{4}_{5}\right]$.
[242°]. Formed from acetyl-di-nitro-toluidine by reduction with ammonium sulphide, and treatment of the resulting hydrazo- compound with boiling dilute HClAq (Bankievitch, *B.* 21, 2407). Prisms, v. e. sol. alcohol.—$B''H_2Cl_2$.—$B''2HNO_3$. [214°]. Yellow needles.

NITRO-ETHENYL-PHENYLENE-DIAMINE
$C_8H_7N_3O_2$ *i.e.* [1:3:4] $C_6H_3(NO_2)\lessdot{}^{NH}_{N}\gtrdot CMe$.
[216°]. Formed by heating nitro-*o*-phenylene-diamine with Ac_2O at 190°, cooling, and boiling with dilute H_2SO_4 (Heim, *B.* 21, 2307). Yellowish-brown needles (from water), v. sol. hot alcohol.

NITRO - ETHENYL - TOLYLENE - DIAMINE
$C_6H_2Me(NO_2)\lessdot{}^{N}_{NH}\gtrdot CMe\left[1:3:{}^{5}_{4}\right]$. [246°].
Formed from acetyl-*p*-toluidine by nitration and reduction (Bankievitch, *B.* 21, 2402). Needles. Yields on reduction ethenyl-tetra-amido-toluene [100°].—$B''H_2Cl_2$.—$B''HNO_3$. [207°]. Yellowish plates.

NITRO - ETHENYL - TOLYLENE - DIAMINE. [185°] (L.); [202°] (N.). Formed by nitrating ethenyl-tolylene-o-diamine (Ladenburg, *B.* 8, 677; Niementowski, *B.* 19, 723). Needles.

NITRO - ETHYL - ALCOHOL $C_2H_5NO_3$ *i.e.* $CH_2(NO_2).CH_2OH$. S.G. $\frac{19·4}{19·4}$ 1·1691. Formed from glycol iodhydrin and $AgNO_2$ (Demuth a. V. Meyer, *B.* 21, 3529; *A.* 256, 29). Yellowish liquid, sol. water, decomposed on distillation. Reacts with diazo- salts yielding azo- dyes (*e.g.* $C_6H_5.N_2.CH(NO_2).CH_2OH$). Nitrous acid converts it into methyl-nitrolic and glycollic acids. —$CH_2(NO_2).CH_2ONa$: white granular powder.

NITRO - ETHYL - AMIDO - BENZOIC ACID $C_9H_{10}N_2O_4$ *i.e.* [1:3:5] $C_6H_3(NO_2)(NHEt).CO_2H$. [208°]. Formed from nitro-amido-benzoic acid and EtBr (Rollwage, *B.* 10, 1704). Yellow needles (from water).—BaA'_2 4aq: red needles.

Nitro-di-ethyl-*m*-amido-benzoic acid $C_6H_3(NO_2)(NEt_2).CO_2H$. Monoclinic crystals; $a:b:c$ = ·893:1:1·095. β = 74° 57′ (Heintze, *J.* 1885, 1454; *cf.* Lehmann, *Dissert.*, Göttingen, 1884).

NITRO-ETHYL-AMIDO-PHENOL. *Nitrosamine of the ethyl ether* $C_{10}H_{13}N_3O_4$ *i.e.*

$C_6H_3(NO_2)(OEt).NEt(NO)$. Formed from $C_6H_4(OEt).NHEt$ and nitrous acid (Förster, *B.* 21, 354). Yellowish prisms. Does not form salts.

o-**NITRO-TETRA-ETHYL-DI-*p*-AMIDO-TRI-PHENYL-METHANE** $C_{27}H_{33}N_3O_2$ *i.e.* $C_6H_4(NO_2).CH(C_6H_4NEt_2)_2$. [110°]. Formed by heating o-nitro-benzoic aldehyde with di-ethyl-aniline and dehydrated oxalic acid (Fischer a. Schmidt, *B.* 17, 1898). Orange triclinic prisms.

p-Nitro-tetra-ethyl-di-*p*-amido-tri-phenyl-methane. [113°]. Obtained from *p*-nitro-benzoic aldehyde and di-ethyl-aniline (Kaeswurm, *B.* 19, 744). Thick needles or monoclinic plates.

NITRO-ETHYLAMINE $C_2H_5NH.NO_2$. *Ethyl-nitramine.* [3°]. Formed from ethylamine by treatment with $ClCO_2Me$ and decomposition of the resulting $C_2H_5NH.CO_2Me$ by ammonia (Franchimont a. Klobbie, *R. T. C.* 7, 356).

o-**NITRO-ETHYL-ANILINE** $C_8H_{10}N_2O_2$ *i.e.* $C_6H_4(NO_2).NHEt$ [1:2]. Formed by heating o-nitro-phenol with alcoholic ethylamine for 12 hours at 175°. Formed also by heating the ethylene ether of o-nitro-phenol with alcoholic ethylamine at 140° (Hempel, *J. pr.* [2] 39, 199; 41, 162). Red oil, sol. acids, but reppd. by water. Yields on reduction o-phenylene-ethyl-diamine (249°). Nitrous acid converts it, in ethereal solution, into di-nitro-ethyl-aniline [114°].

Nitrosamine $C_6H_4(NO_2).NEt(NO)$. [30°]. Formed from the hydrochloride of the base and $NaNO_2$ in aqueous solution. Yellow needles (from dilute alcohol or HOAc).

m-Nitro-ethyl-aniline $C_6H_4(NO_2)NHEt$ [1:3]. [60°]. Formed by heating *m*-nitro-aniline (16 g.) with EtBr (14 g.) and aqueous NaOH (6 g.). Formed also by adding HNO_3 (41·5 g. of S.G. 1·39) to a cooled solution of ethyl-aniline (50 g.) in H_2SO_4 (1,000 g.) (Nölting a. Stricker, *B.* 19, 546). Reddish-yellow needles, volatile with steam. With diazotised *p*-bromo-aniline it yields $C_6H_4Br.N_2.NEt.C_6H_4NO_2$ [136°] (Meldola a. Streatfeild, *C. J.* 55, 429).

Nitrosamine $C_6H_4(NO_2).NEt(NO)$. [47°].

Acetyl derivative $C_6H_4(NO_2).NEtAc$. [89°].

p-Nitro-ethyl-aniline $C_6H_4(NO_2)(NHEt)$ [1:4]. [95°]. Obtained by nitration of acetyl-ethyl-aniline dissolved in H_2SO_4 (5 pts.), the product being saponified (Weller, *B.* 16, 31; Nölting a. Collin, *B.* 17, 267). Formed also by heating *p*-nitro-aniline with EtBr and alcoholic potash at 110° (Schweitzer, *B.* 19, 142). Yellow prisms with violet reflex (from alcohol). Somewhat volatile with steam. With diazotised *p*-bromo-aniline it yields $C_6H_4Br.N_2.NEt.C_6H_4NO_2$ [125°].

Nitrosamine $C_6H_4(NO_2).NEt(NO)$. [120°]. Yellow needles (from alcohol) (Meldola a. Streatfeild, *C. J.* 49, 61).

Acetyl derivative $C_6H_4(NO_2).NEtAc$. [118°].

Benzoyl derivative $C_6H_4(NO_2).NEtBz$. [98°]. Needles, v. sl. sol. hot water (Meldola a. Salmon, *C. J.* 53, 774).

m-Nitro-di-ethyl-aniline $C_6H_4(NO_2).NEt_2$ [1:3]. (289°). Formed, together with a small quantity of the *p*- isomeride, by nitration of di-ethyl-aniline dissolved in H_2SO_4 (20 pts.) (Groll, *B.* 19, 199). Obtained also by heating *m*-nitro-aniline (20 g.) with EtI (46 g.) and NaOH (12 g.) in alcoholic solution for 8 hours at 100° (Nölting a. Stricker, *B.* 19, 550). Dark-yellow oil.

p-Nitro-di-ethyl-aniline $C_6H_4(NO_2).NEt_2$ [1:4]. [78°]. Formed by oxidation of nitroso-di-ethyl-aniline with $KMnO_4$ and H_2SO_4; and also by the action of nitrous acid on di-ethyl-amido-benzene-azo-di-ethyl-aniline (Lippmann a. Fleissner, *B.* 16, 1422; Groll). Yellow monoclinic needles with blue reflex.—$B'_2H_2PtCl_6$: thin prisms.

Di-nitro-ethyl-aniline $C_6H_3(NO_2)_2.NHEt$ [4:2:1]. [114°]. Formed from bromo-di-nitro-benzene and alcoholic ethylamine (Van Romburgh, *R. T. C.* 2, 104). Formed also by boiling $C_6H_5.NEtAc$ with dilute HNO_3 (S.G. 1·029) (Norton a. Allen, *B.* 18, 1997); and by the action of nitrous acid on an ethereal solution of o-nitro-ethyl-aniline (Hempel, *J. pr.* [2] 39, 199; 41, 168). Yellow needles (from alcohol). Decomposed by boiling conc. KOHAq into ethylamine and di-nitro-phenol.

Di-nitro-di-ethyl-aniline $C_6H_3(NO_2)_2NEt_2$ [4:2:1]. [80°]. Prepared by nitrating di-ethyl-aniline, and also by treating bromo-di-nitro-benzene with diethylamine (Van Romburgh, *R. T. C.* 2, 35; 8, 251). Yellow needles. Decomposed by boiling aqueous KOH into di-ethylamine and di-nitro-phenol. When gently oxidised by CrO_3 it yields di-nitro-aniline [175°].

Tri-nitro-ethyl-aniline $C_6H_2(NO_2)_3NHEt$. *Ethylpicramide.* [84°]. Formed from chloro-tri-nitro-benzene (picryl chloride) and NH_2Et in alcohol (Van Romburgh, *R. T. C.* 2, 107). Crystals (from alcohol) which turn brown in air.

Tri-nitro-di-ethyl-aniline $C_6H_2(NO_2)_3.NEt_2$. [164°]. Prepared by adding a hot alcoholic solution of $NHEt_2$ to (1,2,4,6)-chloro-tri-nitro-benzene. Orange crystals (from benzene). Decomposed by potash into picric acid and di-ethylamine.

Tetra-nitro-ethyl-aniline $C_6H_2(NO_2)_3.NEt(NO_2)$. *Nitramine* of *tri-nitro-ethyl-aniline.* [96°]. Obtained by the action of HNO_3 and H_2SO_4 on ethyl-aniline and on di-ethyl-aniline (Van Romburgh, *R. T. C.* 2, 31, 114). Yellow plates (from alcohol). Decomposed by 10 p.c. aqueous Na_2CO_3 into picric acid and ethylamine. Reduced by tin and HClAq to tri-amido-phenol.

NITRO-ETHYL-ANTHRONE $C_{16}H_{13}NO_3$ *i.e.* $C_6H_4{<}{\genfrac{}{}{0pt}{}{CO}{CEt(NO_2)}}{>}C_6H_4$. [102°]. Formed, as a by-product, in the preparation of ethyl-anthracene hydride-nitrite by the action of HNO_3 on ethyl-anthracene hydride dissolved in HOAc (Liebermann a. Landshoff, *B.* 14, 474).

o-**NITRO-ETHYL BENZENE** $C_6H_4(NO_2).C_2H_5$. [228°]. S.G. $\frac{21.5}{}$ 1·126. Formed, together with the *p*- isomeride, by dissolving ethyl-benzene in HNO_3 (Beilstein a. Kuhlberg, *A.* 156, 206; *Z.* [2] 5, 524). Oil.

p-Nitro-ethyl-benzene $C_6H_4(NO_2).C_2H_5$. (246°). S.G. $\frac{25}{}$ 1·124. Oil.

Nitro-di-ethyl-benzene $C_6H_3Et_2(NO_2)$ (155° at 23 mm.). Formed from di-ethyl-benzene and fuming HNO_3 at 0° (Voswinkel, *B.* 22, 316). Oil; boils with partial decomposition at 280°–285°.

Di-nitro-tetra-ethyl-benzene $C_6Et_4(NO_2)_2$. [115°]. Pale-yellow prisms (Galle, *B.* 16, 1745).

Tri-nitro-di-ethyl-benzene $C_6H(NO_2)_3Et_2$. [62°]. Yellow prisms (Voswinkel, *B.* 21, 2830).

o-NITRO-ETHYL-BENZENE SULPHONIC ACID $C_8H_9NSO_5$ *i.e.* $C_6H_3(NO_2)Et.SO_3H$. Formed by sulphonation (Beilstein a. Kuhlberg, *A.* 156, 207).—BaA'_2. S. ·54 at 17·5°.

p - Nitro - ethyl - benzene sulphonic acid—$BaA'_2 5aq$. S. 2·61 at 17·5°. Needles.

NITRO-*p*-ETHYL-BENZOIC ACID $C_6H_3Et(NO_2).CO_2H$. [156°]. Formed from *p*-ethyl-benzoic acid and cold-fuming HNO_3 (Aschenbrandt, *B.* 12, 1304; *A.* 216, 220). Needles (from water).—$NaA'2aq$.—$CaA'_2 2aq$.—$SrA'_2 4aq$.—$BaA'_2 4aq$: leaflets, sl. sol. water.

***p* - NITRO - *a* - ETHYL - BENZOYL - ACETIC ETHER** $C_6H_4(NO_2).CO.CHEt.CO_2Et$. [40°]. Formed from $C_6H_4(NO_2).CO.CHNa.CO_2Et$ and EtI (Perkin a. Bellenot, *C. J.* 49, 451). Plates.

DI-NITRO-ETHYLENE-UREA

$CO<\begin{matrix}N(NO_2).CH_2\\N(NO_2).CH_2\end{matrix}>$. [210°]. Obtained from ethylene - urea and HNO_3 (Franchimont a. Klobbie, *R. T. C.* 7, 17). Prisms. On boiling with water it loses CO_2 and forms ethylene-di-nitramine $C_2H_4(NH.NO_2)_2$ [174°].

DI-NITRO-ETHYLIC ACID $C_2H_6N_2O_2$. *Ethyl-nitramine*? Formed from $ZnEt_2$ and NO. Prepared by passing nitric oxide into a benzene solution of $ZnEt_2NaEt$, obtained by adding sodium (12·7 g.) to cold zinc ethyl (100 g.). The product is successively treated with ether, alcohol, and water; zinc is ppd. by CO_2; the filtrate evaporated, and the sodium salt extracted by alcohol (Frankland a. Graham, *C. J.* 37, 570; *cf.* Frankland, *C. J.* 9, 89; Zuckschwerdt, *B.* 7, 291; *A.* 174, 302). The free acid is unstable. Its salts yield ethylamine on reduction by sodium-amalgam. Alcoholic potash forms ethylamine and nitric acid (Zorn, *B.* 15, 1008).—$NaC_2H_5N_2O_2$.—$CaA'_2 3aq$.—BaA'_2.—MgA'_2.—ZnA'_2.—$ZnA'_2 aq$.—$CuA'_2 \frac{1}{2}aq$: flat dark-blue needles (from alcohol).—AgA'.—$AgA'AgNO_3$.

NITRO-*o*-ETHYL-PHENOL $C_6H_3Et(NO_2).OH$. (212°–215°). Formed in small quantity by the action of nitrous acid on $C_6H_4Et.NH_2$ (Suida a. Plohn, *Sitz. W.* [2] 81, 245).—$BaA'_2 aq$: orange plates.

Di-nitro-*o*-ethyl-phenol $C_6H_2Et(NO_2)_2OH$. Formed from *o*-ethyl-phenol and cold HNO_3 (S. a. P.). Heavy oil.—BaA'_2 (at 100°). Yellow plates (from alcohol).

NITRO -*p*- ETHYL - ISOPROPYL - BENZENE $C_6H_3EtPr.NO_2$. (265°). Obtained from [4:1] C_6H_4EtPr and HNO_3 (Von der Becke, *B.* 23, 3194).

DI-NITRO-(β)-ETHYL-THIOPHENE $C_4H(C_2H_5)(NO_2)_2S$. Formed by nitration of (β)-ethyl-thiophene by passing air charged with its vapour into fuming HNO_3 (Bonz, *B.* 18, 552). Crystalline solid. With alcoholic KOH it yields a blue colouration, becoming red on longer exposure to the air, or by addition of more KOH.

NITRO-o-ETHYL-TOLUENE $C_6H_3MeEt(NO_2)$. Oil (Claus a. Pieszczek, *B.* 19, 3087).

Di-nitro-*o*-ethyl-toluene $C_6H_2MeEt(NO_2)_2$. Oil, not solid at 0°.

Di-nitro-*p*-ethyl-toluene. [52°]. Obtained, with an oily isomeride, by nitrating *p*-ethyl-toluene (Jannasch a. Dieckmann, *B.* 7, 1513).

Tri-nitro-*p*-ethyl-toluene $C_6HMeEt(NO_2)_3$. [92°]. Obtained by nitration (Glinzer a. Fittig, *A.* 136, 303). Prisms (from alcohol).

Nitro-ethyl-*p*-toluidine $C_6H_3Me(NO_2).NHEt$ [4:3:1]. [48°]. Formed from ethyl-*p*-toluidine (1 pt.), H_2SO_4 (20 pts.), and HNO_3 (Nölting a. Stricker, *B.* 19, 549). Flat red prisms, v. sol. alcohol.

Nitro-ethyl-*p*-toluidine $C_6H_3Me(NO_2).NHEt$ [4:2:1]. [59°]. Formed by heating nitro-*p*-toluidine with EtI (Gattermann, *B.* 18, 1483; Niementowski, *B.* 20, 1883). Red crystals (from alcohol), v. sol. ether.

Acetyl derivative (245°–250° at 150 mm.).

Di-nitro-ethyl-o-toluidine. *Nitramine.* [1:3:5:6] $C_6H_2Me(NO_2)_2.NEt(NO_2)$. [72°]. Formed, in small quantity, by the action of HNO_3 on di-ethyl-o-toluidine (Van Romburgh, *R. T. C.* 3, 402). Yellow crystals (from alcohol).

Di nitro-ethyl-*p*-toluidine $C_6H_2Me(NO_2)_2NHEt$ [1:3:5:4]. [126°]. Formed by nitration of nitro-ethyl-*p*-toluidine (Gattermann, *B.* 18, 1485). Orange crystals.

Nitrosamine $C_7H_5(NO_2)_2.NEt(NO)$. [78°].

Nitramine $C_6H_2Me(NO_2)_2.NEt(NO_2)$. [116°] (R.; G.); [106°] (N. a. L.). Formed from di-ethyl-*p*-toluidine and fuming HNO_3 (Van Romburgh, *R. T. C.* 3, 408). Formed also from $C_6H_4Me(NEtAc)$ and dilute (10 p.c.) HNO_3 (Norton a. Livermore, *B.* 20, 2271). Converted by boiling NaOHAq into di-nitro-*p*-cresol [83°].

TRI-NITRO-ETHYL-o-XYLENE $C_6Me_2Et(NO_2)_3$. [121°]. Needles (from alcohol) (Fittig a. Ernst, *A.* 139, 193; Stahl, *B.* 23, 992).

Tri-nitro-ethyl-*m*-xylene. [127°]. Formed from ethyl-*m*-xylene, HNO_3, and H_2SO_4 (Stahl). White needles, m. sol. alcohol.

Tri-nitro-*s*-ethyl-*m*-xylene. [138°]. Needles, v. sl. sol. alcohol (Jacobsen, *B.* 7, 1434).

Tri-nitro-ethyl-*p*-xylene. [129°]. Prisms (from hot alcohol) (Jacobsen, *B.* 19, 2516).

NITRO-EUGENOL $C_{10}H_{11}NO_4$ *i.e.* $C_6H_2(C_3H_5)(NO_2)(OMe)(OH)$ [1:5:3:4]. [44°]. Formed by nitration of eugenol (Weselsky a. Benedikt, *M.* 3, 387). Triclinic crystals, sl. sol. water. Volatile with steam.

Acetyl derivative [61°]. Tables.

NITRO-EUXANTHIC ACID *v.* EUXANTHIC ACID.

NITRO-PSEUDO-FLAVENOL *v.* FLAVENOL.

NITRO-FLUORANTHENE *v.* FLUORANTHENE

***p*-NITRO-FLUORENE** $C_{13}H_9NO_2$ *i.e.*

$CH_2<\begin{matrix}C_6H_3(NO_2)\\C_6H_4\text{——}\end{matrix}>$. [151°] (H.); [154°] (S.).

Formed from fluorene, HOAc, and HNO_3 (Hodgkinson, *C. J. Proc.* 1, 37; Strasburger, *B.* 17, 107). Prisms, v. sl. sol. alcohol.

Di-nitro-fluorene $CH_2<\begin{matrix}C_6H_3(NO_2)\\C_6H_3(NO_2)\end{matrix}>$. [201°].

Formed by nitrating fluorene (Fittig a. Schmitz, *A.* 193, 134). Needles (from HOAc).

DI-NITRO-FLUORESCEÏN $C_{20}H_{10}(NO_2)_2O_5$. Formed from fluoresceïn (1 pt.), H_2SO_4 (20 pts.), and HNO_3 (2 pts.) at 0° (Baeyer, *A.* 183, 1). Amorphous yellow powder.

Di-acetyl derivative. Pale-yellow needles (from alcohol). On boiling for some minutes with dilute (15 p.c.) KOH it forms a blue solution.

Tetra - nitro - fluoresceïn $C_{20}H_8(NO_2)_4O_5$. Formed from fluoresceïn (1 pt.) and fuming HNO_3 (5 pts.) Colourless crystals (from HOAc). Its alcoholic solution is yellowish-red, and, on

adding an acid, becomes first reddish-violet and then colourless.

NITROFORM *v.* TRI-NITRO-METHANE.

NITRO-FURFURYL-ETHYLENE $C_4H_3O.CH:CH(NO_2)$. [184°]. From furfuraldehyde and an alkaline solution of nitro-ethane (P.). Yellow prisms.

Nitro-furfuryl-nitro-ethylene $C_4H_2(NO_2)O.CH:CH(NO_2)$. [144°]. Yellow felted needles. Formed by nitration of furfuryl-nitro-ethylene. It is oxidised by CrO_3 to nitro-pyromucic acid.

Dibromide: [111°]; yellow prisms (Priebs, *B.* 18, 1362).

NITROGEN. N. (*Azote.*) At. w. 14·01. Mol. w. 28·02. Boils at −194·4° (Olszewski, *W.* 31, 58). According to Sarrau (*C. R.* 94, 639, 718, 845) the critical temperature of N is −123·8°, and the critical pressure is 42·1 atmos. S.G. (gas) ·97247 (air = 1). S.G. (liquid) ·885 (water = 1) at b.p. (O., *l.c.*; *cf.* Wroblewski, *C. R.* 102, 1011). S.G. (gas) at 3000 atmos. (water = 1) ·823 (Amagat, *C. R.* 107, 522). V.D. 14 (von Jolly, *W.* 6, 536). S.H.p. (equal wt. of water = 1) ·2368; (equal volume of air = 1) ·2377 (Regnault, *Acad.* 26, 302). C.E. ·0036677 (von Jolly, *P. Jubelbd.* 82). S. ·01843 at 4°, ·01751 at 6·2°. ·0152 at 12·6°, ·01436 at 17·7°, ·01392 at 23·7°; the absorption-coefficient $= ·020346 - ·00053887t + ·000011156t^2$ (Bunsen, *Gasom. Methoden* [2nd ed.] 209). S. (alcohol) ·12561 at 1·9°, ·12384 at 6·3°, ·12241 at 11·2°, ·12148 at 14·6°, ·12053 at 19°, ·11973 at 23·8°; absorption-coefficient $= ·126338 - ·000418t + ·000006t^2$ (Carius, *A.* 94, 136; Bunsen, *Gasom. Methoden* [2nd ed.] 209). Refraction-equivalent $\left(\frac{\mu-1}{d} . \text{At. w.}\right) = 4·1 \text{ to } 5·3$ (Gladstone, *Pr.* 18, 49). Mean value of μ for white light = 1·0003019; dispersion-power = ·2086 (Croullebois, *A. Ch.* [4] 26, 236; *v.* also Mascart, *P.* 153, 149). M.M. N^{V} c. ·114; N^{III} c. ·611 (Perkin, *C. J.* 55, 736). T.C. (air = 1) ·98 (Narr, *P.* 142, 123); ·993 (Plank, *Carl Rep.* 13, 164). H.C. $[N^2,O] = -17,740$; $[N,O] = -21,575$; $[N,O^2] = -2,005$; $[N^2,O^3,Aq] = -6,820$; $[N^2,O^5,Aq] = 29,820$ (*Th.* 2, 198); $[N^2,O^3] = -22,200$; $[N^2,O^5] = -1,200$; $[N^2,O^3,Aq] = -8,400$; $[N^2,O^5,Aq] = 28,600$ (Berthelot, *A. Ch.* [5] 20, 255). Coefficient of compressibility 750–1,000 atmos. ·000407, 1000–1500 atmos. ·000265, 1500–2000 atmos. ·00017, 2000–2500 atmos. ·000122, 2500–3000 atmos. ·000091 (Amagat, *C. R.* 107, 522). Transpiration-coefficient (O = 1) ·873 (Meyer a. Springmühl, *P.* 148, 526); ·885 (von Obermayer, *W. A. B.* 73 [2nd part], 433). Friction-coefficient at 0° = ·000184 (M. a. S., *l.c.*); ·0001659 (von O., *l.c.*). The spectrum of N varies much; there are two distinct spectra, known as the elementary line spectrum and the band-spectrum (for measurements of lines, *v. B. A.* 1884. 429; also Ames, *P. M.* [5] 30, 48).

Occurrence.—In the atmosphere, forming c. $\frac{4}{5}$ths by volume. In the fluid-cavities of some specimens of rock-crystals (Davy, *T.* 1822. 367). In the air-bladders of fishes, and in other cavities of the bodies of animals and vegetables. In the gases from some fumaroles. In certain wells (*v.* L. Smith, *Am. S.* [2] 12, 366). Probably in the sun (Young, *Am. S.* [3] 4, 356; Draper, *ibid.* [3] 14, 89). Compounds of N occur in very large quantities throughout the animal, vegetable, and mineral, kingdom.

In 1772 Rutherford (*De aere mephitico*; Edinburgh, 1772) showed that the expired breath of animals contained a gas which extinguished flame, but which was not carbonic acid, as it was not absorbed by potash. A little later Lavoisier proved that this gas was present in air. As this gas did not support animal life, Lavoisier called it *azote* (ἀ and ζωή). Chaptal afterwards gave it the name *nitrogen*, because it was present in nitre.

Formation.—1. From air; by removing CO_2 by KOHAq, moisture and NH_3 by conc. H_2SO_4, and O by passing over red-hot Cu (*v. Preparation*, No. 1).—2. By passing air through a mixture of sawdust and Fe sulphide (obtained by saturating ppd. Fe_2O_3 with H_2S), and then through alkaline pyrogallate solution, and finally through conc. H_2SO_4. When the process is completed, passage of H_2S re-forms Fe sulphide, which may be used again.—3. By burning P in an inclosed quantity of air, over water, and allowing the P_2O_5 formed to dissolve in the water.—4. By passing air through conc. NH_3Aq, and then sending the mixture of air and NH_3 over Cu heated to redness; the CuO formed is reduced by the NH_3 (Lupton, *C. N.* 33, 90).—5. Berthelot (*Bl.* [2] 13, 314) partly covers with NH_3Aq c. 200 grams pure Cu turnings in a 10–14 litre flask, closes the flask by a cork carrying a safety funnel-tube, and a delivery tube which is stopped by a caoutchouc cap, and shakes from time to time. The O is thus completely removed from the air in the flask; the N may be obtained by pouring into the flask water previously freed from O by shaking with NH_3Aq and Cu; the gas should be passed through KOHAq, conc. H_2SO_4, and then through $CrCl_2Aq$ (B., *Bl.* [3] 2, 643).—6. By shaking FeO_2H_2, or MnO_2H_2, with air; the hydroxides are obtained by adding NaOHAq to conc. $FeSO_4Aq$ or $MnSO_4Aq$, and at once stopping the ingress of air.—7. By placing pyrogallic acid in a flask, adding NaOHAq, corking, and shaking for some time (*v.* Liebig, *A.* 77, 107).—8. By passing over Pt black a mixture of 100 vols. air (from which CO_2 has been removed) with 42 vols. H (Dumoulin, *L'Institut*, 1851. 11).—9. By passing Cl into rather dilute NH_3Aq, keeping the NH_3 always in large excess; $8NH_3 + 3Cl_2 = 6NH_4Cl + N_2$ (the experiment is dangerous, as NCl_3 may be formed and explode).—10. By warming conc. NH_4NO_2Aq; or more easily conc. KNO_2Aq mixed with 3 vols. conc. NH_4ClAq, whereby KCl and NH_4NO_2 are formed and the NH_4NO_2 is decomposed ($NH_4NO_2 = 2H_2O + N_2$; Corenwinder, *A.* 72, 225). Addition of conc. $K_2Cr_2O_7Aq$ oxidises N oxides (which are generally produced) to HNO_3 (*v. Preparation*, No. 2). Loew (*B.* 23, 3018) has found that a 4–5 p.c. solution of NH_4NO_2 is decomposed at the ordinary temperature by Pt black, with evolution of N.—11. By heating in a retort an intimate mixture of equal parts dry NH_4Cl and $K_2Cr_2O_7$, and passing the gas through $FeSO_4Aq$ to absorb NO which is generally formed. The chief change is represented approximately thus: $2NH_4Cl + K_2Cr_2O_7 = 2KCl + 4H_2O + Cr_2O_3 + N_2$.—12. By heating powdered $(NH_4)_2Cr_2O_7$, which decomposes to Cr_2O_3, H_2O, and N.—13. By

adding conc. NH_4ClAq to a strongly alkaline conc. solution of NaBrO (prepared by adding Br to cold NaOHAq); N is evolved rapidly (? $3NaBrO + 2NH_4Cl = 3NaBr + 3H_2O + 2HCl + N_2$). Solution of bleaching-powder may be used, but there is danger of formation and explosion of NCl_3.—14. By heating a mixture of NH_4NO_3 and MnO_2 to c. 200° (not over 215°) ($4NH_4NO_3 + MnO_2 = Mn(NO_3)_2 + 8H_2O + 3N_2$; Gatehouse, *B.* 10, 1007).—15. N is evolved in the reactions of several metals with HNO_3; the gas evolved by the action of Zn on HNO_3Aq in presence of much NH_4NO_3 consists of c. 90 p.c. N, with N_2O and NO (Acworth, *C. J.* 28, 839).

Preparation.—1. A very slow stream of air is passed from a gasholder through U tubes containing slightly moistened KOH, to absorb CO_2, then through U tubes containing $CaCl_2$, to absorb H_2O, and then through a long hard glass tube, containing Cu turnings, or better Cu obtained by reducing CuO in H (Carius, *A.* 94, 126), and heated to bright redness in a furnace; the gas which issues is allowed to bubble through a solution of $CrCl_2$, to remove any traces of O which may remain, and is then dried by passing through $CaCl_2$ in several U tubes, and then over P_2O_5. Before the air-stream is started, the tube containing the Cu should be heated and a stream of H passed through it, to remove traces of CuO (this is not necessary, of course, if the Cu has been prepared by reducing CuO by H); after cooling, one end of the tube should be sealed and the other connected with a Sprengel-pump, and the Cu should be heated in a vacuum for some time. If this precaution is not taken, the N will contain H (von Jolly, *W.* 6, 536). The solution of $CrCl_2$ is prepared before use by digesting $CrCl_3Aq$ with scrap Zn and HClAq until a clear blue liquid is obtained, which is poured into Na acetate solution, in an atmosphere of CO_2; the red pp. of chromium acetate is washed with H_2O containing CO_2, and is then placed in a flask closed by a cork with entrance tube (to be attached to the N apparatus), exit tube, and a funnel though which HClAq is dropped on to the acetate, which is thereby changed to $CrCl_2$; the whole of the acetate is not dissolved, to avoid free HCl; the N apparatus is at once attached to the flask (O. von der Pfordten, *A.* 228, 112).—2. Solid NH_4Cl is added to an almost saturated cold solution of $NaNO_2$, when no more NH_4Cl dissolves the liquid is poured into a capacious flask, cold conc. $K_2Cr_2O_7Aq$ is added, about 1 pt. $K_2Cr_2O_7$ for each 1 pt. $NaNO_2$ used, and the mixture is gently warmed. The $K_2Cr_2O_7$ oxidises any oxides of N to HNO_3 (*v.* Gibbs, *B.* 10, 1387). It is advisable to pass the N through KOHAq to absorb any traces of Cl compounds coming from impurities in the salts used (Gibbs, *l.c.*).—3. A solution of 1 pt. $K_2Cr_2O_7$, 1 pt. NH_4NO_3, and 1 pt. $NaNO_2$, in 3 pts. water is warmed in a fair-sized flask (Böttger, *Jahr. des phys. Vereins zu Frankfort*, 1876–77. 24).

Properties.—A tasteless, colourless, odourless gas, which does not burn, nor support combustion, nor form a pp. with CaOAq. Liquid N is obtained by cooling the gas to −136° under a pressure of some hundred atmos., and then reducing pressure, not too suddenly, to not less than 50 atmos.; the N does not remain liquid for more than a few seconds. Liquid N is colourless, transparent, and shows a very sharp meniscus (Wroblewski a. Olszewski, *A. Ch.* [6] 1, 112). According to Cailletet (*A. Ch.* [5] 5, 132), N is liquefied, for a second or two, by subjecting the gas to 200 atmos. pressure at 13°, and then suddenly reducing the pressure. It has not been solidified. N is slightly lighter than air; 1 litre at the sea-level, lat. 45°, weighs 1·2574614 grams (von Jolly, *W.* 6, 536). N is very slightly sol. water (for S. *v.* beginning of this art.). Small quantities of N are absorbed by molten pig-iron, cast-iron, and steel (Parry, *Am. Ch.* 6, 107; Troost a. Hautefeuille, *C. R.* 76, 482, 562; 80, 909; Ledebur, *C. C.* 1873. 810). Wood charcoal also absorbs N; according to R. A. Smith, charcoal which has absorbed N and O, when exposed to the air for a time gives off O only (*Pr.* 12, 424; *cf.* Montmagon a. de Laire, *Bl.* [2] 11, 261). N is chemically inert; it combines slowly with O when electric sparks are sent through a mixture of the gases for some time; HNO_3 is formed when electrolytic gas ($H_2 + O$) is strongly compressed and then exploded in compressed air in presence of a little KOHAq, and also when C is burnt in a mixture of strongly compressed air and O (in presence of a little KOHAq) (Hempel, *B.* 23, 1455). N and H combine under the influence of the electric discharge. At or towards white heat N combines with B, Cr, Mg, Si, and V; probably also with Al, Fe, and Zn. The compounds of N are extremely numerous and exhibit great differences of properties. N is related chemically to P, V, As, Nb, Sb, Di, Er, Ta, and Bi; these elements form Group VI. Most of the oxides of N are acidic, none is basic; NH_3, however, is markedly basic and alkaline (*v.* NITROGEN GROUP OF ELEMENTS, p. 571).

The influence exerted on the molecular volumes of N compounds by the N atoms has not yet been measured satisfactorily (for a synopsis of data *v.* Kopp, *A.* 250, 1). The molecular rotatory power of N compounds varies according as the N atom is in direct union with 3 or 5 other atoms; but the exact numerical value to be assigned to N^{III} and N^{V} has not yet been finally determined (*v.* Perkin, *C. J.* 55, 680). Neither have final values been yet determined for the atomic refractions of N^{III} and N^{V}.

The atomic wt. of N has been determined (1) by finding the ratio of Ag to $AgNO_3$, the at. wts. of Ag and O being known (Marignac, *A.* 59, 289; Stas, *Rech.* 50; *Nouv. R.* 281); (2) by finding the ratio of NH_4Cl to Ag needed to ppt. the Cl (M., *l.c.*; Stas, *Rech.* 87; *Nouv. R.* 57).

Supposed allotropic form of nitrogen.—By passing a succession of powerful electric sparks through N at not more than 20 mm. pressure, Thomson a. Threlfall (*Pr.* 40, 329) observed a diminution in the volume of the N; at 8 mm. the diminution amounted to 8 to 10 p.c. of the original volume; after long warming to 100° the gas attained its original volume. T. a. T. supposed that an allotropic form of N is produced under these conditions. According to Johnson (*C. J.* 39, 130), when N, obtained from KNO_2Aq and NH_4ClAq, is mixed with H, and the gases are passed over spongy Pt, NH_3 is formed; but NH_3 is not produced if the gases are passed through a hot tube before coming in contact with the spongy Pt. Johnson concluded that N can exist

in two forms: one active and the other inactive, the latter being formed by the action of heat on the former (*v.* also Johnson's pamphlet, *Elementary Nitrogen, and on the Synthesis of Ammonia* [Churchill, 1885]).

Fixation of nitrogen by growing plants.—Experiments conducted in recent years tend to show that certain plants, notably *Leguminosæ*, are able to absorb N from the air and build up nitrogenous material therewith. The absorption of N seems to occur in nodules which grow on the roots of the plants. For an account of the more important experiments up to the early part of 1890 *v.* Lawes a. Gilbert, *Pr.* 46, 85; abstract in *N.* 42, 41: *v.* also Atwater a. Woods, *Am.* 12, 526; also Schloesing a. Laurent, *C. R.* 111, 750; abstracts in *C. J.* 60, 353.

Reactions and Combinations.—1. Combines with *oxygen* to form NO_2 when electric sparks are sent through the gases for some time. When air is strongly compressed and mixed with compressed O and some electrolytic gas (H_2+O), an open tube containing KOHAq is placed in the vessel, and a spark is passed, a considerable quantity of KNO_3 is found in the KOHAq (Hempel, *B.* 23, 1455). HNO_3 is also formed by exploding H_2+O in air at the ordinary pressure standing over Hg (Bunsen, *Gasom. Methoden* [2nd ed.], 71). Nitrites, or HNO_2, are formed in very small quantities in certain cases of combustion in air, *e.g.* when P, H, or ether is slowly burnt (Schönbein, *J. pr.* 84, 193; 86, 129; Berthelot, *A. Ch.* [5] 12, 440; *C. R.* 108, 543; Kolbe, *A.* 119, 176; Zöller a. Grete, *B.* 10, 2145; Ilosva, *Bl.* [3] 2, 734). It is doubtful whether the nitrites are produced by the oxidation of N or of NH_3 in the air; the experiments of L. T. Wright (*C. J.* 35, 42) tended to show that nitrites are not formed by burning H in air from which NH_3 has been carefully removed. According to Ilosva (*Bl.* [3] 2, 734), nitrites are formed by passing air over Pt black heated to c. 250°. Loew (*B.* 23, 1443) showed that small quantities of nitrites are produced when pure Pt black is treated with pure NaOHAq in the air. Neither of these sets of experiments proves conclusively that the N, and not the NH_3, of the air was the source of the N of the nitrites produced. Schönbein's statement that N combines with *ozone* has been disproved by Carius (*A.* 174, 31).—2. N combines with *hydrogen* to form NH_3 under the influence of the electric discharge (Chabrier, *C. R.* 75, 484; Donkin, *Pr.* 21, 281; Morren, *C. R.* 48, 432; Perrot, *C. R.* 49, 204; *cf.* Johnson, *C. J.* 39, 130; and Wright, *C. J.* 39, 359). Ramsay a. Young assert that a trace of NH_3 is formed when a mixture of moist N and H is passed through a red-hot tube containing iron filings (*C. J.* 45, 93).—3. At a very high temperature N combines with *boron, chromium, magnesium*, and *silicon*, and probably also with *aluminium, iron*, and *zinc*, to form nitrides (*v.* these elements).—4. N combines with *carbon* to form C_2N_2, when induction-sparks are passed between C poles in an atmosphere of N (Morren, *C. R.* 48, 342). Cyanides are formed when a mixture of C with oxide of an alkali, or alkaline earth, metal is heated in N; Hempel (*B.* 23, 3390) has shown that considerable quantities of cyanides are thus formed if the reaction occurs at pressures from 10 to 60 atmospheres.

Detection of nitric nitrogen, i.e. N in combination as nitrite or nitrate. One part of N existing as a nitrite or nitrate in 20,000,000 parts of water suffices to give a violet-blue colour with a drop of diphenylamine sulphate in H_2SO_4 followed by 2 c.c. conc. H_2SO_4 and stirring (*v.* Warington, *C. J.* 45, 644).

Nitrogen, acids of. The compound N_3H, known as *hydrazoïc acid*, is described under *Nitrogen, hydrides of*, p. 559; for the *Oxyacids of nitrogen v.* p. 567.

Nitrogen, boride of, *v.* BORON NITRIDE, vol. i. p. 527.

Nitrogen, bromide of. ? NBr_3. According to Millon (*A. Ch.* [2] 69, 75) the red, very explosive, oily, liquid formed by adding KBrAq to N chloride covered with a little water is a bromide of N.

Nitrogen, chloride of. NCl_3. This compound is frightfully explosive. Experiments must be conducted with small quantities and with the greatest care. V. Meyer (*B.* 21, 26) describes a glass case in which experiments with NCl_3 may be conducted.

Preparation.—1. A stick of NH_4Cl is suspended in as conc. HClOAq as can be obtained; an oily liquid slowly collects in a small leaden basin placed at the bottom of the vessel in which the reaction proceeds (*cf.* Troost a. Hautefeuille, *C. R.* 69, 152).—2. NH_4ClAq saturated at 35° is poured into a glass basin, and a glass cylinder, closed at one end by parchment, and partly filled with the same NH_4ClAq, is placed upright in the liquid in the basin; a Pt plate, forming the positive pole of a battery of at least 6 to 8 Grove or Bunsen cells, is immersed in the NH_4ClAq in the cylinder, and the negative pole—also a Pt plate—is placed obliquely under the parchment which closes the lower end of the cylinder. A very thin layer of turpentine is spread on the surface of the NH_4ClAq in the cylinder. When the current is sent through the liquid very small oily drops form at the positive pole and float to the surface, where they explode on coming into contact with the turpentine (Böttger a. Kolbe, *A.* 64, 236; Böttger, *J. pr.* 68, 374).—3. About 30 grams pure NH_4Cl are dissolved in hot water, the solution is filtered if necessary, diluted to 1½ litres, and placed in a perfectly clean leaden basin; a small leaden basin with a handle is placed in the centre of the larger basin; a fair-sized, very clean flask is filled with Cl, and this flask is immersed in the NH_4ClAq, so that the mouth of the flask covers the small leaden dish. The apparatus is placed out of direct sunlight, in a glass case with double walls, having an open door at one end (*v.* V. Meyer, *B.* 21, 26). The Cl is slowly absorbed by the NH_4ClAq which rises in the jar; when about ½ of the Cl has disappeared, oily drops begin to be formed in the liquid; these drops increase in quantity and size, and at last sink into the small leaden dish. The leaden dish is very carefully removed, and its contents are poured into a small separating funnel made of very thin glass; the NH_4ClAq is removed by a pipette, the greatest care being taken that the liquid does not come into contact with any kind of organic matter; the oil in the funnel is repeatedly washed in the cold water till the washings are free from Cl, and a gentle stream of air is sent through the oil to remove

the last traces of Cl. The oil is now allowed to drop from the funnel into a very small glass vessel, where it is dried by contact with a little bit of dry $CaCl_2$; the oil is then poured into a little weighed tube holding about 1 c.c., and closed by a loosely-fitting stopper. The very greatest care is required in conducting these operations, especially the removal of the oil from the separating funnel, as the rubbing of the glass tap against the funnel is very apt to cause explosion; when a little of the oil has been dropped into the vessel in which it is to be dried, another clean glass dish must at once be placed beneath the funnel, as explosion would occur if a trace of the oil should drop on to the table. (For more details *v.* Gattermann, *B.* 21, 751.) The oil thus obtained is a mixture of chlorinated ammonias $NH_{3-x}Cl_x$ (G., *l.c.*); the composition of portions of the oil varies. To prepare pure NCl_3, after washing the oil in a separating funnel till free from Cl, and separating the water as completely as possible, Gattermann passes a fairly rapid stream of pure Cl over the oil, which is in the narrow part of the funnel, for about ½ an hour; he then washes and dries the oil in the way described. The analysis was made by decomposing the oil by NH_3Aq, when N and HCl are formed (the HCl combining with excess of NH_3 to form NH_4Cl), and estimating Cl. The process is carried out by Gattermann (*l.c.*) by dropping the little weighing tube and the stopper (which is removed from the tube) into water in a flask, closed by a cork carrying a small dropping funnel and a tube passing downwards into a beaker of water, allowing about 20 c.c. conc. NH_3Aq to flow *very slowly* into the flask, when the decomposition is complete (about 4 hours are required) adding the water in the beaker to the contents of the flask, and boiling for a short time, adding HNO_3Aq and $AgNO_3Aq$, and weighing the AgCl formed.

Properties and Reactions.—A dark-yellow oil; S.G. c. 1·6 (determined by finding that the oil very slowly sank in $Fe_2(SO_4)_3Aq$, S.G. 1·578, Porret, Wilson, a. Kirk, *G. A.* 47, 56). Explodes when exposed to direct sunlight or the light of burning Mg. Explodes at c. 90°–95° when heated in a perfectly clean tube (*v.* G., *l.c.*); explodes on contact with wood, grease, oil, or almost any kind of organic matter. The explosion of NCl_3 is frightfully violent. The older observers said that explosions occurred under most curious and apparently contradictory conditions; *e.g.* contact with P, As, or Se caused explosion, but no explosion occurred by contact with C, S, gum, starch, or wax. Gattermann (*l.c.*) thinks that light was the cause of many of these explosions. The vapour of NCl_3 acts on the eyes and mucous membrane of the nostrils. NCl_3 is decomposed by conc. HClAq, giving NH_4Cl and Cl; NH_3Aq produces NH_4Cl and N; Hg forms $HgCl_2$ and N; SO_2Aq produces NH_3, H_2SO_4, and HCl; As_2O_3Aq and SH_2Aq also set free N.

The formation of NCl_3 from N and Cl would be accompanied by the disappearance of much heat. Deville a. Hautefeuille give $[N, Cl^3] = -38{,}000$ (*C. R.* 69, 152; *cf.* Ogier, *A. Ch.* [5] 20, 5).

References.—Dulong, *G. A.* 47, 43; Porret, Wilson, a. Kirk, *G. A.* 47, 56; H. Davy, *T.* 1813. 1, 242; Serullas, *P.* 17, 304; Millon, *A. Ch.* [2] 69, 75; Bineau, *A. Ch.* [3] 15, 82; Gladstone, *C. J.* 7, 51; Deville a. Hautefeuille, *C. R.* 69, 152; Böttger a. Kolbe, *A.* 64, 236; Böttger, *J. pr.* 68, 374; Gattermann, *B.* 21, 751.

Nitrogen, chlorophosphide, *v.* *Nitrogen, phosphochloride of*, p. 570.

Nitrogen, chlorosulphide of, *v.* *Nitrogen, sulphochloride of*, p. 571.

Nitrogen, fluoride of. Warren (*C. N.* 55, 289) says that a yellow oil, probably a fluoride of N, is obtained by electrolysing NH_4FAq; the oil explodes by contact with a gold wire.

Nitrogen, hydrides of.

Three compounds of N and H have been isolated, viz. *ammonia*, NH_3; *hydrazine*, N_2H_4; and *hydrazoïc acid* N_3H. Ammonia is described in vol. i. p. 196, and hydrazine in vol. ii. p. 706. As hydrazoïc acid has been isolated since the publication of vol. ii. this compound is described here:—

HYDRAZOÏC ACID N_3H. $\begin{matrix} N : N \\ \diagdown\ \diagup \\ NH \end{matrix}$. (*Azoimide. Hydrogen nitride.*) This acid was discovered by Curtius in 1890 (*B.* 23, 3023).

Formation.—Ethyl benzoylglycollate reacts with N_2H_4 to form benzoyl-hydrazine and the ethyl salt of hydrazine acetic acid; thus,

$$C_6H_5CO.O.CH_2COOEt + 2N_2H_4$$
$$= C_6H_5CO.NH.NH_2 + NH_2.NH.CH_2.CO_2Et + H_2O.$$

By the reaction of benzoyl-hydrazine with $NaNO_2$ and acetic acid, benzoyl-azoimide is formed; thus, $C_6H_5CO.NH.NH_2 + NOOH = C_6H_5CO.N{<}{N \atop N} + 2H_2O$. By boiling this imide with NaOH the Na salts of benzoic and hydrazoïc acids are produced; thus,

$$C_6H_5CO.N{<}{N \atop N} + 2NaOH = C_6H_5COONa + NaN{<}{N \atop N} + H_2O.$$

By adding dilute H_2SO_4Aq and warming, hydrazoïc acid gas is evolved.

Preparation.—Ethyl hippurate is dissolved in as small a quantity as possible of boiling alcohol, $N_2H_4.H_2O$ is added in the ratio $C_6H_5CO.NH.CH_2.COOEt{:}N_2H_4.H_2O$; hippuryl hydrazine, $C_6H_5CO.NH.CH_2.CO.NH.NH_2$, separates on cooling. The crystals are recrystallised from alcohol, and dissolved in much warm water, with addition of rather more than a molecular proportion of $NaNO_2$; the solution is cooled to 0°, and mixed with excess of acetic acid, when lustrous tablets of a nitroso-compound (probably $C_6H_5CO.NH.CH_2.CO.N{<}{NO \atop NH_2}$) separate; the crystals are collected by help of a filter-pump, washed with cold water, and dissolved in very dilute NaOHAq. This solution is gently warmed for a short time on the water-bath, and is then placed in a flask connected with a condenser and furnished with a dropping funnel. A flask containing $AgNO_3Aq$ is used as a receiver; dilute H_2SO_4Aq is allowed to drop very slowly into the boiling liquid in the flask; N_3H distils over with steam, and, reacting with the $AgNO_3$ in the receiver, produces AgN_3; the operation is continued so long as a pp. is produced in the receiver. The AgN_3 is collected by the help of the pump, and well washed with cold water; it must not be heated above 60°, else there is danger of a severe explosion. The AgN_3 is decomposed by boiling with dilute HClAq, the dis-

tillate is fractionated, and the portion which distils over in the early stages is collected separately from the rest. In this way a solution of N_3H containing 27 p.c. N_3H is obtained. By repeatedly fractionating with great care, N_3HAq containing over 90 p.c. N_3H is obtained; and all water can be removed from this solution by fused $CaCl_2$ (Curtius a. Radenhausen, *J. pr.* [2] 43, 207). The process of fractionation is often attended with explosions.

Properties and Reactions.—A 27 p.c. solution of N_3H is a thickish liquid, which sinks in water; it possesses an extremely offensive odour; with NH_3 it gives white clouds. Pure N_3H is a clear, colourless, very foully smelling, liquid. It boils at 37°. It is very explosive. When touched with a hot substance it explodes with violence; it also explodes when placed in a barometric vacuum. The solution of N_3H corrodes the skin and causes headache and giddiness. N_3HAq is a strong monobasic acid; it dissolves Fe, Zn, Cu, Al, and Mg with rapid evolution of H; it appears to dissolve slightly Au and Ag. With $AgNO_3Aq$ and $HgNO_3Aq$ white pps. of AgN_3 and HgN_3 are obtained. The affinity of N_3HAq is a little greater than that of acetic acid. The salts of N_3H are also very explosive, with the exception of those of the alkali and alkaline earth metals.

The following salts are described by Curtius (*B.* 23, 3032): $N(NH_{43})$, $(N_3)_2Ba$, N_3Hg, N_3Ag; salts of Cu, Fe, and Na were also prepared.

In connexion with N_3H *v.* Mendelejeff, *B.* 23, 3464.

Nitrogen, iodides of. (*Iodamines.*) Very explosive compounds containing N and I are obtained by rubbing I with conc. NH_3Aq, by pouring an alcoholic solution of I into NH_3Aq or alcoholic NH_3, by pouring NH_3 into alcoholic I, by pouring a solution of I in *aqua regia* into NH_3Aq or NH_4ClAq, by adding bleaching-powder solution (neutralised by acetic acid) to NH_4IAq, by adding NH_3Aq to a mixed solution of HCl and HIO_3, by the action of N chloride on KIAq, and by adding I and alcohol to 'white precipitate.' The products of these reactions are very dark-coloured powders, which explode, more or less readily and violently, by rubbing or striking. Analyses of these substances seemed to show that at least three different explosive compounds existed, viz. NI_3, NH_2I, and $N_2H_3I_3(=NH_3.NI_3)$. For details and analyses *v.* Serullas, *P.* 17, 304; Millon, *A. Ch.* [2] 69, 78; Marchand, *J. pr.* 19, 1; Bineau, *A. Ch.* [3] 15, 71; Gladstone, *C. J.* 4, 34; 7, 51; Bunsen, *A.* 84, 1; Stahlschmidt, *P.* 119, 421; Champion a. Pellet, *Bl.* [2] 24, 447; Mallet, *Am.* 1, 4; Guyard, *A. Ch.* [6] 1, 358. Guthrie (*C. J.* [2] 1, 239), by adding I to conc. NH_4NO_3Aq or $(NH_4)_2CO_3Aq$ containing KOH, obtained a brown-black liquid, which, he said, had the composition $NH_3I.I$ (*v. post*).

Raschig (*A.* 230, 212) has re-examined the various methods of preparing and analysing N iodides. According to R., three compounds exist, NI_3, NH_2I, and NHI_2; but only NI_3 and NH_2I have been isolated by R.

Tri-iodamine NI_3. NH_4Cl and I in the ratio $NH_4Cl:6I(1:14\cdot24)$ were dissolved in KIAq, and NaOHAq was added in the ratio $NH_4Cl:4NaOH$, *i.e.* 2·99 parts NaOH for each part NH_4Cl used; the black pp. which forms was collected immediately (with the help of a filter-pump) and washed 6–8 times with cold water, as rapidly as possible, then dissolved in HClAq and analysed. Raschig (*l.c.*) expresses the reaction thus, $NH_4ClAq + 6IAq + 4NaOHAq$
$= NI_3 + NaClAq + 3NaIAq + 4H_2O$. NI_3 is rapidly decomposed by water to NHI_2. Mallet (*Am.* 1, 4) obtained NI_3 by triturating I with a large excess of the most conc. NH_3Aq, keeping temperature at or below 0°, pouring off the liquid and triturating with more NH_3Aq, repeating this several times, then agitating 2 or 3 times in a cooled flask with absolute alcohol, then with dry ether, and allowing the ether to evaporate. NI_3 is a heavy, nearly black, powder. According to Raschig (*l.c.*), the NI_3 prepared by the action of NH_3Aq on I is much more explosive than the iodide formed by the action of NH_4ClAq and NaOHAq on I. NI_3 dissolves in KCyAq, forming ICy, KOHAq, and NH_3Aq (Millon, *A. Ch.* [2] 69, 78; Raschig, *A.* 230, 212); KSCyAq reacts similarly, producing ICy, HI, KOH, NH_3, and H_2SO_4 (R., *l.c.*).

Di-iodamine NHI_2. Prepared similarly to NI_3, using the materials in the ratio $NH_4Cl:4I:3NaOH$ (Raschig, *l.c.*). Mallet (*Am.* 1, 4) obtained this compound by triturating I with not very conc. NH_3Aq at the ordinary temperature, washing with water till NH_3 could not be detected in the washings, keeping under water for three days, washing with alcohol and ether, and allowing to dry. Gladstone obtained NHI_2 by acting on an alcoholic solution of I with NH_3 (*C. J.* 4, 34; 7, 51); with H_2S it gave HI and NH_3, with SO_2Aq the products were NH_3, HI, and H_2SO_4. Stahlschmidt obtained NHI_2 by adding alcoholic NH_3 to an alcoholic solution of I (*P.* 119, 421).

Mono-iodamine NH_2I. Raschig (*A.* 230, 212) expected to obtain this compound by the reaction of NH_4Cl and NaOH with I, using these materials in the ratio $NH_4Cl:2I:2NaOH$; but the pp. was very quickly decomposed by water to $NH_3.NI_3$. Millon (*A. Ch.* [2] 69, 78) gave the formula NH_2I to the iodide prepared by him, and Marchand (*J. pr.* 19, 1) confirmed this composition. Guyard (*A. Ch.* [6] 1, 358) describes a light-brown explosive compound, decomposed by light, exploding in contact with water, prepared by NH_3Aq reacting with I in an iodide solution; to this compound he gives the formula NH_2I; with an ammoniacal solution of a Cu salt it forms $Cu_2I_2.2NH_2I$.

Tri-iod-diamine $N_2H_3I_3(=NH_3.NI_3)$. Obtained by mixing cold nearly saturated alcoholic solution of I and NH_3; decomposed by HClAq giving NH_3 and ICl in the ratio $2NH_3:3ICl$. This compound seems to have been obtained by Raschig (*A.* 230, 212) by mixing NH_4ClAq, I, and NaOHAq in the ratio $NH_4Cl:2I:2NaOH$, and washing the pp. with water.

Other compounds of nitrogen, iodine, and hydrogen. (1) *Iodammonium iodide*, $NH_3I.I$; a mobile brownish-red liquid, formed by adding finely powdered I to saturated NH_4NO_3Aq or $(NH_4)_2CO_3Aq$ mixed with about $\frac{1}{4}$ of an equivalent of KOH (Guthrie, *C. J.* [2] 1, 239). Soluble alcohol, ether, $CHCl_3$, CS_2, and KIAq; decomposes by heat, giving I and probably NH_3I; decomposes in the air to NH_3 and I; water forms NH_4I, HI, and NHI_2 which explodes producing N, I, and H_2O. According to Seamon (*C. N.* 44, 188), this compound is formed by act-

ing on dry I with dry NH_3, and absorbing the excess of NH_3 by standing near H_2SO_4. S. describes the compound as a nearly black liquid, S.G. 2·46 at 15°, solidifying at −2°, decomposing slowly at 15°, quickly at 70°.

(2) *Compounds of ammonia with iodine.* *a.* $NH_3.I$, obtained by the action of NH_3 on I at 10° (Millon, *A. Ch.* [2] 69, 78); formed at 80° according to Raschig (*A.* 241, 253). *β.* $(NH_3)_3I$ formed at 20° (Bineau, *A. Ch.* [3] 15, 71; Raschig, *l.c.*). *γ.* $(NH_3)_2I$, formed at 0°. *δ.* $(NH_3)_5I_2$ formed at −10° (R., *l.c.*). It is doubtful whether these bodies are true compounds or not.

Nitrogen, oxides of. N forms five oxides: N_2O, NO, N_2O_3, NO_2, N_2O_5. N_2O_3 and N_2O_5 are the anhydrides of HNO_2 and HNO_3 respectively; NO_2 reacts with water to produce both HNO_2 and HNO_3; N_2O is obtained by the decomposition of HNOAq, but the acid has not been obtained from the oxide; NO is a neutral oxide. Whether N_2O_3 exists in the gaseous state is not yet finally settled; the other oxides, with the exception of N_2O_5, are gases under ordinary conditions. NO_2 exhibits polymerism; at low temperature the molecular weight corresponds with the formula N_2O_4, and at higher temperatures with the formula NO_2. Besides these five oxides, there is said to exist a pernitric oxide NO_3 or N_2O_6.

Nitrous oxide N_2O. (*Nitrogen monoxide. Laughing gas.*) Mol. w. 43·98. Melts at −99°, and boils at −92° (Wills, *C. J.* [2] 12, 21). S.G. 1·527. S.G. liquid N_2O ·9756 at −5°, ·937 at 0°, ·8964 at 10°, ·8365 at 20° (Andréeff, *A. Ch.* [3] 56, 317; *cf.* Wills, *C. N.* 28, 170; Wroblewski, *C. R.* 97, 166; Cailletet a. Mathias, *C. R.* 102, 1202). V.D. 22·1. S.H.p. (equal wt. of $H_2O = 1$) 16° to 207° = ·22616 (Regnault, *Acad.* 26, 1), 26° to 103° = ·2126, 27° to 206° = ·2241 (Wiedemann, *P. M.* [5] 2, 81). $\frac{\text{S.H.p.}}{\text{S.H.v.}}$ 1·3106 at 0°, 1·27238 at 100° (Clausius, *Mechan. Wärmetheorie*, i. 62). C.E. (22° to 98°) ·0037067 (von Jolly, *P. Jubelbd.* 82). S. 1·305 at 0°, 1·095 at 5°, ·92 at 10°, ·778 at 15°, ·67 at 20°; absorption-coefficient $= 1·30521 - ·045362t + ·0006843t^2$ (Carius, *A.* 94, 139). Absorption-coefficient in alcohol $= 4·17805 - ·069816t + ·000609t^2$ (Carius, *l.c.*). H.F. $[N^2, O] = -17,740$; $[NO, N] = 3835$ (*Th.* 2, 198). For vapour-pressures from −25° to 40° *v.* Regnault, *J.* 1863. 66.

Nitrous oxide was discovered by Priestley in 1776, and carefully studied by Davy.

Formation.—1. By dissolving Zn in HNO_3Aq (S.G. 1·2 diluted with an equal vol. of water).—2. By decomposition of NH_2OHAq by $AgNO_3$, $K_2C_2O_4$, &c., *v.* Hydroxylamine, *Reactions*, No. 1 (vol. ii. p. 735).—3. By the gradual decomposition of $H_2N_2O_2Aq$ (*v. Hyponitrous acid*, p. 569).—4. By the action of $SnCl_2$ in HCl on HNO_3Aq or a nitrate.—5. By passing NO through SO_2Aq or an acid sulphite.—6. By the action of HNO_3Aq on Cu in presence of much $Cu2NO_3$; if NH_4NO_3 is present, much N_2O and N, with little NO, are produced (Acworth, *C. J.* 28, 828).

Preparation.—1. Pure NH_4NO_3 is slowly heated in a retort to a temperature at which gas begins to be given off. The gas flame is then lowered, and the decomposition allowed to proceed: $NH_4NO_3 = N_2O + 2H_2O$. It is best to make the NH_4NO_3 by neutralising pure dilute HNO_3Aq with pure NH_3Aq or $(NH_4)_2CO_3Aq$, evaporating till the B.P. gets to c. 120° and a drop solidifies on a cold plate, allowing to cool, and breaking up into small pieces. If the temperature rises above 250°, decomposition to N, O, and H_2O may occur with explosive violence; in the change $NH_4NO_3 = N_2O + 2H_2O$ c. 31,100 cals. are produced, whereas the change $NH_4NO_3 = N_2 + O + 2H_2O$ is accompanied by the production of c. 48,700 cals. (*Th.* 2, 205). To obviate explosions, Caseneuve (*D. P. J.* 257, 435) recommends to dry NH_4NO_3 carefully over a low flame, to bring the salt while warm into a retort or flask, to heat with a very small flame which is gradually increased till decomposition begins, and then to withdraw the flame. The gas is collected over hot water, brine, or Hg. If the gas is to be used as an anæsthetic, the greatest care should be taken that the NH_4NO_3 used is pure, and especially that it is quite free from NH_4Cl, else the N_2O may contain Cl; the gas should be passed through KOHAq and $FeSO_4Aq$, to absorb traces of Cl, NO_2, and NO.—2. A mixture of 5 parts $SnCl_2$, 10 parts HClAq S.G. 1·21, and ·9 parts HNO_3Aq S.G. 1·38, is heated to boiling, when pure N_2O is evolved in a regular stream; any alteration in the proportions may cause explosions (Campari, *C. C.* 1888. 1569).

Properties.—A colourless gas, with a slightly sweetish smell and taste. Supports combustion almost as well as O. When breathed, N_2O produces insensibility, which lasts for a short time only. It is often used as an anæsthetic in dental operations; for this purpose it is usually much compressed in iron bottles. N_2O is decomposed by heat, the decomposition being complete at c. 900°. H and N_2O forms an explosive mixture; most inflammable gases burn in N_2O. N_2O is liquefied at 0° by a pressure of c. 30° atmos.; the liquid occupies c. $\frac{1}{30}$ of the volume of the gas (Faraday, *A.* 56, 157). Liquid N_2O is colourless and very mobile; a drop burns when let fall on the skin; on evaporation much cold is produced; liquid N_2O boils in liquid CO_2. Metals dropped into liquid N_2O generally hiss as hot iron does in water. Glowing C swims on the liquid and burns briskly. Hg sinks and freezes; S, I, P do not react. Water freezes when added to liquid N_2O, but so sudden an evolution of vapour occurs that an explosion generally takes place (Faraday, *A.* 56, 157); nitric and sulphuric acids are frozen by liquid N_2O; alcohol, ether, and CS_2 mix, without freezing. By evaporating liquid N_2O in an air-stream, Wills (*C. J.* [2] 12, 21) obtained solid N_2O in some quantity; the solid is a snow-like substance, more compact than solid CO_2; when slightly warmed it melts, at c. −99°, and then boils, at c. −92°.

Reactions.—1. Decomposed by heat to N and O; change is complete at c. 900° (Langer a. V. Meyer, *Pyrochemische Untersuchungen* [Brunswick, 1885], 65; *cf.* Berthelot, *C. R.* 77, 1448).—2. Decomposed to N and O, by *electric sparks.* 3. Passed over red-hot *iron*, Fe_2O_3 and N are formed.—4. Potassium or sodium burns in N_2O setting free N.—5. Mixed with *hydrogen*, or other *combustible gas* such as CO, PH_3, H_2S, or a hydrocarbon, and brought to a flame, combustion ensues at the expense of the O of the N_2O (explosions occur with H).—6. *Easily burnt sub-*

stances, when inflamed and plunged into N_2O, burn almost as rapidly as in O; *e.g.* C, P, S, Na, &c.—7. Mixed with *oxygen*, and subjected to the electric discharge, NO_2 is formed.—8. A solution of N_2O in *water* is neutral to litmus; N_2O is, however, related to the acid $H_2N_2O_2$, as it is obtained by the decomposition of this acid in aqueous solution (*v. Hyponitrous acid*, p. 569). The hyponitrites may be regarded as compounds of the negative radicle N_2O with more positive oxides, *e.g.* $Ag_2O.N_2O$.

References to older memoirs.—Gay-Lussac, *G. A.* 58, 29; W. Henry, *Annals of Phil.* 24, 299, 344; Pleischl, *S.* 38, 461; Davy, *G. A.* 6, 105; Natterer, *P.* 62, 133; Dumas, *C. R.* 27, 463.

Nitric oxide NO. (*Nitrogen dioxide. Deutoxide of nitrogen. Nitrous gas* or *air.*) Mol. w. 29·97. V.D. 15; not changed from $-100°$ to 1200° (Daccomo a. V. Meyer, *B.* 20, 1832; Langer a. Meyer, *Pyrometrische Untersuchungen* [1885] 66). S.H.p. (equal wt. of H_2O = 1) 13° to 172° = ·23173 (Regnault, *Acad.* 26, 1); S.H.v. (equal wt. of H_2O = 1) ·1652 (Clausius, *Mechan. Wärmetheorie*, 1, 62). S. c. ·05 at ordinary temp. S. (in alcohol) ·309 at 2°, ·282 at 11·8°, ·266 at 20° (Bunsen, *Gasom. Methoden*, [2nd ed.] 227). S. (in H_2SO_4 S.G. 1·84) at 13° = 3·5; S. (in H_2SO_4Aq S.G. 1·5) at 18° = 1·7 (Lunge, *B.* 18, 1391). H.F. [N, O] = $-21{,}575$; [N^2O,O] = $-25{,}410$.

NO is liquefied at the following temperatures and pressures (Olszewski, *C. R.* 100, 940):—

Pressure in atmos.	71·2	57·8	49·9	41
Temperature . .	$-93·5°$	$-97·5°$	$-100·9°$	$-105°$
Pressure in atmos.	31·6	20	10·6	5·4
Temperature . .	$-110·9°$	$-119°$	$-129°$	$-138°$
Pressure	1 atmo.	138 mm.	18 mm.	
Temperature . .	$-153·6°$	$-167°$	$-176·5°$.	

The critical temp. is c. $-93·5°$ according to Olszewski; but according to Cailletet (*C. R.* 85, 1016) NO is liquefied at $-11°$ under a pressure of 104 atmos., but not at 8° even under 270 atmos. pressure. NO solidifies at $-167°$ (Olszewski, *l.c.*).

NO was discovered by Priestley and called by him *saltpetre-gas*.

Formation.—1. NO is probably formed in the first stages of those combustions in air whereby nitrites and nitrates are produced, *e.g.* in burning air with compressed O, in slowly burning P, ether, &c., in air (*v.* Nitrogen, *Reactions*, No. 1; p. 558). NO is also probably formed when electric sparks are passed through a mixture of N and O.—2. By reducing HNO_3Aq or HNO_2Aq; *e.g.* by reaction with Cu, by passing in SO_2, by electrolysis, &c. (*v.* Nitric acid, *Reactions*, Nos. 3, 4, 5; p. 520).—3. By reacting on KNO_3 with $FeCl_2Aq$ and HClAq, or with $FeSO_4Aq$ and H_2SO_4Aq.

Preparation.—1. A quantity of HClAq is divided into 2 equal parts; one portion is converted into $FeCl_2Aq$ by dissolving iron wire in it until it is saturated; the two portions are then mixed and placed in a retort or flask, KNO_3 is added in quantity nearly equal to that of the Fe used, and the whole is warmed ($6FeCl_2Aq + 8HClAq + 2KNO_3$ $= 6FeCl_3Aq + 2KClAq + 4H_2O + 2NO$). $FeSO_4Aq$ and H_2SO_4Aq may be substituted for $FeCl_2Aq$ and HClAq.—2. Cu cuttings are added to HNO_3Aq, S.G. 1·2, in a flask arranged so that it can be surrounded by cold water when desired; action begins after a little and red fumes of NO_2 are evolved; when the gas in the flask is quite colourless it is collected over cold water, or if required dry it is passed over solid dry KOH and then through conc. H_2SO_4. About 130 c.c. acid are used for 15 grams Cu. The HNO_3Aq used should not be more conc. than S.G. 1·2, and temperature must be kept as low as possible, else N_2O and N_2O_3 may be formed. If the action proceeds for some time the gas contains considerable quantities of N_2O, as the reaction of Cu with much $Cu(NO_3)_2Aq$ in presence of HNO_3 produces this gas (Acworth, *C. J.* 28, 828). But with all precautions, NO prepared by this method is always liable to contain N_2O and N (*v.* Acworth, *l.c.*). Carius (*A.* 94, 138) says NO can be obtained pure by passing the products of the reaction of Cu with HNO_3Aq into $FeSO_4Aq$, which absorbs NO but not N_2O or N, and then gently warming the solution thus obtained.—3. Kämmerer (*B.* 18, 3064) recommends to fill a Wolff's bottle with Cu turnings, add enough cold saturated $NaNO_3Aq$ to fill the bottle $\frac{1}{3}$, and then allow conc. H_2SO_4 to drop in little by little.—4. Thiele (*A.* 253, 246) prepares NO by adding conc. $NaNO_2Aq$ (free from carbonate) to $FeCl_2$ or $FeSO_4$ in HClAq.—5. SO_2 is prepared by heating Cu with conc. H_2SO_4, and passed into slightly warmed HNO_3Aq S.G. 1·15; the issuing gas is passed through wash-bottles wherein excess of SO_2 is absorbed ($3SO_2 + 2HNO_3Aq + 2H_2O = 3H_2SO_4Aq + 2NO$).

Properties.—A colourless gas; at great pressure and very low temperature, a colourless liquid; becomes solid at $-167°$. As NO combines with O immediately on coming into contact with air, it cannot be determined whether pure NO is or is not tasteless and odourless. Sl. sol. water, v. sl. sol. H_2SO_4, less sol. H_2SO_4Aq. NO does not change the colour of litmus. Substances which produce much heat when burning, *e.g.* P and C, continue to burn in NO if plunged into the gas when burning vigorously; burning S or H, or a burning taper, ceases to burn in NO. A mixture of NO and H is not explosive. NO is reduced to N_2O by Zn, Fe, SO_2, &c. At a very high temperature, c. 1700°, NO is decomposed to N and O.

The S.G. of NO has been determined from $-100°$ to 1200° (*v.* beginning of this article), for this temperature-interval the molecular formula is NO.

NO is a neutral oxide. In the compound NOCl, formed by the union of NO and Cl, NO acts as the more positive radicle; it also perhaps takes the part of the positive radicle in nitrosulphuric acid, which may be regarded as SO_2.OH.ONO.

Reactions.—1. Decomposed into N and O by *heat*, but only at a very high temperature; c. 1700°, according to Langer and V. Meyer (*Pyrochemische Untersuchungen*, 66).—2. *Electric sparks* produce N_2O (which then goes to N and O) and O (Berthelot, *Bl.* [2] 26, 101).—3. Reduced to N_2O by many *easily oxidised* substances, *e.g.* moist *zinc* or *iron* filings (NH_3 also is produced), *sulphur dioxide and water* (reductions occurs even in presence of O if H_2SO_4 is

also present, *v.* Lunge, *C. J.* 47, 465), *hot copper*, &c.—4. Heated with *potassium* or *sodium*, K_2O or Na_2O and N are formed.—5. Passed over red-hot *carbon* N and CO_2 are obtained.—6. Mixed with *hydrogen* and inflamed, H_2O and N are formed; NH_3 is formed by passing a mixture of NO and H over spongy Pt (L. Wright, *C. J.* 39, 357).—7. The *copper-zinc couple* acting on NO in presence of water produces NH_3 (Gladstone a. Tribe, *C. J.* 43, 341).—8. *Stannous chloride*, in presence of HClAq, produces $NH_2OH.HCl$, N, and $SnCl_4$; the action ceases at 100° (Divers a. Haga, *C. J.* 47, 623).—9. When a flame is brought to a mixture of NO and *carbon disulphide*, CO_2, SO_2, and N are produced very rapidly, and with a brilliant white flash.—10. In contact with *water* in the dark slowly produces HNO_2Aq, N, and a little N_2O (Cooke, *C. N.* 58, 115; *cf.* Russell a. Lapraik, *C. J.* 32, 37).—11. Contact with conc. *potash solution* causes a slow formation of KNO_2Aq, N_2O, and N (Gay-Lussac, *Gm.* 2, 378; Russell a. Lapraik, *C. J.* 32, 35).—12. With *alkaline solution of pyrogallol* N_2O and N are formed (R. a. L., *l. c.*).—13. Reduced to NH_3, with separation of I, by conc. *hydriodic acid* solution (Chapman, *C. J.* [2] 5, 166).—14. An *alkaline solution of stannous hydroxide* ($=K_2SnO_2$) produces $K_2N_2O_2$ and K_2SnO_3 (Divers a. Haga, *C. J.* 47, 361).—15. *Ferrous hydroxide*, in presence of much conc. KOHAq, reduces N_2O to NH_3 (D. a. H., *l. c.*).—16. Oxidised to HNO_3Aq by an alkaline solution of *potassium permanganate*, with separation of $MnO_2.xH_2O$ (Wanklyn a. Cooper, *P. M.* [5] 6, 288).—17. Oxidised to NO_2 and N_2O_3 by *nitric acid* of S.G. >1·15.—18. With *nitric acid in sulphuric acid*, $SO_2.OH.ONO$ is produced.—19. With *oxygen and water* NO is wholly oxidised to HNO_3Aq (Lunge, *C. J.* 47, 465).—20. With *oxygen and conc. sulphuric acid* forms $SO_2OH.ONO$ (L., *l.c.*).

Combinations.—1. With *oxygen* to form NO_2. According to Lunge (*C. J.* 47, 465), NO_2 is the chief or only product when excess of O is used, but with excess of NO both NO_2 and N_2O_3 are formed.—2. With *ferrous salts* in solution, to form deep-brown coloured liquids. Gay (*A. Ch.* [6], 5, 145) finds that the quantity of NO absorbed is independent of the kind of ferrous salt used and of dilution. It is proportional to the quantity of Fe in solution, and varies with temperature and pressure. The relation between quantity of NO absorbed and pressure is a special one; it resembles that which holds good in the solution of NH_3 by water. The solutions lose all NO *in vacuo*, or by passing a stream of H into them. The quantity of NO absorbed at 8° and 760 mm. nearly agrees with the formula $2NO.3FeSO_4$; between 8° and nearly 25° the formula $NO.2FeSO_4$ approximately expresses the quantity of NO absorbed; and at c. 25° the NO agrees with that required by $NO.5FeSO_4$. NO is also absorbed by *chromous*, *stannous*, and *mercurous salt solutions*.—3. With *antimony chloride*, to form $NO.2SbCl_3$; also with *aluminium*, *bismuth*, and *ferric chloride* (Beeson, *C. R.* 108, 1012).—4. NO combines with liquid N_2O_4 to form N_2O_3 (*q. v.*).

References to older memoirs.—Gay-Lussac, *A. Ch.* [3] 28, 229; Millon, *C. R.* 14, 908; Carius, *A.* 94, 138.

NITROGEN TRIOXIDE N_2O_3. (*Nitrous anhydride. Nitrogen sesquioxide.*) Mol. w. 75·9 (*v. infra*).

Formation.—1. By passing NO into liquid N_2O_4 at c. 20°, more or less pure liquid N_2O_3 is formed (Dulong, *A. Ch.* 2, 317; Péligot, *A.* 39, 327; Ramsay, *C. J.* 57, 590). According to Hasenbach (*J. pr.* [2] 4, 1), N_2O_3 is produced by passing a mixture of NO and NO_2 through a hot tube, and then into a vessel surrounded by a freezing mixture. Ramsay a. Cundall (*C. J.* 47, 672) showed that no contraction occurs when NO_2 and NO are mixed at the ordinary temperature.—2. By reacting on starch or As_2O_3 with HNO_3Aq S.G. 1·3 to 1·35 (Lunge, *B.* 11, 1641; Stenhouse a. Groves, *C. J.* 31, 545).—3. Fritzsche (*J. pr.* 22, 14) gently warmed red fuming HNO_3, condensed the vapour, again very gently warmed this liquid, and passed the vapour into a strongly cooled receiver; to 92 parts of the liquid thus obtained (chiefly N_2O_4) he added 45 parts of cold water very slowly, the liquid being kept very cold. Two layers of liquid were thus obtained; the under was very deep blue, and was regarded by Fritzsche as fairly pure N_2O_3; the upper layer, which was grass-green, was a solution of N_2O_3 and NO_2 in HNO_3Aq. By placing both liquids in a retort kept at 0°, the lower layer boiled, and a pure indigo-blue liquid condensed in the very strongly cooled receiver; this liquid consists chiefly of N_2O_3 according to Fritzsche. F. (*l.c.*) obtained a deep-blue liquid, containing, according to him, at least 93·4 p.c. N_2O_3, by distilling a large quantity of nitric acid which had been used in a battery, condensing the distillate in a vessel surrounded by snow and $CaCl_2$, and redistilling several times at the lowest possible temperature.—4. By the reaction of O on excess of NO, considerable quantities of N_2O_3 are produced (Lunge, *C. J.* 47, 466).—5. By dropping water on to 'chamber-crystals' (nitrosyl sulphate, $SO_2.OH.ONO$) (Streiff, *B.* 5, 285).

Preparation.—Pure N_2O_3 has not been obtained. 1. The gas obtained by reacting on starch or powdered As_2O_3 with HNO_3Aq S.G. 1·35 is nearly pure N_2O_3, according to Lunge (*B.* 11, 1229, 1641); the starch is made into a paste with water, and the acid is added from a dropping funnel; the flask is at first gently warmed, and then plunged into cold water. Stenhouse a. Groves (*C. J.* 31, 545) also recommend HNO_3Aq S.G. 1·35. They say that the reaction proceeds at 70° with production of nearly pure N_2O_3.—2. Pure NO is passed into cold liquid N_2O_4. The product is not pure N_2O_3 (Ramsay, *C. J.* 57, 591).

Properties. — The liquid obtained by condensing the gaseous product of the reaction between As_2O_3 and HNO_3Aq, S.G. 1·3, at 70°, passing the vapour of this liquid over P_2O_5, and condensing again, is deep blue; it does not solidify at −90°; it is miscible with liquid N_2O; O passed into liquid N_2O_3, mixed with N_2O_4, very slowly, if at all, combines with the N_2O_3; liquid N_2O_3 appears to dissociate slightly to NO and N_2O_4 at −90° (Ramsay, *C. J.* 57, 597). Gaines (*C. N.* 48, 97) says that N_2O_3 liquefies at −14·4°. According to Geuther, liquid N_2O_3 boils at 3·5°, and has the following S.G. 1·464 at −8°, 1·4555 at −4°, 1·451 at −1°, 1·449 at 0°, 1·4485 at 1°, 1·447 at 2°. Birhaus

(*C. R.* 109, 63) says that N_2O_3 solidifies at $-82°$; Ramsay found the blue liquid to remain liquid at $-90°$. (Birhaus's liquid probably contained N_2O_4, as it was formed by the action of O on excess of NO_2.)

Molecular weight of nitrogen trioxide.—Ramsay determined the lowering of the freezing-point of N_2O_4, after passing in NO and calculating the quantity of N_2O_3 produced by the increase in weight; his results, on the whole, are in favour of the formula N_2O_3 for the liquid compound. There has been much discussion as to the existence of this oxide in the state of gas. Some chemists deny the existence of a compound nN_2O_3, and say that the reactions of this supposed compound are those of a mixture of NO and NO_2 (containing variable quantities of N_2O_4 according to the temperature). As NO rapidly combines with O, a mixture of NO and NO_2 would also surely combine with O; but Ramsay a. Cundall have shown (*C. J.* 47, 187) that O acts very slowly on the blue liquid which, on the hypothesis of the non-existence of N_2O_3, is a mixture of NO and N_2O_4; this result is confirmed by Ramsay's later observations (*C. J.* 57, 597), and also by observations made by Richardson (*C. J.* 51, 397). Lunge has shown (*D. P. J.* 233, 63) that the gas from the blue liquid which has the empirical composition N_2O_3 is not wholly transformed into NO_2 even in presence of 10 times as much O as is required on the assumption that the gas in question is a mixture of NO and N_2O_4. Moreover, Ramsay a. Cundall (*C. J.* 47, 672) showed that although no change in appearance or volume occurs when NO_2 gas is mixed with NO, yet on lowering the temperature of the mixed gases, by HClAq and ice, a dark-blue liquid was formed (liquid NO is colourless, and liquid N_2O_4 is yellow-red). Again, Ramsay (*C. J.* 57, 597) found that the blue liquid does not freeze at $-90°$, but part of a mixture of NO and N_2O_4 would freeze at $-10°$, as this is about the freezing-point of N_2O_4. Some of the reactions of N_2O_3 with alkalis, H_2SO_4, &c., are scarcely those of a mixture of two substances (*v. Reactions*, 1, 2, and 5). According to Gay-Lussac (*G. A.* 58, 29) a mixture of excess of NO with O allowed to stand for a long time over KOHAq forms KNO_2Aq, and the gases disappear in the ratio required to form N_2O_3.

As regards the existence of N_2O_3 as a gas, Lunge's experiments show that the oxidation of the gas obtained by heating starch with HNO_3Aq S.G. 1·35 to NO_2 is not completed by a very large excess of O (*D. P. J.* 233, 63; *B.* 12, 357). Now, as Lunge has also shown (*C. J.* 47, 465), that NO_2 is the sole product, or almost the sole product, of the action of excess of O on NO, and therefore as soon as O is added to NO there must be present a mixture of NO, NO_2, and O, it is difficult to escape the conclusion that the action of a large excess of O on a mixture of NO and NO_2 must result in the formation of much NO_2; and that, therefore, the gas obtained by HNO_3Aq acting on starch, contains N_2O_3, which is not oxidised by O to N_2O_4. Ramsay a. Cundall (*C. J.* 47, 672) found that no contraction occurred on mixing NO_2 with NO; if any N_2O_3 were formed contraction must have occurred. R. a. C. prepared a blue liquid having the composition N_2O_3 (by action of HNO_3Aq on As_2O_3), and determined the V.D. of the gas obtained by gently warming the liquid. The V.D. was 22·35 at 18·2°; V.D. corresponding to $N_2O_3 = 38$. If the gas was supposed to be a mixture of NO, NO_2, and N_2O_3 (without any N_2O_4), there must have been present 17·63 p.c. N_2O_3 to raise the S.G. of $NO + NO_2$ to 22·35; hence the maximum percentage of N_2O_3 gas which could be present was 17·63; but as the gas certainly contained some N_2O_4, the percentage of N_2O_3 gas must have been less than 17·63. R. a. C. show that a mixture of NO, NO_2, and N_2O_4, having the same percentage of N and O as N_2O_3, would have the V.D. 23·42 under the conditions of their experiment, assuming a formula given by Willard Gibbs to be correct; hence they conclude that the gas examined by them was more probably a mixture of NO, NO_2, and N_2O_4, than a mixture of these gases with N_2O_3. R. a. C. also draw attention to the remarkable result of Lunge's experiments, which he has himself stated, that the dissociation of N_2O_3 (supposing it to exist as a gas) is almost independent of temperature. According to Luck (*Fr.* 8, 402) and Moser (*W.* 2, 139), the absorption-spectrum of the gas supposed to be N_2O_3 is identical with that of NO_2 (containing N_2O_4). On the question of the existence or non-existence of gaseous N_2O_3, besides the memoirs referred to, *v.* Lunge, *B.* 11, 1232, 1641; 12, 357; 15, 495; Witt, *B.* 12, 2188; Geuther, *A.* 245, 96.

Reactions.—1. Dissolves in *water* at 0°, forming a blue liquid; on warming, NO is evolved and HNO_3Aq remains; if the solution is neutralised by alkali, a mixture of a nitrite (MNO_2) and nitrate (MNO_3) is obtained. According to Fremy (*C. R.* 79, 61) addition of a little water causes evolution of pure NO, and HNO_3 is formed, but addition of much cold water produces a fairly stable solution, which may be kept unchanged for some days, and which slowly evolves NO and N_2O_3 on warming. Addition of sand, powdered $CaSO_4$, or other indifferent substance, causes rapid decomposition to HNO_3Aq and NO. The solution is a strong reducer; cold SO_2Aq forms various nitro-derivatives of S oxy-acids, warm SO_2Aq forms NO, N, NH_3, and H_2SO_4 (F., *l.c.*; *cf.* Reinsch, *J. pr.* 28, 399).—2. Passed into *alkali solution*, nitrite and nitrate are formed (*cf. Nitrous acid* and *Nitrites*, p. 567). Gay-Lussac (*G. A.* 58, 29) says that KNO_2 is formed by allowing O, mixed with a large excess of NO, to stand over KOHAq, and that the gases disappear in the ratio required to form N_2O_3.—3. Decomposes *urea* evolving N.—4. With *benzenoid primary amido- compounds*, forms diazo- compounds (*q. v.* vol. i. p. 397). With *paraffinoid amido-compounds*, the general result is to substitute OH for NH_2 and evolve N.—5. With conc. *sulphuric acid*, nitrosyl sulphate (SO_2.OH.ONO) is formed. As NO_2 reacts with conc. H_2SO_4 to form SO_2.OH.ONO and HNO_3, and as NO passed into H_2SO_4 containing HNO_3 forms SO_2.OH.ONO and H_2O, it is sometimes argued that the reaction of N_2O_3 with H_2SO_4 is easily explained by the view that regards N_2O_3 as a mixture of NO and NO_2; if this view is held, then the two reactions

(1) $2NO_2 + H_2SO_4 = SO_2.OH.ONO + HNO_3$;

(2) $HNO_3 + 2NO + 3H_2SO_4$

$= 3SO_2.OH.ONO + 2H_2O$ must proceed simultaneously and at equal rates, and the supposed mixture must never contain more NO than is shown by the ratio $NO:NO_2$, otherwise some NO would pass on unabsorbed. According to Lunge (*l.c.*) (confirmed by Groves, *C. S. Proc.* 1, 24), NO only slowly converts H_2SO_4 containing HNO_3 into $SO_2.OH.ONO$.

Combinations.—According to Weber (*P.* 118, 471) N_2O_3 combines with $SnCl_4$ and $TiCl_4$, *e.g.* to form $SnCl_4.N_2O_3$.

NITROGEN DIOXIDE NO_2; and TETROXIDE N_2O_4 (*Nitrogen peroxide. Nitroso-nitric anhydride*). The mol. w. of the compound N_nO_{2n} varies with temperature; at low temperatures and small pressure (c. $-12°$ at 115 mm.) the mol. w. is $91{\cdot}86 = N_2O_4$, and at moderately high temperatures (c. 150°) the mol. w. is $45{\cdot}93 = NO_2$ (*v. infra*). N_2O_4 melts at $-10°$ (Deville a. Troost, *C. R.* 64, 257; Ramsay, *C. J.* 57, 590). Boils at 21·64° (760 mm.; Thorpe, *C. J.* 37, 224). S.G. (liquid) $\frac{0°}{4°} = 1{\cdot}4903$ (Thorpe, *l.c.*). V.D. at $-12°$ and 115·4 mm. = 42·54 (Natanson, *W.* 27, 606); at 130° a. 718 mm. = 23·26 (Richardson, *C. J.* 51, 397); at 183° a. 760 mm. = 22·7 (Deville a. Troost, *C. R.* 64, 237); at 27° a. 16 to 35 mm. = 23·1 (Troost, *C. R.* 86, 1395). S.H. (liquid) ·46 (Ramsay, *C. J.* 57, 590); for S.H. at different temperatures *v.* Berthelot a. Ogier (*A. Ch.* [5] 30, 382). For heat of fusion *v.* Ramsay (*l.c.*). H.F. $[N,O^2] = -2{,}005$; $[NO,O] = 19{,}570$; $[N,O^2,Aq] = 5{,}750$ (*Th.* 2, 199). For electrical resistance of liquid N_2O_4 *v.* Boguski (*Z. P. C.* 5, 69). For absorption-spectrum *v.* Kundt (*P.* 141, 157), Gernez (*C. R.* 74, 465), Luck (*Z.* [2] 6, 287). For thermal expansion *v.* Thorpe (*C. J.* 37, 224).

Molecular weights of nitrogen peroxide.—The V.D. at low temperatures near the liquefying point corresponds with the formula N_2O_4, and the same formula expresses the molecular composition at c. 27° under a pressure of 16 to 35 mm.; when heated to c. 150° the V.D. shows that the molecular formula is NO_2. Measurements of V.D. are given by Deville a. Troost (*C. R.* 64, 257); Troost (*C. R.* 86, 1395); Playfair a. Wanklyn (*C. J.* 15, 156); E. a. L. Natanson (*W.* 27, 606); Richardson (*C. J.* 51, 397). That the change in V.D. measures a process of dissociation from N_2O_4 to NO_2 has been shown by Natanson (*l.c.*); Naumann (*A. Suppl.* 6, 205; *B.* 11, 2045); Salet (*C. R.* 67, 488). The amount of dissociation is increased by raising temperature or lowering pressure (*v.* especially Natanson, *l.c.*). Ramsay determined the lowering of the freezing point of acetic acid by dissolving N peroxide in it (*C. J.* 53, 621), and also the lowering of f. p. of C_6H_5Cl and $CHCl_3$ by the peroxide (*C. J.* 57, 590); both results tend to show that the mol. w. of the liquid compound is N_2O_4.

Formation.—1. By passing electric sparks through a mixture of O and N.—2. By bringing NO into contact with excess of air or O.—3. By heating $Pb(NO_3)_2$. — 4. By the action of $AgNO_2 + NO_2Cl$ (Exner, *C. C.* 1872. 273); but the existence of NO_2Cl is denied by Williams (*C. J.* 49, 226).—5. According to Hasenbach (*J. pr.* [2] 4, 1), by passing O into the liquid obtained by heating starch with HNO_3Aq and condensing; but the observations of Ramsay a. Cundall (*C. J.* 47, 187) show that O very slowly, if at all, combines with N_2O_3.—6. By the reaction between NOCl and KNO_3 (Girard a. Pabst, *Bl.* [2] 30, 351).

Preparation.—1. A mixture of dry NO and about an equal volume of dry O is passed over dry KOH, and then into a vessel cooled to $-20°$; solid N_2O_4 is thus obtained (Péligot, *A.* 9, 259; 39, 327; *cf.* Dulong, *G. A.* 58, 53; a. Lunge, *C. J.* 47, 465).—2. Dry powdered $Pb(NO_3)_2$ is heated in a tube of hard glass, and the gas is passed into a U tube cooled to c. $-8°$; a stream of dry O is passed through the liquid in the U tube for some time (Péligot, *l.c.*; Thorpe, *C. J.* 37, 224).—3. By very gently heating As_2O_3 with HNO_3Aq S.G. 1·5 and a little conc. H_2SO_4, and passing O into the liquid thus obtained (*cf.* Ramsay a. Cundall, *C. J.* 47, 187, with Lunge, *B.* 11, 1641).—4. By distilling fuming HNO_3 at a low temperature, and fractionating the distillate in a stream of dry O (Fritzsche, *J. pr.* 22, 21). Setlick (*C. C.* 1888. 461) has determined the yields of NO_2 obtained by the various processes.

Properties.—At temperatures below $-10°$ a white, crystalline (? prismatic), deliquescent solid; between $-10°$ and 21·6° a liquid, which is nearly colourless at $-9°$, yellow at 0°, and orange at 21°; at temperatures above 21·6°, a gas, the colour of which deepens from orange-yellow to nearly black as temperature rises. At c. 180°–200° decomposition to NO + O begins and is complete at c. 620° (Richardson, *C. J.* 51, 397; *cf. Reactions*, No. 1). The colourless liquid is N_2O_4; as this dissociates into NO_2 the colour becomes deeper and deeper red (*v.* Salet, *C. R.* 67, 488; also *v. supra*). The gaseous compound at ordinary temperatures is a mixture of NO_2 and N_2O_4; this gas is reddish-brown, has a pungent odour, is irrespirable, and stains the skin yellow. NO_2 dissolves in cold water, forming HNO_2Aq and HNO_3Aq; it is dissolved, apparently without change, by $CHCl_3$, C_6H_5Cl, CS_2 (Friedburg, *C. N.* 47, 52), and $C_6H_5NO_2$. As solution of NO_2 in HNO_3 does not show the absorption-lines of gaseous and liquid N_nO_{2n} it is probable that the solution in HNO_3 contains a compound or compounds of the two substances (Gernez, *C. R.* 74, 465). NO_2 probably combines with NO at low temperatures to form N_2O_3 (*cf. Combinations*, No. 1).

NO_2 is an acidic oxide, inasmuch as it reacts with H_2O to form HNO_2Aq and HNO_3Aq; because of this reaction it may be looked on as nitroso-nitric anhydride, or perhaps better (as there is no nitroso-nitric acid) as a mixed anhydride. There are no salts corresponding with NO_2. Numerous nitro- compounds are known, obtained by substituting the monovalent radicle NO_2 for H.

Reactions.—1. *Heat* dissociates N_2O_4 to $2NO_2$ (*v.* beginning of this article). At c. 180° a. 755 mm. decomposition to NO + O begins; at c. 400° about 33 p.c. of the NO_2 is decomposed, at c. 500° 60 p.c. is decomposed, and at c. 620° the change is complete; on cooling, the NO + O recombine to form NO_2 (Richardson, *C. J.* 51, 397).—2. *Electric sparks* are said to decompose NO_2 to N and O; according to Richardson (*C. J.* 51, 402) a very small quantity of a white solid is produced.—3. NO_2 dissolves in *water*; added to a little ice-cold H_2O a green solution is obtained, which becomes blue on dilution, and then colour-

less; the solution gives the reactions of HNO_2 and HNO_3. On warming NO_2Aq, or on adding NO_2 to hot water, NO is evolved and HNO_3Aq remains ($3NO_2 + H_2O + Aq = 2HNO_3Aq + NO$). The cold colourless solution of NO_2 in water may be raised to the boiling-point without a complete decomposition of the HNO_2Aq to HNO_3Aq and NO; addition of Pt wire or powdered glass, &c., causes decomposition of NO_2Aq with evolution of NO. NO_2Aq decomposes HIAq and iodides in solution with separation of I; it also deoxidises $KMnO_4Aq$.—4. With *aqueous solution of an alkali* NO_2 produces a nitrite and a nitrate.—5. *Sulphydric acid in solution* absorbs NO_2, evolving NH_3 and depositing S. — 6. NO_2 passed into *conc. sulphuric acid* forms HNO_3 and nitrosyl sulphate (lead-chamber crystals, $SO_2.OH.ONO$) (*v.* Lunge, *D. P. J.* 233, 65).—7. NO_2 dissolves in very *conc. nitric acid*, forming a yellow liquid, which is probably not merely a solution of NO_2 in HNO_3, inasmuch as it does not show the absorption-lines of gaseous or liquid N_2O_4, whereas a solution in CS_2 does show these lines (*v.* Gernez, *C. R.* 74, 465).—8. NO_2 reacts with many *carbon compounds* replacing H by NO_2; with *alcoholic iodides* it usually produces nitrates of the alcoholic radicle, *e.g.* $C_2H_5I + N_2O_4 = C_2H_5NO_3 + NO + I$.—9. With cold *boron chloride*, crystals $BCl_3.NOCl$ are formed (Geuther, *J. pr.* [2] 8, 854).—10. *Carbon monoxide* is said to be partly oxidised to CO_2, while part of the CO combines with NO_2.—11. When NO_2 is mixed with *hydrogen*, and the mixed gases are passed over spongy Pt, H_2O and NH_3 are formed.—12. Ordinary *combustibles* are extinguished in NO_2; but strongly burning *phosphorus* and *carbon* continue to burn.—13. Many *metals* decompose NO_2, forming oxides and N; Fe, Cu, &c., at a red heat, K and Na at the ordinary temperature.—14. Liquid N_2O_4 reacts with *mercury* to form $HgNO_3$ and NO without any nitrite; the equation $2N_2O_4 + 2Hg = 2HgNO_3 + 2NO$ is almost realised quantitatively (Divers a. Shimidzu, *C. J.* 47, 630). With *silver*, liquid N_2O_4 forms $AgNO_3$; *copper* probably forms $Cu_2(NO_3)_2$ (D. a. S., *l.c.*).—15. Liquid N_2O_4 reacts with *liquid sulphur dioxide* to form $(NO_2)_2.S_2O_5$ (De la Provostaye, *A. Ch.* [3] 73, 362).—16. With *sulphuric anhydride*, NO_2 gas forms $NO_2.S_2O_5.O.NO_2$ (Weber, *P.* 123, 337).

Combinations.—1. With *nitric oxide*, at low temperatures, to form a blue liquid which is chiefly N_2O_3 (Dulong, *A. Ch.* 2, 317; Peligot, *A.* 39, 327; Ramsay, *C. J.* 57, 590; Richardson, *C. J.* 51, 397). Ramsay a. Cundall (*C. J.* 47, 672) found that no contraction occurs when dry NO_2 and NO are mixed at the ordinary temperature. According to Hasenbach (*J. pr.* [2] 4, 1), N_2O_3 is formed by passing NO and NO_2 through a hot tube, and then into a well-cooled receiver.—2. With *chlorine*, and *bromine*, to form NO_2Cl, and NO_2Br, respectively (Gay-Lussac, *A. Ch.* [3] 23, 203; Landolt, *A.* 116, 177; but denied by Williams, *C. J.* 49, 226).—3. With *antimonic chloride*, to form $3SbCl_5.N_2O_4$; obtained by heating in a sealed tube at 100° (Besson, *C. R.* 108, 1012).—4. NO_2 also combines with the *chlorides of aluminium, antimony* ($SbCl_3$), *bismuth*, and *iron*; the compounds are decomposed by water, and also by a gentle heat (B., *l.c.*).—5. With *phosphorus pentafluoride*, to form crystals of $NO_2.PF_5$; very easily decomposed (Tassel, *C. R.* 110, 1264).—6. With *magnesium hydrogen phosphate*, to form $2MgHPO_4.NO_2$ (Luck, *Fr.* 1874. 255).—7. With *amylene* (and some other hydrocarbons) to form $C_5H_{10}(NO_2)_2$.

Constitution of N_2O_4.—From the reactions of liquid N_2O_4 with Hg and Ag, whereby $HgNO_3$, or $AgNO_3$, and NO are produced, Divers a. Shimidzu conclude that N_2O_4 is best represented as $NO.NO_3$ (*C. J.* 47, 630). This formula is in keeping with the reaction $AgO.NO + NO_2Cl = AgCl + NO.ONO_2$ (Exner, *C. C.* 1872, 273); this argument, however, assumes $AgNO_2$ to have the structure $AgO.NO$ (*v. Nitrites*, p. 567); it also assumes the existence of NO_2Cl. The formation of nitrosyl sulphate by the reaction of N_2O_4 with H_2SO_4 is also in keeping with the formula $NO.NO_3$; $NO.NO_3 + H_2SO_4 = NO.HSO_4 + HNO_3$. Also, if nitrous acid is assumed to be $HO.NO$, then the formation of this acid and HNO_3 by the reaction of N_2O_4 with water points to the formula $NO.ONO_2$ ($NO.ONO_2 + H_2O = NO.OH + HO.NO_2$). The formation of diazo-benzene nitrate by the reaction of N_2O_4 with amido-benzene is in keeping with the formula $NO.ONO_2$; thus $C_6H_5.NH_2 + NO.ONO_2 = NO_2.O.N{:}N.C_6H_5 + H_2O$. The formation of $C_2H_5.ONO_2$ by the reaction of N_2O_4 with C_2H_5I is best expressed by writing N_2O_4 as $NO.ONO_2$ ($C_2H_5I + NO.ONO_2 = C_2H_5.ONO_2 + I + NO$). The fact that $C_5H_{10}(NO_2)_2$ when reduced by Sn and HClAq yields NH_4Cl and not an NH_2 compound, induced V. Meyer (*A.* 171, 5) to assign to N_2O_4 the formula $NO.O_2.NO$, and to write $C_5H_{10}(NO_2)_2$ as $C_5H_{10}(ONO)_2$; because had the C been in direct union with N, an NH_2 compound would have been formed on reduction. N_2O_4 is dissociated by heat to $2NO_2$; this reaction seems to point to the constitution $O_2N.NO_2$, or perhaps to $NO.O_2.NO$. Whichever formula is adopted, the reactions of N_2O_4 make it evident that some substances separate the group NO_2, and others the group ONO, and that the way in which the molecule N_2O_4 splits up depends largely on the conditions of the reaction.

NITROGEN PENTOXIDE N_2O_5 (*Nitric anhydride*). Mol. w. uncertain, as compound has not been gasified.

Formation.—1. By passing Cl over $AgNO_3$ ($2AgNO_3 + Cl_2 = 2AgCl + N_2O_5 + O$).—2. By dehydrating conc. HNO_3 by P_2O_5 ($2HNO_3 + P_2O_5 = 2HPO_3 + N_2O_5$).—3. By the reaction of NO_2Cl on $AgNO_3$ at 60° – 70° ($AgNO_3 + NO_2Cl = AgCl + N_2O_5$; Odet a. Vignon, *C. R.* 69, 1142; 70, 96; but the existence of NO_2Cl is very doubtful, *v.* Williams, *C. J.* 49, 226).

Preparation.—1. Perfectly dry $AgNO_3$ is placed in a dry U tube, which is connected by a glass tube, without corks or caoutchouc, with another dry U tube having a small reservoir at the bottom; the U tube containing $AgNO_3$ is immersed in a water-bath, and the other U tube is surrounded by ice and salt; a very slow stream of dry CO_2 is passed through the apparatus, the $AgNO_3$ being kept at c. 180° (to expel every trace of moisture); a very slow stream of dry Cl is then passed from a gasholder (the Cl being stored over conc. H_2SO_4, and driven out by the inlet of H_2SO_4), the $AgNO_3$ being heated to 95°, and the temperature then lowered to 58°–68°. After a time crystals of N_2O_5 appear

in the cooled U tube, while a little liquid (N_2O_4 or N_2O_3) collects in the small reservoir. Not more than 3 to 4 litres Cl should pass in 24 hours. To transfer the N_2O_5 to another vessel, the Cl is replaced by a current of dry CO_2, the U tube is connected by a glass tube with the vessel, which is immersed in a freezing mixture, the U tube is removed from its freezing mixture, and the N_2O_5 is poured into the vessel (Deville, *A. Ch.* [3] 28, 241).—2. Very conc. HNO_3 is surrounded by ice and salt, rather more P_2O_5 than the wt. of HNO_3 is added little by little, so that the temperature does not rise above 0°, the thick mass is brought into a wide retort and distilled at as low a temperature and as slowly as possible, the retort being cooled if the liquid froths; pure N_2O_5 condenses in the cooled receiver, but towards the end of the reaction liquid $2N_2O_5.H_2O$ is formed (Berthelot, *Bl.* [2] 21, 53; a modification of the process given by Weber, *J. pr.* [2] 6, 342). About 80 grams N_2O_5 are obtained from 150 gr. HNO_3.

Properties and Reactions.—Very lustrous, translucent, rhombic prisms; melts c. 30°, with partial decomposition to N_2O_4 and O, and boils between 45° and 50°. N_2O_5 should be kept in stoppered bottles over H_2SO_4. At c. 15° the crystals become yellowish, but are colourless when kept in a freezing mixture (Weber, *l.c.*). S.G. c. 1·64. H.F. $[N^2,O^5] = -31,600$ (Berthelot, *A. Ch.* [5] 6, 145); $[N^2,O^5,Aq] = 29,820$ (*Th.* 2, 199), N_2O_5 decomposes slowly when kept, rapidly in sunlight, giving N_2O_4 and O (Berthelot, *Bl.* [2] 21, 53). Burning P burns brightly in slightly-warmed N_2O_5; C burns in the vapour of N_2O_5, but not in the solid or liquid compound; K burns brightly, but most of the metals are without action on N_2O_5; with S there is formed $(NO_2)_2S_2O_5$ (Weber, *l.c.*). N_2O_5 reacts with water to form HNO_3. With conc. HNO_3, it produces $H_2N_4O_{11}$ ($=2N_2O_5.H_2O$, or $N_2O_5.2HNO_3$; *v. Dinitric acid*, under NITRIC ACID, p. 520). The reactions of N_2O_5 point to the constitution $NO_2.O.NO_2$.

PERNITRIC OXIDE NO_3 or N_2O_6. According to Hautefeuille a. Chappuis (*C. R.* 92, 80, 134; 94, 1111, 1306), a very unstable compound of this composition is obtained by the action of the silent electric discharge on a mixture of N and O at a low temperature. When a certain quantity is formed, the substance begins to decompose to NO_2 and O. Berthelot (*Bl.* [2] 35, 227) says that the compound is obtained by the action of the induction discharge on a mixture of O and NO_2. The compound is described as a liquid which does not solidify in a freezing mixture of ice and salt, and is extremely unstable, decomposing to NO_2 and O.

Nitrogen, oxyacids of. The only oxyacids of N which have been isolated are nitric (HNO_3) and dinitric ($H_2N_4O_{11}$); nitrous acid (HNO_2) and hyponitrous acid ($H_2N_2O_2$) are known in aqueous solution. Nitric and dinitric acids are described under the heading NITRIC ACID (p. 517). The present article contains descriptions of nitrous and hyponitrous acids and their salts.

NITROUS ACID and NITRITES; HNO_2Aq and M^INO_2. Nitrites are usually, if not always, accompanied by nitrates in nature. Nitrites are present int he atmosphere; Warington (*C. J.* 39, 229) has shown that when distilled water is exposed to the air it soon gives the reactions of nitrites. Small quantities of nitrites are present in many river and well waters (*v.* Warington, *C. J.* 55, 537; Munro, *C. J.* 49, 632). The juices of many plants contain nitrites (Genadius, *Am. Ch.* 5, 7). Nitrites are sometimes, but not generally, found in saliva (Wurster, *B.* 22, 1901). Nitrites are formed in the soil by oxidation of various nitrogenous compounds (*v.* NITRIFICATION, p. 521). $NaNO_2$ is formed by exposing Pt black to air and NaOHAq (Loew, *B.* 23, 1443). NH_4NO_2 is produced by passing O and air over Pt black at 180°-300° (Ilosva, *Bl.* [3] 2, 734). NH_4NO_2 is also produced by burning H in air (Struve, *J.* 1870. 199, 209; Schönbein, *J.* 1862. 94; Zöller a. Grete, *B.* 10, 2145); and also during the slow combustion in air of P or ether (Berthelot, *A. Ch.* [5] 12, 440; *C. R.* 108, 543; Kolbe, *A.* 119, 176; Ilosva, *Bl.* [3] 2, 734). It was formerly stated that NH_4NO_2 is formed by the direct union of N and H_2O (by evaporating H_2O in air), but this has been disproved (Carius, *A.* 174, 31; Weith a. Weber, *B.* 7, 1745); Berthelot, however, asserts that NH_4NO_2 is produced by subjecting H_2O and pure N to the action of a very powerful induction-coil (*Bl.* [2] 27, 338). NH_4NO_2 is also formed by the oxidation of NH_3 by ozone (Carius, *l.c.*; Goppelsröder, *J. pr.* [2] 4, 139, 383). Fe nitrite is said to be formed by passing air over reduced Fe at 190°–250° (Ilosva, *Bl.* [3] 2, 734). Alkali nitrites are formed, along with nitrates, by the reaction of N_2O_3 on alkali solutions (*v. Nitrogen trioxide*; *Reactions*, No. 2, p. 564). Nitrous acid, along with HNO_3, is produced by the action of cold water on N_2O_3 (*v. Nitrogen trioxide*; *Reactions*, No. 1, p. 564). Nitrites are also formed by the reduction of nitrates; *e.g.* by heating KNO_3, O is evolved and KNO_2 remains; or by the action of amalgamated Zn on KNO_3Aq, KNO_2Aq is produced.

The normal nitrites have the composition M^INO_2 and $M^{II}(NO_2)_2$; several basic nitrites are known. Most of the normal nitrites are soluble in water and alcohol; $AgNO_2$ is one of the least soluble nitrites, from it most of the other nitrites may be obtained. Nitrites are decomposed by heat, evolving NO or NO_2, and leaving metallic oxide or metal; solutions of nitrites are decomposed by boiling, generally with evolution of NO and formation of nitrates. Nitrites in solution are decomposed by dilute H_2SO_4Aq, giving HNO_2Aq, which soon decomposes to HNO_3Aq and NO. Acidulated solutions of nitrites reduce $KMnO_4Aq$, $K_2Cr_2O_7Aq$, H_2SAq, &c.; they ppt. Au from $AuCl_3Aq$, and Hg from mercurous solutions. These solutions decompose KIAq with separation of I, and give a brown colour with $FeSO_4Aq$; these reactions serve to distinguish nitrites from nitrates. (For details regarding the detection and estimation of nitrites, a *manual of analysis* must be consulted.) Nitrites may be regarded either as MO NO or as $M.NO_2$; Divers (*C. J.* 47, 226) endeavours to show that the second view is preferable.

Nitrous acid HNO_2Aq. This acid is known only in aqueous solution; and it is doubtful whether HNO_2Aq has been obtained free from HNO_3Aq. Fremy (*C. R.* 70, 61) says that a solution of N_2O_3 in a considerable quantity of cold water may be kept for some days without change, and that on boiling NO and N_2O_3 are

evolved. The solution very probably contains HNO_2, but whether it is free from HNO_3 or not is undecided. This solution acts as a strong reducer. Thomson gives the thermal data $[N^2,O^3,Aq] = -6,820$; $[H,N,O^2,Aq] = 30,770$; $[2NO,O,Aq] = 36,330$; $[H,NO,O,Aq] = 52,345$ (*Th.* 2, 199).

Nitrites $M^IN O_2$ and $M^{II}(NO_2)_2$; also basic salts, $xMO.yN_2O_3$, and $xM_2O_3.yN_2O_3$. The nitrites have been examined chiefly by Fischer (*P.* 74, 115), Lenz (*P.* 118, 282), Hampe (*A.* 125, 295), Stromeyer (*A.* 96, 230), Lang (*J. pr.* 86, 299).

Ammonium nitrite NH_4NO_2. A crystalline mass, decomposed by heat to N and H_2O (*v.* NITROGEN, *Preparation*, No. 2, p. 557). Obtained by decomposing NH_4ClAq by $AgNO_2Aq$. Berthelot (*Bl.* [2] 21, 55) says this salt is formed, along with N, by the action of dry NH_3 on NO and O. It was formerly stated that NH_4NO_2 is produced by evaporating water in air free from NH_3, but this was disproved by Carius (*A.* 174, 31) and by Weith a. Weber (*B.* 7, 1745). According to Berthelot (*Bl.* [2] 27, 238) NH_4NO_2 is produced by the action of a powerful induction-coil on a mixture of H_2O and pure N. NH_4NO_2 is also formed by oxidising NH_3Aq by ozone (Carius, *l.c.*; Goppelsröder, *J. pr.* [2] 4, 139, 383); and also, along with ozone and H_2O_2, by burning H in air (Struve, *J.* 1870. 199, 209; Zöller a. Grete, *B.* 10, 2145).

Barium nitrite $Ba(NO_2)_2.H_2O$ (Fischer).

Cadmium nitrite $Cd(NO_2)_2.H_2O$ (Hampe; Lang).

Calcium nitrite $Ca(NO_2)_2.H_2O$ (Fischer; Hampe; Lang).

Cobalt nitrite. This salt is not known, but several double salts of $Co(NO_2)_3$ have been isolated.

Cobalt-potassium nitrite $2Co(NO_2)_3.6KNO_2.xH_2O$ (*x* varies from 0 to 1, 3, and 4). Prepared by mixing KNO_2Aq and $Co(NO_3)_2Aq$, or $CoCl_2Aq$, adding excess of acetic acid, washing the pp. with K acetate solution, and then with 80 p.c. alcohol, and drying below 100°. A bright-yellow powder, consisting of small 4-sided prisms; very slightly sol. water, insol. alcohol or ether. At 200° gives NO_2, Co_2O_3, and KNO_2 (Fischer, *P.* 67, 245; Saint-Evre, *J. pr.* 54, 85; 58, 185; Braun, *Fr.* 6, 42; 7, 313; Stromeyer, *A.* 96, 220; Erdmann, *J. pr.* 97, 385; Sadtler, *Am. S.* [2] 49, 189). Various other Co-K nitrites are formed under different conditions of concentration and acidification (*v.* especially Sadtler, *l.c.*). If Ca salts are present a triple nitrite of Co, Ca, and K is ppd. (Erdmann, *l.c.*). A triple nitrite of Co, Pb, and K is described by Stromeyer (*l.c.*). Erdmann (*l.c.*) also describes a compound of $Co(NO_2)_3$, KNO_2, and NH_3.

Cobalt-cæsium nitrite $Co(NO_2)_3.3CsNO_2.H_2O$ (Rosenbladt, *B.* 19, 2531).

Cobalt-sodium nitrites $2Co(NO_2)_3.4NaNO_2.H_2O$ and $2Co(NO_2)_3.6NaNO_2.H_2O$ (Sadtler, *l.c.*).

Copper nitrites, basic salts (Hampe; van der Meulen, *B.* 12, 758).

Lead nitrites. These salts were examined by Proust, Chevreul (*G. A.* 46, 176), and Berzelius (*G. A.* 40, 194; 46, 156). Péligot (*A.* 39, 338) revised and classified the work; Bromeis (*A.* 72, 38), von Lorenz (*W. A. B.* [2nd part] 84, 1133), and Meissner (*J. Z.* [2] 3, 26), more recently have examined these salts. The lead nitrites are all basic salts; many seem best looked on as compounds of basic nitrites with basic nitrates. They are obtained by digesting $Pb(NO_3)_2Aq$ with Pb; von Lorenz says that 14 different salts are thus obtained.

Magnesium nitrite $Mg(NO_2)_2.3H_2O$ (Lang); $Mg(NO_2)_2.2H_2O$ (Hampe).

Mercuric nitrite $Hg(NO_2)_2.2HgO.H_2O$ (Lang).

Nickel nitrite $Ni(NO_2)_3$ (Lang). The *double salts*, $Ni(NO_2)_3.4KNO_2$; $Ni(NO_2)_3.2KNO_2.Ba(NO_2)_2$; $Ni(NO_2)_3.2Ba(NO_2)_2$; $Ni(NO_2)_2.Ca(NO_2)_2.2KNO_2$ have been isolated (Erdmann, *J. pr.* 97, 385).

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Potassium nitrite KNO_2. Colourless, microscopic, prismatic crystals (according to Lang, *J. pr.* 86, 295, the crystals are $2KNO_2.H_2O$); very sol. water, insol. absolute alcohol. KNO_2Aq with H_2SO_4 evolves NO, and forms KNO_3Aq. KNO_2 is prepared by passing into cold KOHAq the gas obtained by heating starch with HNO_3Aq S.G. 1·35, evaporating till crystallisation begins, pouring off from the crystals of KNO_3, adding dilute acetic acid and 2 vols. alcohol, separating the lower layer which forms and evaporating it (Fischer). Stahlschmidt (*P.* 128, 466) reduces KNO_3Aq by Zn in presence of NH_3Aq. Erdmann (*J.* 1866. 154) reduces KNO_3 by fusion with Fe, and crystallises from water.

Double salts of KNO_2 with the nitrites Ba, Cd, Ca, Co, Cu, Pb, Mg, Hg, Ni, Pd, Ag, Sr, and Zn are described by Hampe, Lang, and Fischer.

Silver nitrite $AgNO_2$. Obtained by adding $AgNO_3Aq$ to the solution produced by passing into KOHAq the gas formed by heating starch with HNO_3Aq S.G. 1·35, after neutralising this solution by acetic acid. Small white crystals. Dissolves in 300 pts. water at ordinary temperatures, easily in boiling water. The decomposition of $AgNO_2$ by heat has been examined by Divers a. Shimidzu (*C. J.* 47, 630). Treated with H_2S, $AgNO_2$ yields Ag_2S, S, NO, NH_3, and NH_2OH (Divers a. Haga, *C. J.* 51, 48).

Sodium nitrite $NaNO_2$. A crystalline salt, prepared similarly to KNO_2. Etard (*Bl.* [2] 27, 434) recommends to fuse $NaNO_3$ with an equivalent quantity of K_2SO_4, and to extract with alcohol.

Strontium nitrite $Sr(NO_2)_2$ (Hampe).

Zinc nitrite $Zn(NO_2)_2.3H_2O$ (Lang; Hampe).

HYPONITROUS ACID and HYPONITRITES; $H_2N_2O_2Aq$ and $M_2N_2O_2$. Hyponitrites were first obtained by Divers in 1871, by reducing nitrates by Na-amalgam (*Pr.* 19, 425). The salts were examined by Zorn (*B.* 10, 1306; 11, 1630, 2217; 12, 1509; 15, 1007, 1258); van der Plaats (*B.* 10, 1507); Menke, (*C. J.* 33, 401); Berthelot a. Ogier (*C. R.* 96, 30, 84). In 1884 Divers and Haga (*C. J.* 45, 78) showed that the silver salt is *n*AgNO. The investigation has been continued by Divers and Haga (*C. J.* 47, 364; 55, 760), Dunstan and Dymond (*C. J.* 51, 646), and Berthelot and Maquenne (*C. R.* 108, 1286, 1303).

Zorn prepared ethyl hyponitrite and determined its molecular formula (from V.D.) to be $(C_2H_5)_2N_2O_2$; hence the formula for the salts is better written $M_2N_2O_2$ than MNO.

Hyponitrites are produced (1) by reducing

nitrates or nitrites in solution by Na-amalgam (Divers); (2) by electrolysing nitrite solution, using Hg as negative electrode (Zorn; Divers a. Haga); (3) by the reaction of $Fe(OH)_2$ on alkaline nitrite solution, or on NO in presence of alkali (Zorn; Dunstan a. Dymond); (4) by decomposing oxyamidosulphonates [salts of $NH(SO_3H).OH$] by alkali (Divers).

Silver hyponitrite $Ag_2N_2O_2$ (*Nitrosyl silver*).

Preparation.—1. Na-amalgam is added to KNO_3Aq in the ratio KNO_3:4Na, the liquid being kept cold. When evolution of gas ceases the solution is neutralised by acetic acid, and $AgNO_3$ is added; the pp. is washed in the dark with cold water, dissolved in cold dilute HNO_3Aq, and reppd. by Na_2CO_3Aq; the pp. is thoroughly washed in the dark and dried *in vacuo* over H_2SO_4 (Divers, *Pr.* 19, 425; D. a. Haga, *C. J.* 45, 78).—2. Zorn (*B.* 12, 1509) reduces $Ba(NO_2)_2$ by Na-amalgam, and ppts. by $AgNO_3Aq$; the pp. of $Ag_2N_2O_2$ thus obtained is pure. The $Ba(NO_2)_2$ is obtained by boiling $Ba(NO_3)_2Aq$ with Pb, prepared by ppg. dilute Pb acetate solution by Zn; the boiling is continued till all the Pb is changed to PbO; the PbO in solution is removed by CO_2, and the last traces by H_2S; the filtrate is evaporated to a thick oil, which cools to a mass of $Ba(NO_2)_2$; the salt is obtained pure by crystallising from 80 p.c. alcohol. For preparing large quantities of $Ag_2N_2O_2$, Zorn (*l.c.*) places the Na-amalgam, in large pieces, in the middle bulb of a Kipp's apparatus, the $Ba(NO_2)_2Aq$ being in the lower bulb, and the upper he half-fills with distilled water. By regulating the stopcocks so that a slow stream of gas escapes, the reduction proceeds satisfactorily.—3. Pure $FeSO_4Aq$ is mixed with enough milk of lime to ppt. the Fe as $Fe(OH)_2$; $NaNO_2Aq$ is added (1 part $NaNO_2$ to 10 parts $FeSO_4$), and the apparatus is kept cold. When the reaction is finished the solution is ppd. by $AgNO_3Aq$ (Zorn, *B.* 15, 1258; *cf.* Dunstan a. Dymond, *C. J.* 51, 646).

Properties and Reactions.—$Ag_2N_2O_2$ is a yellowish amorphous salt. By standing in NH_3Aq over H_2SO_4, it is obtained in small crystals (Zorn). The salt is not hygroscopic; insol. water; may be kept in boiling water without decomposition; is decomposed at c. 100°, probably giving $AgNO_3$; when quickly heated to c. 150°, $Ag_2N_2O_2$ explodes, evolving brown vapours. $Ag_2N_2O_2$ dissolves in HNO_3Aq and H_2SO_4Aq, it is reppd. by NH_3Aq or Na_2CO_3Aq. Unacted on by CO_2. Decomposed by NaOHAq at c. 70°. Decomposed by H_3PO_4Aq, H_2S, or boiling $H.C_2H_3O_2Aq$, with production of $H_2N_2O_2Aq$. $Ag_2N_2O_2$ reacts with C_2H_5I to form $(C_2H_5)_2N_2O_2$ (Zorn, *B.* 11, 1630), the formula of which compound is molecular, as its V.D. has been determined.

Barium hyponitrite BaN_2O_2 is described by Zorn (*B.* 15, 1007).

Calcium and *Strontium hyponitrites* $CaN_2O_2.4H_2O$ and $SrN_2O_2.5H_2O$ are described by Maquenne (*C. R.* 108, 1303).

Hyponitrous acid $H_2N_2O_2Aq$. Known only in solution. Moist $Ag_2N_2O_2$ is suspended in water, such a quantity of dilute HClAq is added that a little $Ag_2N_2O_2$ remains unchanged, and the liquid is filtered from AgCl (van der Plaats, *B.* 10, 1507). $H_2N_2O_2Aq$ is an acid liquid, fairly stable; may be boiled with HNO_3Aq or $H.C_2H_3O_2Aq$ without decomposition; reduces $KMnO_4Aq$, and separates I from KIAq. The solution slowly decomposes, and after a few weeks not a trace of $H_2N_2O_2$ remains. The liquid thus obtained is neutral; probably N_2O and H_2O are formed. It was proved by van der Plaats (*l.c.*) that conc. H_2SO_4 evolves N_2O from $H_2N_2O_2Aq$.

Constitution of hyponitrites.—The compound $(C_2H_5)_2N_2O_2$ reacts not as an ethereal salt but as a diazo- compound; with reducers it evolves N and forms C_2H_5OH; water produces C_2H_5OH, $CH_3.CHO$, and N. The constitution of this compound is $C_2H_5.O.N{:}N.O.C_2H_5$, and hence the constitution of the acid is probably HO.N:N.OH (Zorn, *B.* 11, 1630). This formula is confirmed by the production of hyponitrites, along with sulphites, by the action of KOHAq on $NH(SO_3K).OH$. This reaction shows that the O in hyponitrites is in direct union both with N and H (Divers a. Haga, *C. J.* 55, 760).

Nitrogen, oxybromide of, NOBr (*Nitrosyl bromide*). Mol. w. not determined directly; probably = 109·72, from analogy with NOCl. A very dark-brown liquid. Obtained by passing NO into Br at −7° to −15° (Landolt, *A.* 116, 177); also by distilling nitrosyl sulphate $(NO.H.SO_4)$ with KBr (Girard a. Pabst, *Bl.* [2] 30, 531). Landolt gives b.p. as −2°; Girard a. Pabst as 19°. Easily decomposed to NO and Br by heat. With cold water forms HBrAq and HNO_2Aq; with KOHAq forms KBrAq and KNO_2Aq.

Nitryl tribromide. Landolt (*A.* 116, 117) supposed that a compound $NOBr_3$ is obtained (along with NOBr) by passing Br into well-cooled Br. That the amount of NO absorbed by Br, at c. 15°, is nearly independent of pressure, and corresponds approximately with the quantity required to form $NOBr_3$, was shown by Pattison Muir (*C. J.* 28, 844). The experiments of Fröhlich (*A.* 224, 270), and of Roozeboom (*R. T. C.* 4, 381) have shown that the so-called nitryl tribromide is probably only a mixture of NOBr and Br.

Nitrogen, oxychlorides of. The compound NOCl has been isolated; the existence of NO_2Cl is very doubtful; according to Hautefeuille a. Chappuis (*A. Ch.* [6] 2, 282), a compound $N_2Cl_2O_{13}$ is formed by passing N with O and Cl through an induction-apparatus. The non-existence of $NOCl_2$, said by Gay-Lussac to be produced by the reaction of conc. HClAq with HNO_3 (*A. Ch.* [3] 23, 203), has been proved by Tilden (*C. J.* 27, 633), and this has been confirmed by Goldschmidt (*A.* 205, 372).

Nitrosyl chloride NOCl (*Chloronitrous gas*). Mol. w. 65·34. V.D. 33 at c. 15° to 700° (Sudborough a. Millar, *C. J.* 59, 73). S.G. at −18° 1·433, at −12° 1·4165 (Geuther, *A.* 245, 97; Tilden, *C. J.* 27, 630). Boils at c. −8° (Tilden). An orange-red gas; liquefied by passing through a U tube cooled by ice and salt; the liquid is reddish yellow. Dissociation into NO and Cl begins at c. 780°, at 985° about 42 p.c. is dissociated (S. a. M., *l.c.*). For absorption-spectrum *v.* Magnanini (*Z. P. C.* 4, 427). Formed by combination of NO with Cl (Gay-Lussac, *A. Ch.* [3] 23, 203); by the reaction of PCl_5, PCl_3, or $AsCl_3$ with NO_2 or N_2O_3; and by the reaction of $POCl_3$ with KNO_2 (Naquet, *J.* 1860. 102); by passing

HCl into N_2O_4 at a low temperature; by heating conc. HClAq and HNO_3, and by heating NO.H.SO_4 with NaCl.

NOCl is more readily prepared by warming HNO_3Aq S.G. 1·42 with c. 4 vols. HClAq S.G. 1·16, passing the gases over $CaCl_2$ and then into conc. H_2SO_4 until the acid is saturated, then adding perfectly dry NaCl, and heating gently (Tilden, *C. J.* 27, 630; *cf.* Girard a. Pabst, *Bl.* [2] 30, 531).

NOCl reacts with H_2O to form HClAq and HNO_2Aq; with KOHAq it produces KClAq and KNO_2Aq; Hg decomposes it, forming NO and HgCl; it dissolves Au and Pt more slowly (Tilden, *l.c.*). With conc. H_2SO_4, nitrosyl sulphate (NO.H.SO_4) is formed (Tilden). NOCl reacts energetically with SO_3 to produce $NO_2.SO_2.Cl$ (Weber, *P.* 123, 333). Forms double compounds with many metallic chlorides, *e.g.* $AlCl_3$, $SbCl_3$ (*v.* Sudborough, *C. J.* 59, 655).

Nitryl chloride NO_2Cl. A compound with this composition was supposed to be formed by the reaction of $POCl_3$ with $AgNO_3$ or $Pb(NO_3)_2$, also by passing a very slow stream of Cl over $AgNO_3$ at c. 95° (Odet a. Vignon, *C. R.* 69, 1142; 70, 96); Hasenbach obtained a liquid which he took to be NO_2Cl by passing Cl and NO_2 through a hot tube and cooling the issuing gases (*J. pr.* [2] 4, 1); Williamson (*Pr.* 7, 15) poured SO_2.OH.Cl on to KNO_3, and obtained a gas which formed HNO_3Aq and HClAq with cold water, and was supposed by W. to be NO_2Cl; Müller (*A.* 122, 1) supposed that NO_2Cl was formed by the reaction of NO_2 with PCl_5; and Schiff thought he had obtained the compound as a product of the reaction of HNO_3 with PCl_5. Meissner (*J. Z.* 10, 27) failed to obtain any NO_2Cl by the processes used by Odet a. Vignon, Schiff, Müller, and Williamson. Geuther (*A.* 245, 96) could not form NO_2Cl by the reaction of PCl_5 with HNO_3, NO_2, or a nitrate. Williams (*C. J.* 49, 222) showed that NO_2Cl is not produced by the reaction (1) of $POCl_3$ with $Pb(NO_3)_2$, (2) of $POCl_3$ with HNO_3, (3) of SO_2.OH.Cl with KNO_3, (4) of SO_2Cl_2 with KNO_3; he also established a very large probability in favour of the conclusion that the products of the reaction of NO_2 with Cl, at different temperatures, are NOCl, and N_2O_4 holding more or less Cl in solution.

Nitrogen, phosphide of, *v.* Phosphorus nitride.

Nitrogen, phosphochloride of, $N_3P_3Cl_6$ (*Phosphorus chloronitride. Nitrogen chlorophosphide. Phosphorus nitrogen chloride*). Mol. w. 347·13. V.D. 176·7 (Gladstone a. Holmes, *C. J.* 17, 225; Wichelhaus, *B.* 3, 163). S.G. 1·98 (G. a. H.). Melts at c. 110° (G. a. H.); at 114° (W.); boils at 240° (G. a. H.); at 250°–260° (W.). Crystallises in trimetric forms; $a{:}b{:}c$ = ·4417:1:1·8165 (Groth, *B.* 3, 166), $\frac{\mu-1}{d}$ M = 109·9 (G. a. H.).

Formation.—By heating PCl_5 with NH_4Cl, NH_3, or NH_2HgCl.

Preparation.—1. PCl_5 is saturated with dry NH_3, the product is distilled with water, and the crystals which form on the sides of the receiver are washed, dried, and recrystallised from hot ether (Wöhler a. Liebig, *A.* 11, 146).—2. A mixture of 1 pt. PCl_5 and 2 pts. NH_4Cl is heated in a flask connected with a reversed condenser; the mass gets red, then brown, and the $N_3P_3Cl_6$ sublimes; the compound is dissolved out in ether and crystallised, or is blown over in steam (Gladstone, *C. J.* 3, 135; modified by Couldridge, *C. J.* 53, 398). The yield is not more than 10 p.c. of the PCl_5 used.—3. An intimate mixture of white pp. (NH_2HgCl) and PCl_5 is gently heated in a flask; the product is treated with water, which dissolves out $HgCl_2$ and NH_4Cl; the residue is dried and the $N_3P_3Cl_6$ is dissolved out (from $PCl_3N_2H_4$) by ether (Gladstone a. Holmes, *C. J.* 17, 225).

Properties.—Hard, lustrous, trimetric, crystals; sol. alcohol, ether, or $CHCl_3$; insoluble in water, but slowly decomposed (G. a. H.; W.). Gives off white fumes when heated in air; may be sublimed in H or H_2S. Solution in alcohol slowly decomposes, also that in ether if a trace of water is present (even in absence of water, according to Wichelhaus). Is not acted on by I (G.); nor by hot H_2SO_4Aq, HClAq, or HNO_3Aq (Wöhler a. Liebig); decomposed by hot fuming HNO_3 (G.).

Reactions.—1. *Water* forms pyrophosphodiamic acid ($P_2N_2H_6O_6$) and HCl, according to G. a. H.; but W. says the products are many and complicated.—2. *Ammonia* or *potash* decomposes $N_3P_3Cl_6$ in alcoholic solution, the reaction being similar to that of water (G. a. H.).—3. *Ammonia gas* passed over melted $N_3P_3Cl_6$ forms phospham nPN(NH), and HCl (Couldridge, *C. J.* 53, 398).—4. Heated with *aniline*, $P_3N_3(NHC_6H_5)_6$ is formed (Hofmann, *B.* 17, 1909; Couldridge, *l.c.*); *orthotoluidine*, and *phenylhydrazine* produce similar reactions (C., *l.c.*).—5. *Nascent hydrogen* forms PH_3 (W., *l.c.*).—6. Heated with *copper oxide*, NO_2 and N are evolved.—7. Passed over red-hot *iron*, N is evolved and $FeCl_3$ and Fe phosphide remain (W. a. L.).

Nitrogen, selenide of (?NSe). Espenschied (*A.* 113, 101) passed NH_3, diluted with H, over well-cooled $SeCl_4$, shook the product with water, and washed the ppd. mixture of Se and N selenide with CS_2 (to extract Se); he thus obtained an orange-yellow powder, which was extremely explosive and very dangerous to handle. Analyses pointed to the formula NSe, but E. supposed that the substance probably contained H besides N and Se. For details of preparation and properties *v.* Espenschied (*l.c.*).

Nitrogen, silicide of, *v.* Silicon nitride, in vol. iv.

Nitrogen, sulphide of, nNS. Mol. w. unknown. S.G. 2·1166 at 15° (Michaelis, *Z.* [2] 6, 460); 2·22 at 15° (Berthelot, *A. Ch.* [5] 27, 202). Sublimes at 135°; melts at 158°, and decomposes with slight explosions at 160° (M., *l.c.*; at 207° according to B., *l.c.*). Berthelot (*l.c.*) gives [N,S] = −31,900. N sulphide was prepared, but not pure, by Soubeiran (*A. Ch.* [2] 67, 71); Fordos and Gélis obtained it approximately pure (*A. Ch.* [3] 32, 385); it has been examined further by Michaelis (*Z.* [2] 6, 460), and Demarçay (*C. R.* 91, 854, 1066; 92, 726). N sulphide easily explodes when rubbed or struck with a hammer.

Preparation.—1. SCl_2 or S_2Cl_2 is dissolved in 8-10 vols. CS_2, and dry NH_3 is passed in; the liquid darkens in colour, and a cochineal-red pp. is produced, which dissolves after a time and a

brown powder is ppd.; passage of NH_3 is continued until the brown pp. dissolves, and the liquid becomes orange-yellow with a few nearly colourless flocks of NH_4Cl floating in it (addition of more NH_3 decomposes the NS in solution); the liquid is filtered and allowed to evaporate, when orange-red NS separates; the NS is collected and washed with CS_2, to remove traces of S. Omitting intermediate products, the reaction may be represented approximately as $8NH_3 + 3SCl_2 = 2NS + S + 6NH_4Cl$ (F. a. G.).—2. $SOCl_2$ is surrounded by cold water, and NH_3 is passed into it; after a time the cold water is removed, the solid mass is mixed by a glass rod, and NH_3 is passed over it as long as absorption continues; the nearly white mass thus obtained is treated with CS_2, and the solution on evaporation deposits NS; the insol. in CS_2 consists of NH_4Cl, $(NH_4)_2SO_3$, and polythionates of NH_4 (Michaelis).

Properties.—Orange-red, rhombic (or ? triclinic) crystals, with a faint odour, which becomes more marked at c. 120°; the vapour rapidly attacks the mucous membrane of the nose and eyes; detonates at c. 160°; explodes violently when rubbed or struck by a hammer; adheres strongly to glass or paper when rubbed thereon; is electric. Insol. in, but slowly decomposed by, water; slightly sol. alcohol, ether, turpentine; CS_2 is the best solvent, this solution slowly decomposes.

Reactions.—1. *Water* slowly decomposes NS, forming NH_3Aq, $(NH_4)_2S_2O_3Aq$, and $(NH_4)_2S_3O_6Aq$. 2. *Potash* forms NH_3, $K_2S_2O_3Aq$, and K_2SO_3Aq.—3. *Hydrogen chloride* produces NH_4Cl, chlorides of S, and probably a compound of NS with SCl_2.—4. *Chlorine* reacts on NS in $CHCl_3$ with formation of a compound of S chloride and NS; Demarçay (*C. R.* 91, 854) gives the formula SNCl to the product, and says that addition of NS to this produces $(SN)_3Cl$.—5. A large excess of *sulphur chloride* reacting on NS in $CHCl_3$ produces a compound of S, N, and Cl, to which Demarçay (*C. R.* 91, 1066) assigns the formula S_4N_3Cl.—6. *Nitric acid* forms $S_4N_3NO_3$; and *sulphuric acid* produces HCl and $S_4N_3HSO_4$ (D., *l.c.*; also *C. R.* 92, 726).

Combinations.—With *sulphur dichloride* to form several compounds, especially $2NS.SCl_2$, $4NS.SCl_2$, and $6NS.SCl_2$ (Michaelis).

Nitrogen, sulphochloride of. $NS_2Cl(=N_2S_3.SCl_2)$. According to Soubeiran (*A. Ch.* 67, 87, 101), this substance is formed by heating, in a sealed tube at 100°, the compound $2NH_3.SCl_2$, which is obtained by passing a slow stream of NH_3 into SCl_2. NS_2Cl is a citron-yellow solid; decomposed by heat to N, S, and S_2Cl_2; decomposed by water to NH_4Cl and $H_2S_2O_3$. NS_2Cl is also said to be formed by passing CO_2 into a hot solution of NS in S_2Cl_2 (S., *l.c.*). M. M. P. M.

NITROGEN GROUP OF ELEMENTS. *Nitrogen, phosphorus, vanadium, arsenic, niobium, antimony, didymium, erbium, tantalum, bismuth.* Of these ten elements, N, As, Sb, and Bi are found uncombined; the others occur only in combination. N is found in vast quantities in the air; compounds of N and also of P occur in large quantities in rocks and in animal and vegetable matter. Compounds of As, Sb, and Bi are widely distributed in minerals, but no very large quantities are found. Compounds of V are found widely spread about, but they occur only in comparatively small quantities. The compounds of Nb, Di, Er, and Ta have been found in but a few minerals; these four bodies are classed among the rare elements. Sb has been known as a metal from about the end of the fifteenth century, and Bi from the sixteenth century; P was prepared in 1669, As in 1694, and N in 1772; V was obtained by Roscoe in 1867, investigations on this element having been carried on from the beginning of this century; Di was isolated in 1842; Nb and Ta were obtained nearly pure in 1864, after a long series of investigations conducted by different chemists from 1801 onwards; researches on Er have been carried on since 1788 to the present day, but the element has not yet been isolated. Within recent years great doubt has been cast on the elementary character of Di, and although the investigation of Er is yet far from complete it is very probable that the substance known by this name is not a simple body. Of the names given to the ten elements, As is derived from the name by which the chief ore of this metal was known in ancient times; N, P, and Di express characteristic properties of the elements; Er is derived from the locality where the minerals were found from which the compounds of this element have been prepared; V, Nb, and Ta are taken from mythological personages; and the origins of the names Bi and Sb are not known with certainty.

N is obtained from air by removing the O by hot Cu, or other deoxidiser; P is prepared by heating Ca phosphate with SiO_2 to combine with the Ca, and C to remove the O; As, Sb, and Bi are prepared by removing O from the oxides by C; V and Nb by reducing the chlorides at a high temperature by H, and Di by reducing the chloride by Na or K; to obtain Ta, the compound Na_2TaF_7 is reduced by Na; Er has not yet been isolated. N is a gas at ordinary temperatures, but has been liquefied at a very low temperature under great pressure; P is a soft solid with a low melting-point and not high S.G.; the other elements are hard, lustrous, and metal-like; none has a very high S.G., Ta = 11 (?) is the heaviest; and all melt at or below a full red heat (M.P. of V, Nb, and Ta, not determined; Er not isolated). The following table presents some of the chief properties of the ten elements:—

	Nitrogen	Vanadium	Niobium	Didymium	Tantalum
Atomic weights	14·01	51·2	94	144	182
	One or more compound of each element, except Di, has been gasified; specific heat of Di only has been determined directly. Mol. w. of N = At. w. × 2; mol. w. of none of the others known.				
Melting-points	—	—	—	600°–700°	—

	NITROGEN	VANADIUM	NIOBIUM	DIDYMIUM	TANTALUM
Specific gravities (approx.)	(liquid) ·885	5·5	7	6·5	11 (?)
Specific heats	—	—	—	·04563	—
Atomic weight / *Spec. grav.* (approx.)	15·8	9·1	13·4	22·1	16·6 (?)
Occurrence and preparation	In large quantity in air. Many compounds, especially nitrates and NH_3 compounds, are widely distributed in large quantities. Prepared by removing O from air.	Vanadates of Pb, Ca, Bi, &c. occur as comparatively rare minerals. Small quantities of V compounds are very widely distributed. Prepared by long-continued heating VCl_2 in H.	Niobates occur in a few rare minerals. Prepared by repeatedly heating $NbCl_5$ in H.	Silicate of Di is found in several rare minerals. Prepared by heating $DiCl_3$ with K; or by electrolysing molten $DiCl_3$.	Tantalates occur with niobates in a few rare minerals. Prepared by heating K_2TaF_7 with K, or Na_2TaF_7 with Na.
Physical properties	Colourless, tasteless, odourless gas; liquefied at very low temp. and great pressure, liquid boils at c. $-195°$	Grey, lustrous crystalline powder.	Steel grey, lustrous solid.	White solid, with slightly yellow tinge; hard, ductile.	Grey, lustrous, solid; not obtained free from impurities.
Chemical properties	Combines slowly with O under influence of electric discharge; also to a small extent with H. At high temp. combines with B, Cr, Mg, Si, and V; and perhaps also with Al, Fe, and Zn. Compounds exhibit most diverse chem. properties; oxides are generally acidic; one hydride is strongly alkaline, another is acidic. Never replaces H of acids to form salts. Forms the oxychloride NOCl. An allotropic form perhaps exists, proof is not satisfactory. Atom is trivalent in NH_3.	Burns in air to V_2O, then to V_2O_3, and finally to V_2O_5. Burns in Cl to VCl_4. Combines with N to form VN. Dissolved by conc. H_2SO_4 and HNO_3; forms vanadates with molten alkalis. Some oxides are basic, *e.g.* V_2O_3; others are basic and acidic, *e.g.* V_2O_4 which forms salts with acids and also with alkalis. Reacts both as a metal and a non-metal. Forms oxychlorides $VOCl_3$, $VOCl_2$, and VOCl. Does not form a hydride. Atom is tetravalent in VCl_4, perhaps trivalent in $VOCl_3$.	Burns in air to Nb_2O_5. Combines with Cl to $NbCl_5$. Sol. in conc. H_2SO_4, not in HNO_3 or HClAq. Nb_2O_5 forms niobates with basic oxides; also dissolves in H_2SO_4, but no definite salts isolated. No hydride known with certainty, but there are indications of existence of hydride. Forms a nitride. Oxychloride is $NbOCl_3$. Compounds formed by replacing H of acids by Nb not yet isolated, but probably exist. NbF_5 and $NbOF_3$ form many double salts. Atom pentavalent in $NbCl_5$.	Burns in air to Di_2O_3. Di_2O_5 exists and acts as a peroxide. Di_2O_3 is basic, easily sol. dilute acids. Decomposes cold water slowly, and hot water rapidly. Di is almost certainly a mixture or compound of two or more elements. DiOCl is isolated. No hydride. No compounds gasified.	Burns in air to Ta_2O_5. Combines with Cl to form $TaCl_5$. Ta_2O_5 forms tantalates with alkalis; seems to have no basic properties. Sol. only in HFAq, and H_2SO_4 + HFAq. Forms a nitride. No hydride known. No oxychlorides isolated. Atom pentavalent in $TaCl_5$.

	Phosphorus	Arsenic	Antimony	Erbium	Bismuth
Atomic weights	30·96	74·9	120	166	208
Molecular weights	61·92 and 123·84	149·6 and 299·6	(?) 120 (?) 240	—	(?) 208 or (?) 416
	Compounds of all these elements, except Er, have been gasified; and S.H. of each, except Er, has been determined directly.				
Melting-points (approx.)	45°	500° (under pressure)	425°	—	270°
Specific gravities (approx.)	1·9	5·7	6·7	—	9·9
Specific heats	·202	·083	·053	—	·0308
Atomic weight / Spec. grav.	16·3	13·2	18	—	20·5
Occurrence and preparation	Many phosphates occur in large quantities and widely distributed in rocks and waters, also in bones and plants. Compounds of P with C, N, and O, are found in nerve and brain matter. Prepared by heating $Ca_3(PO_4)_2$ with SiO_2 and C.	Is found native in small quantity; compounds with S and other elements are widely distributed, but are not found in very large quantities. Prepared by reducing As_2O_3 by C.	Sb found native in small quantity; Sb_2S_3 occurs in comparatively small quantities, fairly widely distributed; other compounds also occur sparingly. Prepared by reducing Sb_2O_3 by C.	As silicate in a few rare minerals. Er has not yet been isolated.	Bi found native; chief compounds are Bi_2S_3 and Bi_2O_3, not found in any large quantities, but fairly widely distributed. Prepared by reducing Bi_2O_3 by C.
Physical properties	Soft, wax-like, crystalline solid; also a red amorphous solid. Non-conductor of electricity.	Grey, hard, brittle, crystalline, solid; also as a black amorphous powder. Fair conductor of electricity.	White, lustrous, brittle, very crystalline, solid. Fair conductor of electricity.	Not isolated.	White, with slightly reddish tinge; brittle, crystalline, not good conductor of electricity.
Chemical properties	Burns in air to P_2O_3 and P_2O_5. Combines directly with Cl, Br, and I, to form PX_3 and PX_5. Oxidised by HNO_3 to H_3PO_4. Oxides are anhydrides; several oxyacids known. Does not form salts by replacing H of acids. Hydride PH_3 resembles NH_3, but is less alkaline. Exists in two allotropic forms. Atom trivalent and pentavalent in gaseous molecules.	Burns in air to As_2O_3; As_2O_5 also known. Combines directly with Cl, Br, and I, to form AsX_3. Oxidised by HNO_3 to H_3AsO_4. Oxides are acidic, and As_2O_3 is also feebly basic. Does not form salts by replacing H of acids. Hydride AsH_3 is scarcely if at all alkaline. Exists in two allotropic forms. Atom trivalent in gaseous molecules.	Burns in air to Sb_2O_3; Sb_2O_5 also known. Combines directly with Cl, Br, and I, to form SbX_3 and SbX_5. Oxidised by HNO_3 to Sb_2O_4 and $Sb_2O_5.xH_2O$. Oxides are acidic and basic. Forms a few salts by replacing H of acids. Decomposes steam, evolving H. Hydride SbH_3 is not alkaline. Atom trivalent in gaseous molecules.	Reactions of Er not known, as the metal has not yet been isolated. Very probably Er is a mixture or compound of two or more elements. Er_2O_3 is basic, no acidic oxide known. No hydride known. No compound yet gasified.	Burns in air to form Bi_2O_3; Bi_2O_5 also known. Combines directly with Cl, Br, and I, to form BiX_3. Oxidised by HNO_3 to $Bi3NO_3$. Oxides are basic; Bi_2O_5 acts as a basic peroxide with perhaps very feeble acidic properties. Many salts formed by replacing H of acids by Bi. Decomposes steam, evolving H. No hydride isolated. Atom trivalent in gaseous molecules.

General formulæ and characters of chief compounds. MH_3; M = N, P, As, Sb. M_2O_3; M = any element of the group except Nb and Ta. M_2O_4; M = N, P, V, Nb, Sb, Ta, Bi. M_2O_5; M = any of the elements except Er. M_2S_3; M = P, V, As, Sb, Di, Bi. M_2S_5; M = P, V, As, Sb; some other sulphides known, *e.g.* NS, VS, TaS_2; no sulphide of Nb or Er isolated. MCl_3; M = any of the elements except Er and Ta. MCl_5; M = P, Nb, Sb, Ta; some other haloid compounds exist, *e.g.* P_2I_4, VCl_4; no haloid compounds of Er isolated with certainty. HMO_3, H_3MO_3, H_3MO_4, $H_4M_2O_7$; most of these acids exist for M = N, P, V, As, Sb; acids containing Nb and Ta also known; no acids of Di, Er, or Bi isolated. M_23SO_4, &c.; M = Di, Er, Bi. $VO(SO_4)$, $(VO_2)_2(SO_4)_3$, &c. $As_2O_3.xSO_3$; $Sb_2O_3.xSO_3$, &c.

The *hydrides* NH_3, PH_3, AsH_3, and SbH_3 show a gradation of properties, from the strongly alkaline NH_3 to the neutral AsH_3 and SbH_3; NH_3 combines readily with acids, PH_3 only with such strong acids as HI or HCl; AsH_3 and SbH_3 do not combine with acids. AsH_3 and SbH_3 are easily decomposed by heat, while NH_3 and PH_3 are stable in this respect. The hydrides are all oxidised by mixing with O and heating, NH_3 being the most difficult to change in this way. A hydride of Nb (? NbH) probably exists. N forms also the hydrides N_3H and N_2H_4; the former is a fairly strong acid, the latter is basic. Besides PH_3, two hydrides of P, viz. P_2H_4 and P_4H_2, exist.

Regarded broadly, the *oxides* may be divided into three classes: (1) *acidic oxides*, those of N and P; (2) *basic*, those of Di, Er, and Bi; (3) *acidic and basic*, those of V, As, and Sb—acidic and ? basic, oxides of Nb and Ta. The distinctly acidic oxides of N are N_2O_3, NO_2, and N_2O_5; with water N_2O_3 forms HNO_2Aq, and N_2O_5 forms HNO_3Aq, but NO_2 produces both HNO_2 and HNO_3; N_2O may be called the anhydride of $H_2N_2O_2$, inasmuch as it is formed by heating $H_2N_2O_2Aq$, but the acid has not been obtained from N_2O. NO can hardly be classed as acidic or basic; there are compounds in which NO may be regarded as playing the part of the more positive radicle, *e.g.* NOCl and $NO.H.SO_4$, and there are others in which NO seems to form the negative radicle, *e.g.* $(NO)_2H_2$, and perhaps NO.OH. P_2O_3 and P_2O_5 react with water to form H_3PO_3Aq and H_3PO_4Aq respectively; P_2O_4 forms both of these acids. The oxides M_2O_3, where M = Di, Er, or Bi, react with acids to form salts $M_2.3X$ (X = SO_4, $2NO_3$, &c.); Bi_2O_5 forms salts $Bi_2.3X$ and evolves O, this oxide probably forms bismuthates—$Bi_2O_5.xM_2O$—when fused with large excess of alkalis, but these bimuthates cannot be isolated. V_2O_3 probably forms salts with acids; the compound $V_2O_3(SO_3)_4.xH_2O$ has been isolated. V_2O_4 with strong acids forms salts $xV_2O_4.yA$ (A = acidic oxide, SO_3, &c.), and with alkalis it produces salts of the type $xV_2O_4.yM_2O$. V_2O_5 reacts with alkalis to produce vanadates $xV_2O_5.yM_2O$; it also combines with several anhydrides to form salts $xV_2O_5.yA$ (A = acidic oxide, P_2O_5, SO_3, &c.); the acids HVO_3 and $H_4V_2O_7$ have been isolated. As_2O_3 does not form an acid with water, but with KOHAq it produces $KAsO_2$; As_2O_5 with water forms H_3AsO_4. As_2O_3 combines with a few anhydrides of strong acids to form such compounds as $xAs_2O_3.ySO_3$. Neither Sb_2O_3 nor Sb_2O_5 forms an acid with water; a few unstable salts $Sb_2O_3.M_2O$ have been isolated; three weakly acidic hydrates of Sb_2O_5 are known, from each of which salts are derived. With acidic oxides Sb_2O_3 combines to form $xSb_2O_3.yA$ (A = acidic oxide, SO_3, &c.), some of these compounds are fairly well-defined salts, *e.g.* $Sb_2O_3.3SO_3$. The oxides Nb_2O_5 and Ta_2O_5 form salts when fused with alkalis, $xM_2O_5.yM_2O$; these oxides dissolve in some strong acids, probably with formation of salts, although none has yet been isolated.

The *oxyacids* of the nitrogen elements are numerous; oxyacids of all except Di, Er, and Bi are known. The table on p. 575 presents the composition of the most marked of the acids, and the relations between them, their corresponding oxides, and their salts; the symbol Aq added to the formula of an acid means that that acid is known only in aqueous solution; M here stands for a monovalent metal; RO = basic oxide generally, including M_2O, MO, M_2O_3.

The acids of N and P possess the characteristics of acids much more fully than any of the other oxyacids of the N elements. HNO_2, HNO_3; HPO_3, H_3PO_4, $H_4P_2O_7$, H_3PO_3; H_3AsO_4; these acids are produced by the reaction of their corresponding oxides with water—the other acids of the N elements are not obtained directly from their oxides, although in many cases the oxides are formed by heating the acids. HNO_3Aq is a very strong acid, about equal to HClAq; putting the strength or affinity of HNO_3Aq as 100, that of H_3PO_4Aq is approximately about 6, and that of H_3AsO_4Aq about 4. One can scarcely give the name *acid* to the hydrated oxides of Nb and Ta, and it is very doubtful whether $Sb_2O_3.3H_2O$ (= H_3SbO_3) can be called an acid. It should be remembered that the oxides of Nb and Ta have not been very fully examined.

The chief *haloid compounds* of the nitrogen elements are MX_3 and MX_5; no haloid compound of Er has been isolated with certainty; TaX_3 is not known, and pentahaloid compounds of N, V, As, Di, and Bi have not yet been prepared. V forms VCl_4, which has been gasified unchanged. Most of the haloid compounds are formed by the direct union of their elements; they are decomposed by water, forming HXAq, and oxyacids or hydrated oxides in the cases of N, P, V, As, Nb, and Ta, and oxyhaloid compounds in the cases of Di (? Er) and Bi; $SbCl_3$ gives SbOCl if little water is used, but Sb_2O_3Aq if much warm water is employed.

The *sulphides*, M_2S_3, of P, V, As, and Sb react with alkali sulphides to form alkali thiosalts; Di_2S_3 and Bi_2S_3 show no acidic properties; Er and Nb sulphides have not been isolated, and the sulphides of Ta have been studied but slightly; NS is an explosive compound, which forms NH_4 salts of thionic acids when treated with water or potash.

The nitrogen elements form Group V. of the elements in the classification based on the periodic law. This group is composed as follows:—

	2		4		6		8		10		
Even series	N = 14		V = 51		Nb = 94		Di = 144		Ta = 182		
		3		5		7		9		11	
Odd series		P = 31		As = 75		Sb = 120		Er = 166		Bi = 208	

Acid	Salts	Corresponding oxide	Remarks
Nitrogen:			
$H_2N_2O_2Aq$	$M_2N_2O_2$	N_2O	Acid not formed from N_2O, but N_2O obtained by heating $H_2N_2O_2Aq$, and by action of H_2SO_4 on $M_2N_2O_2Aq$.
HNO_2Aq	MNO_2	N_2O_3	Acid obtained by dissolving N_2O_3 in fair quantity of cold water; solution slowly decomposes to HNO_3Aq and NO. Doubtful whether HNO_2Aq has been obtained quite free from HNO_3.
HNO_3	MNO_3; also M_3NO_4; and many basic nitrates $xN_2O_5.yRO$; also probably a few acid salts $M^INO_3.xN_2O_5$	N_2O_5	N_2O_5 reacts with water to form HNO_3Aq; N_2O_5 obtained by removing H_2O from HNO_3 by P_2O_5.
$H_2N_4O_{11}$	None	N_2O_5	Acid formed by adding very conc. HNO_3 to melted N_2O_5, and cooling.
Phosphorus:			
$H.H_2PO_2$	$M.H_2PO_2$	None	Acid obtained by action of equivalent quantity of H_2SO_4Aq on $Ba(H_2PO_2)_2$, which is produced by P reacting with BaOAq. H_3PO_2 decomposes by heat to H_3PO_4 and PH_3.
H_2PO_3	$M.HPO_3$ and M_2PO_3	None	H_2PO_3 obtained by H_2S on $PbPO_3$ in water and evaporation *in vacuo*. H_2PO_3Aq fairly stable; boiled with H_2SO_4Aq forms H_3PO_2Aq and H_3PO_4Aq.
$[H_2.H_2P_2O_5]$	$M_2.H_2P_2O_5$	P_2O_4 (?)	Acid unknown. Na salt got by heating $NaH_2PO_3.5H_2O$ to 160°; Pb salt got by heating $PbH_2(HPO_3)_2$ to 140° *in vacuo*.
$H_2.HPO_3$	$M_2.HPO_3$ and $M.H_2PO_3$	P_2O_3	Acid obtained by slow action of cold water on P_2O_3; decomposed by heat to H_3PO_4 and PH_3.
HPO_3; H_3PO_4; $H_4P_2O_7$	$M.PO_3$; M_3PO_4, M_2HPO_4, MH_2PO_4; $M_4P_2O_7$, $M_2H_2P_2O_7$	P_2O_5	Acids obtained by action of water on P_2O_5. A little cold water gives HPO_3; cold water and P_5O_5 in ratio P_2O_5:$2H_2O$ give $H_4P_2O_7$; much water gives H_3PO_4. H_3PO_4 heated gives $H_4P_2O_7$, and this at higher temperature gives HPO_3. P_2O_5 is not obtained by heating the acids.
Vanadium:			
HVO_3; $H_4V_2O_7$	MVO_3; $M_4V_2O_7$; also salts of types M_3VO_4, $M_2V_4O_9$, $M_2V_4O_{11}$, &c.	V_2O_5	Acids not obtained directly from the oxide; but V_2O_5 obtained by heating the acids.
Arsenic:			
—	$MAsO_2$; M_3AsO_3	As_2O_3	As_2O_3 in water does not form an acid, but reacts with alkalis &c. to form salts.
$HAsO_3$; H_3AsO_4; $H_4As_2O_7$	$MAsO_3$; MH_2AsO_4, M_2HAsO_4, M_3AsO_4; $M_4As_2O_7$	As_2O_5	H_3AsO_4 obtained by action of H_2O on As_2O_5; H_3AsO_4 gives $H_4As_2O_7$, and at higher temperature $HAsO_3$ is formed; on heating $HAsO_3$, As_2O_5 and H_2O are produced.

Acid	Salts	Corresponding oxide	Remarks
Niobium: $xNb_2O_5.yH_2O$ (? acids)	$xNb_2O_5.yRO$; some belong to types $MNbO_3$ and $M_4Nb_2O_7$, others are more complex	Nb_2O_5	Hydrates of Nb_2O_5 are known; but salts are not obtained by reaction of these with alkalis, but by fusing Nb_2O_5 with alkalis and alkaline carbonates.
Antimony: H_3SbO_3 (? acid)	$MSbO_2$	Sb_2O_3	H_3SbO_3 is not obtained directly from Sb_2O_3, but Sb_2O_3 is formed by heating H_3SbO_3. H_3SbO_3 scarcely exhibits acidic properties. $MSbO_2$ are few; produced by dissolving Sb_2O_3 in alkalis.
—	$M_2Sb_2O_5$ (? $MSbO_3.MSbO_2$)	? Sb_2O_4	Said to be formed by fusing Sb_2O_4 with alkalis and alkaline carbonates.
$HSbO_3$; H_3SbO_4; $H_4Sb_2O_7$	$MSbO_3$; $M_4Sb_2O_7$, $M_2H_2Sb_2O_7$	Sb_2O_5	Acids are not obtained directly from Sb_2O_5, but oxide is formed by heating the acids. H_3SbO_4 gives $HSbO_3$ at 175°; $H_4Sb_2O_7$ is obtained from its salts; it is easily decomposed to $HSbO_3$. $HSbO_3$ dissolves in KOHAq, but does not form salts thus; $MSbO_3$, obtained by fusing Sb_2O_5 or $HSbO_3$ with alkalis or alkaline carbonates. $M_4Sb_2O_7$ are formed by action of RO on $MSbO_3$.
Tantalum: $Ta_2O_5.2H_2O$ (? acid)	$MTaO_3$; also complex salts of general form $xTa_2O_5.yRO$.	Ta_2O_5	Acid not formed directly from oxide, but oxide obtained by heating the acid. Salts formed by fusing Ta_2O_5 or $H_4Ta_2O_7$ with basic oxides.

The division into two families is not marked; the properties of the members of the group vary gradually from N, which is a typical non-metal, to Bi, which is distinctly metallic. The properties of these elements and their compounds show that on the whole V, Nb, and Ta form a family; As, Sb, and Bi another family; and N and P a third family. Di and Er have not been much examined, and it is very probable that neither is an elementary substance. For detailed descriptions of the elements and their chief compounds, *v.* NITROGEN, PHOSPHORUS, &c.

M. M. P. M.

NITROGLYCERIN *v.* GLYCERIN.

NITRO-HARMALINE *v.* HARMALINE.

NITRO-HEMIPIC ACID *v.* HEMIPIC ACID.

NITRO-HEPTANE (?) $C_7H_{15}NO_2$. (193°–197°). S.G. $\frac{12}{}$ ·937. Occurs among the products of the action of HNO_3 (S.G. 1·38) on light petroleum oils (95°–100°) (Beilstein a. Kurbatoff, *B.* 13, 2029). Oil, sol. warm KOHAq.

NITRO-HEPTYL-BENZENE $C_7H_{15}.C_6H_4NO_2$. (178° at 10 mm.). Formed by nitration (Auger, *Bl.* [2] 47, 50). Heavy straw-coloured oil.

DI-NITRO-HEPTYLENE $C_7H_{12}(NO_2)_2$. [182°]. From heptinene and HNO_3 (S.G. 1·3) (Morris, *C. J.* 41, 175). Tables (from alcohol). Sol. alcohol, ether, and benzene, volatile with steam.

NITRO-HEXADECYL-BENZENE $C_6H_4(C_{16}H_{33})NO_2$. *Nitro-cetyl-benzene.* [c. 36°]. Formed by nitration of cetyl-benzene (Krafft, *B.* 19, 2984).

NITRO-*p*-HEXADECYL-TOLUENE $C_6H_3(NO_2)Me.C_{16}H_{33}$. [40°]. Obtained by nitration of hexadecyl-toluene (Krafft a. Göttig, *B.* 21, 3182).

DI-NITRO-HEXANE $C_5H_{11}.CH(NO_2)_2$. Obtained from hexyl methyl ketone and HNO_3 (Chancel, *C. R.* 94, 399). Heavy oil. Yields *n*-hexoic acid on reduction.—$KC_6H_{11}N_2O_4$: yellow plates (from hot water).—AgA'.

Tetra-nitro-hexane $C_6H_{10}(NO_2)_4$. Crystals, obtained by passing NO_2 into an ethereal solution of diallyl at 0° (Henry, *B.* 2, 279).

NITRO-HEXOIC ACID $C_6H_{11}NO_4$. [112°]. Formed by reducing di-nitro-hexoic acid in alcoholic solution by sodium-amalgam (Kullhem, *A.* 167, 45; Kachler, *A.* 191, 159). Four-sided prisms, v. sol. water and alcohol. With tin and HClAq it yields methyl isopropyl ketone, hydroxylamine, and CO_2. On adding H_2SO_4 to a solution of the K salt mixed with KNO_2, there is produced a blue colour, which can be taken up by ether.—NaA' 3aq.—BaA'$_2$ 3aq.—$BaC_6H_9NO_4$.—AgA'.

Di-nitro-hexoic acid $C_6H_{10}N_2O_6$. [215°]. Formed by boiling camphor with HNO_3 (Kull-

hem, *A.* 163, 231; Kachler, *A.* 191, 144). Plates (from water).—NH_4A'.—NaA′4aq.—CaA'_2 3aq: slender needles.—BaA'_2 5aq.—BaA'_2 3aq.—AgA′. Formerly supposed to be $C_7H_{12}N_2O_6$, *v. Di-nitro-heptoic acid*, under CAMPHER, vol. i. p. 672.

NITROHEXYLENE $C_6H_{11}NO_2$ (?). (210°–215°). A product of the action of HNO_3 (S.G. 1·34) on the fraction 95°–100° of the petroleum of Baku (Beilstein a. Kurbatoff, *B.* 13, 1820).

m-**NITRO-HIPPURIC ACID** $C_9H_8N_2O_5$ *i.e.* $C_6H_4(NO_2).CO.NH.CH_2.CO_2H$. [162°]. S. ·36 at 23°. Formed by the action of HNO_3 and H_2SO_4 on hippuric acid; and occurs in dogs' urine after administration of *m*-nitro-benzoic acid (Bertagnini, *A.* 78, 100; Schwanert, *A.* 112, 69; Conrad, *J. pr.* [2] 15, 254). Needles. Split up by HClAq into glycocoll and *m*-nitro-benzoic acid. CaA'_2 3aq. — BaA'_2.—CuA'_2 5aq. — ZnA'_2 6aq. — PbA'_2 5aq.—AgA′.

p-Nitro-hippuric acid $C_9H_8N_2O_5$. [129°]. Occurs in urine after a dose of *p*-nitro-toluene (Jaffé, *B.* 7, 1673). Orange prisms (from alcohol).—BaA'_2 4aq.—AgA′: long needles.—Urea salt $HA'CON_2H_4$. [180°]. Occurs in dogs' urine after a dose of *p*-nitro-benzoic aldehyde (Sieber a. Smirnoff, *M.* 8, 90). Pearly plates.

NITRO-HYDANTOÏN $C_3H_3N_3O_4$ *i.e.* $NH<\begin{matrix}CO.NH\\CO.CH(NO_2)\end{matrix}>$. [170°]. Formed from hydantoïn and HNO_3 (Franchimont a. Klobbie, *R. T. C.* 7, 12).

DI-*p*-NITRO-HYDROBENZOÏN.

Acetyl derivative $C_6H_4(NO_2).CH(OAc).CH(OAc).C_6H_4NO_2$. [340°]. From the dibromide of di-*p*-nitro-di-phenyl-ethylene and alcoholic KOAc (Elbs a. Bauer, *J. pr.* [2] 34, 346). Small yellow crystals, m. sol. alcohol, ether, and glacial HOAc.

NITROHYDROCHLORIC ACID *v.* CHLORHYDRIC ACID, *Reactions*, No. 17, vol. ii. p. 8.

NITRO-HYDROCINNAMIC ACID *v.* NITRO-*β*-PHENYL-PROPIONIC ACID.

DI-NITRO-HYDRO-*p*-COUMARIC ACID *v.* DI-NITRO-*p*-OXY-*β*-PHENYL-PROPIONIC ACID.

NITRO-HYDRO-*ψ*-CUMOQUINONE $C_9H_{11}NO_4$ *i.e.* $C_6Me_3(NO_2)(OH)_2$. [106°]. Formed from nitro-*ψ*-cumoquinone and SO_2 (Nef, *A.* 237, 18). Yellow needles (from ether).

NITRO-HYDRO-(*β*)-NAPHTHOQUINONE $C_{10}H_7NO_4$ *i.e.* $C_{10}H_5(NO_2)(OH)_2$. [159·5°]. Formed from nitro-(*β*)-naphthoquinone and SO_2 (Zaertling, *B.* 23, 177; *cf.* Groves, *C. J.* 45, 299). Red needles, sol. boiling water.

NITRO-HYDROQUINONE. *Mono-methyl ether* $C_6H_3(NO_2)(OMe)(OH)$. [83°]. Formed from HNO_3 and $C_6H_4(OMe)(OH)$ in ether (Weselsky a. Benedikt, *M.* 2, 369). Orange needles.

Di-methyl ether $C_6H_3(NO_2)(OMe)_2$. [71°]. Formed from $C_6H_4(OMe)_2$ and cold dilute (1:10) HNO_3 (Habermann, *B.* 11, 1034; Mühlhäuser, *A.* 207, 253). Felted needles.

Mono-ethyl ether $C_6H_3(NO_2)(OEt)(OH)$. [83°]. Yellow needles (W. a. B.).

Di-ethyl ether $C_6H_3(NO_2)(OEt)_2$. [49°]. Formed by nitration (Nietzki, *A.* 215, 148).

Mono-benzyl derivative $C_6H_3(NO_2)(OC_7H_7)(OH)$. [158°]. Formed by boiling the benzyl derivative of nitro-arbutin with dilute H_2SO_4 (Schiff a. Pellizzari, *A.* 221, 371; *G.* 14, 501). Yellow needles (from water).

Di-benzyl derivative $C_6H_3(NO_2)(OC_7H_7)_2$. [83°]. Obtained by nitration of $C_6H_4(OC_7H_7)_2$. Yellow needles (from alcohol).

Di-propionyl derivative $C_6H_3(NO_2)(O.COEt)_2$. [86°]. Obtained by nitration (Hesse, *A.* 200, 247).

Di-nitro-hydroquinone $C_6H_4N_2O_6$ *i.e.* $C_6H_2(NO_2)_2(OH)_2$ [5:2:4:1]. [136°]. Obtained by saponification of its di-acetyl derivative (Nietzki, *B.* 11, 469; *A.* 215, 145) and also by boiling di-nitro-arbutin with dilute H_2SO_4 (Strecker, *A.* 118, 293). Flat golden needles (from water). Its alkaline solutions are violet.—BaA″: violet-black needles with bronze lustre.

Di-acetyl derivative. [96°]. Obtained by nitrating the di-acetyl derivative of hydroquinone. Yellow needles.

Mono-methyl ether [102°]. Needles.

Di-methyl ether. The two crystalline isomerides $C_6H_2(NO_2)_2(OMe)_2$[3:2:1:4] [177°] and $C_6H_2(NO_2)_2(OMe)_2$[5:2:1:4] [202°] are formed by nitrating $C_6H_4(OMe)_2$ (Nietzki a. Rechberg, *B.* 23, 1216).

Mono-ethyl ether [71°]. Yellow needles.

Di-ethyl ether. The two crystalline isomerides $C_6H_2(NO_2)_2(OEt)_2$[3:2:1:4] [130°] and $C_6H_2(NO_2)_2(OEt)_2$[5:2:1:4] [176°] are formed by nitration of the di-ethyl derivative of hydroquinone (Nietzki, *A.* 215, 150; N. a. R.).

Methyl ethyl ether $C_6H_2(NO_2)_2(OMe)(OEt)$. [144°]. Formed from $C_6H_2(NO_2)_2(OMe)(OEt)$ (Fiala, *M.* 6, 914).

Benzyl ether $C_6H_2(NO_2)_2(OC_7H_7)(OH)$. [137°]. Formed by nitration (S. a. P.). Golden needles.—KA′ aq: explosive scarlet needles.—$C_{13}H_{10}N_2O_6 2NH_3$. Loses NH_3 in air, forming NH_4A', which is stable.

Tri-nitro-hydroquinone. *Di-methyl ether* $C_6H(NO_2)_3(OMe)_2$. [101°]. Formed by adding a solution of $C_6H_4(OMe)_2$ in HOAc to a cold mixture of H_2SO_4 and fuming HNO_3 (H.). Yellow needles (from alcohol).

Di-ethyl ether $C_6H(NO_2)_3(OEt)_2$. [130°]. Formed from either $C_6H_2(NO_2)_2(OEt)_2$ by further nitration (Nietzki). Yellow needles. Aniline forms red crystals of $C_6H(NO_2)_2(NHPh)(OEt)_2$ [133°] whence alcoholic potash yields yellow crystals of $C_6H(NO_2)_2(OH)(OEt)_2$ [152°].

Tetra-nitro-hydroquinone. *Di-isobutyl ether* $C_6(NO_2)_4(OC_4H_9)_2$. Formed by nitrating $C_6H_4(OC_4H_9)_2$ (Schubert, *M.* 3, 686). Needles (from alcohol), v. sol. hot HOAc.

DI-NITRO-HYDROTOLUQUINONE $C_6HMe(NO_2)_2(OH)_2$. [149°–153°]. Obtained by saponifying its mono-acetyl derivative, which is got by nitrating the di-acetyl derivative of hydrotoluquinone (Kehrmann a. Brasch, *J. pr.* [2] 39, 377). Yellowish-red crystals (containing aq).

Acetyl derivative $C_6HMe(NO_2)_2(OAc)(OH)$. [146°]. Yellow crystals.

Di-acetyl derivative $C_6HMe(NO_2)_2(OAc)_2$. [154°–157°]. Colourless silky needles.

NITRO-DI-IMIDO-HYDROQUINONE $C_6H(NO_2)(NH)_2(OH)_2$[3:5:2:4:1]. Formed from di-amido-hydroquinone sulphate, HOAc, and HNO_3 (S.G. 1·4) (Nietzki a. Schmidt, *B.* 22, 1658). Needles or prisms. Reduced by $SnCl_2$ to tri-amido-hydroquinone.

NITRO-IMIDO-DI-PHENYL-SULPHOXIDE $NH<{C_6H_4 \atop C_6H_3(NO_2)}>SO$. Formed by nitration of imido-di-phenyl-sulphoxide (Bernthsen, *B.* 17, 2858).

(a)-**Di-nitro-imido-di-phenyl-sulphoxide** $NH<{C_6H_3(NO_2) \atop C_6H_3(NO_2)}>SO$. Formed, together with the (β)-isomeride by nitration of imido-di-phenyl-sulphide (Bernthsen, *A.* 230, 115). Orange needles. Reduced by $SnCl_2$ and HCl to (a)-di-amido-imido-di-phenyl sulphide.

Acetyl derivative $C_{12}H_5Ac_2N_3SO_5$.

(β)-**Di-nitro-imido-di-phenyl-sulphoxide.** Lemon-yellow powder. Reduced by $SnCl_2$ and HCl to (β)-di-amido-imido-di-phenyl sulphide.

NITRO-DI-IMIDO-RESORCIN $C_6H(NH)_2(NO_2)(OH)_2$[6:4:2:3:1]. Formed from di-amido-resorcin sulphate, HOAc, and HNO_3 (Nietzki a. Schmidt, *B.* 22, 1659). Needles.—K_2A'': orange needles.

NITRO-INDAZINE $C_7H_5(NO_2)N_2$. [181°]. Formed, together with nitro-cresol, by heating diazotised (4, 1, 2)-nitro-*o*-toluidine sulphate with water (Witt, Nölting, a. Grandmougin, *B.* 23, 3636). Needles. Yields a methyl derivative $C_7H_4Me(NO_2)N_2$ [159°], an acetyl derivative [140°], and a bromo- derivative $C_7H_4Br(NO_2)N_2$ [229°].

DI-NITRO-INDIN *v.* INDIN.

DI-NITRO-INDIGO *v.* INDIGO.

NITRO-INOSITE *v.* INOSITE.

NITRO-IODO- compounds *v.* IODO-NITRO-compounds.

NITRO-ISATIN *v.* ISATIN.

NITRO-ISATOIC ACID *v.* ISATOIC ACID.

NITRO-LACTIC ACID *v.* NITRO-OXY-PROPIONIC ACID.

TRI-NITRO-LAURENE $C_{11}H_{13}(NO_2)_3$(?). [84°]. From laurene, HNO_3, and H_2SO_4 (Fittig, *A.* 145, 150).

NITROLIC ACIDS. Compounds of the form $R.CH(NO)(NO_2)$ or $R.C(NO_2)$:NOH. They are formed by the action of nitrous acid (*i.e.* KNO_2 and H_2SO_4) on the sodium derivatives of primary nitro-paraffins, and by the action of hydroxylamine on the compounds $R.C(NO_2)Br_2$. Their alkaline solutions are red (V. Meyer, *B.* 7, 1510; *cf.* vol. i. p. 101). The compounds of the form $RR'C(NO)(NO_2)$ formed by the action of nitrous acid on secondary nitro-paraffins are called pseudonitroles. The pseudonitroles are also formed by the action of NO_2 upon ketones; thus acetone yields $(CH_3)_2C(NO)(NO_2)$ (Scholl, *B.* 21, 506). The pseudonitroles may perhaps be formulated RR'C:N.O.NO_2 (V. Meyer, *B.* 21, 1291). The pseudonitroles do not form salts; their solutions are blue.

NITRO-MALONIC ETHER $CH(NO_2)(CO_2Et)_2$. Formed from malonic ether (1 pt.) and HNO_3 (5 pts. of S.G. 1·5), the product being extracted with ether (Franchimont a. Klobbie, *R. T. C.* 8, 283). Heavy oil, decomposing carbonates and forming a white crystalline compound with NH_3, decomposing at 150°.

Methyl nitro-malonate forms the analogous $CH(NO_2)(CO_2Me)_2NH_3$ [c. 166°].

o-**NITRO-MANDELIC ACID** $C_8H_7NO_5$ *i.e* $C_6H_4(NO_2).CH(OH).CO_2H$. [140°]. Formed from di-ω-bromo-*o*-nitro-acetophenone and very dilute KOH (Engler a. Wöhrle, *B.* 20, 2201). Formed also from *o*-nitro-benzoic aldehyde, KCy, MeOH, and HCl (Engler a. Zielke, *B.* 22, 207). Small crystals, v. sol. water.

Methyl ether MeA'. [74·5°]. Sol. alcohol.

m-**Nitro-mandelic acid.** [120°]. Formed from *m*-nitro-α-amido-phenyl-acetic acid and HNO_2 (Plöchl a. Loë, *B.* 18, 1181) and also from di-ω-bromo-*m*-nitro-acetophenone and dilute KOH (E. a. W.). Yellowish rhombohedra with bitter taste.—NH_4A'.—AgA'.

Ethyl ether EtA'. [63°].

m-**Nitro-mandelic imido-ether** $C_6H_4(NO_2).CH(OH).C(NH)OEt$. [84°]. Formed from *m*-nitro-benzoic aldehyde, KCy, alcohol, and HCl (Beyer, *J. pr.* [2] 31, 393). Dendritic needles (from ligroïn).—B'HCl. [129°]. Needles. Cold dilute HClAq converts it quickly into *m*-nitro-mandelic ether [63°].

p-**Nitro-mandelic acid** [126°]. Formed in like manner (E. a. Z.). Yields *p*-oxy-phenyl-glyoxylic acid on boiling with aqueous Na_2CO_3.

Methyl ether MeA'. [87°]. Prisms.

Ethyl ether EtA'. [76°]. Needles.

NITRO-MESIDINE *v.* NITRO-AMIDO-MESITYLENE.

NITRO-MESITOL $C_6HMe_3(NO_2)(OH)$. [64°]. From nitro-amido-mesitylene and HNO_2 (Knecht, *B.* 15, 1376; *A.* 215, 98). Yellow plates (from water), volatile with steam.

NITRO-MESITYLENE $C_6H_2Me_3(NO_2)$. [42°]. (255°). Formed, together with much di-nitro-mesitylene, from mesitylene and HNO_3 (S.G. 1·38) (Fittig, *A.* 141, 132; 147, 2). Formed also from nitro-amido-mesitylene and HNO_2 (Ladenburg, *A.* 179, 170; Klobbie, *R. T. C.* 6, 31). Triclinic prisms (from alcohol). CrO_3 in HOAc oxidises it to $C_6H_2Me_2(NO_2).CO_2H$[6:2:1:4] [200°–225°] (Emerson, *Am.* 8, 268).

Di-nitro-mesitylene $C_6HMe_3(NO_2)_2$. [86°]. Obtained by dropping mesitylene into cooled fuming HNO_3. Trimetric prisms, m. sol. hot alcohol.

Tri-nitro-mesitylene $C_6Me_3(NO_2)_3$. [232°]. Formed from mesitylene, HNO_3, and H_2SO_4. Colourless needles (from hot alcohol) or triclinic prisms (from acetone). Yields NH_3 and di-amido-mesitylene on reduction by tin and HClAq.

NITRO-MESITYLENE SULPHONIC ACID $C_9H_{11}NSO_5$ *i.e.* $C_6HMe_3(NO_2)(SO_3H)$. [131°]. S. 100 in the cold. Formed from mesitylene sulphonic acid and HNO_3 (Roze, *Z.* [2] 6, 74; *A.* 164, 65). Prisms (containing $1\frac{1}{2}$ aq).—KA'aq.—BaA'_2.—CuA'_2 3aq.—PbA'_2 aq.

(a)-**NITRO-MESITYLENIC ACID** $C_9H_9NO_4$ *i.e.* $C_6H_2Me_2(NO_2)(CO_2H)$ [5:3:2:1]. [212°]. Formed by nitrating mesitylenic acid (Schmitz, *A.* 193, 162). Colourless crystals (from alcohol).—BaA'_2 4aq: needles, v. e. sol. water.

Ethyl ether EtA'. [64°]. Tables.

(β)-**Nitro-mesitylenic acid** $C_6H_2Me_2(NO_2)(CO_2H)$ [5:3:4:1]. [223°]. Found, in small quantity, in preparing the preceding acid (Fittig, *A.* 141, 149; 147, 48; Schmitz). Formed also by oxidising nitro-mesitylene (*q.v.*) monoclinic crystals (from alcohol). Melts at 179° when crystallised from water.—BaA'_2 4aq. — BaA'_2 2aq. — BaA'_2 6aq. — CaA'_2 6aq. — MgA'_2 11aq.—AgA'.

Ethyl ether EtA' [72°]. Needles.

NITRO-MESITYL-PHTHALIMIDE $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N.C_6HMe_3(NO_2)$. [210°]. Formed by nitration of mesityl-phthalimide (Eisenberg, *B.* 15, 1018). Prisms, sol. alcohol.

Di-nitro-mesityl-phthalimide $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N.C_6Me_3(NO_2)_2$. [242°]. Formed from mesityl-phthalimide, HNO_3, and H_2SO_4(E.). Needles, sol. alcohol.

NITRO-METHANE $CH_3.NO_2$. Mol. w. 61. (101°). S.G. $\frac{15}{15}$ 1·1441; $\frac{25}{25}$ 1·1330. M.M. 1·858 (Perkin, *C. J.* 55, 687). S.V. 59·5 (Schiff; Lossen, *A.* 254, 73). H.F.p. 18,600. H.F.v. 17,440 (Thomsen, *Th.*). Formed, unaccompanied by methyl nitrite, from MeI and $AgNO_2$ (V. Meyer, *A.* 171, 32). Formed also by heating potassium chloroacetate with potassium nitrite (Kolbe, *J. pr.* [2] 5, 427; Preibisch, *J. pr.* [2] 7, 480; 8, 316). Heavy oil. With alcoholic potash it gives a pp. of $CH_2K.NO_2(EtOH)$, the aqueous solution of which is ppd. by $HgCl_2$, the pp. being explosive. Iron and acetic acid reduce it to methylamine. Fuming H_2SO_4 forms hydroxylamine and CO. HClAq (S.G. 1·14) at 150° forms formic acid and hydroxylamine. Benzoic aldehyde yields $C_6H_5.CH:CH.NO_2$ (characteristic) (Priebs, *A.* 225, 319). Nitro-methane converts dichlorhydrin $CH_2Cl.CH(OH).CH_2Cl$ into di-chloro-formin $CH_2Cl.CH(OCHO).CH_2Cl$ (Pfungst, *J. pr.* [2] 32, 237). $ZnEt_2$, followed by water, yields methyl-di-ethyl-hydroxylamine (Bevad, *J. R.* 20, 125).

Di-nitro-methane. *Potassium salt* $CHK(NO_2)_2$. Formed by passing H_2S into a solution of $CBrK(NO_2)_2$ mixed with ammonia (Villiers, *Bl.* [2] 41, 282). Yellow explosive crystals.

Tri-nitro-methane $CH(NO_2)_3$. *Nitroform.* [15°]. Formed by boiling with water tri-nitro-acetonitrile, a product of the action of HNO_3 and H_2SO_4 on fulminuric acid (Schischkoff, *A.* 103, 364). White crystals, m. sol. water. Explodes when quickly heated. Reduced by tin and HCl to hydroxylamine, NH_3, and HCy (V. Meyer a. Locher, *A.* 180, 172).

Tetra-nitro-methane $C(NO_2)_4$. Mol. w. 196. [13°]. (126°). Formed from tri-nitro-methane, conc. H_2SO_4, and fuming HNO_3 (Schischkoff, *A.* 119, 248). White crystals, which will not burn.

NITRO-METHANE TRICARBOXYLIC ETHER $C(NO_2)(CO_2Et)_3$. Formed from $CH(CO_2Et)_3$ and HNO_3 (S.G. 1·52) (Franchimont a. Klobbie, *R. T. C.* 9, 220). Oil.

NITRO-METHANE DISULPHONIC ACID $CH(NO_2)(SO_3H)_2$. The salt K_2A'', formed by the action of conc. H_2SO_3Aq on chloropicrin crystallises in minute plates, v. sl. sol. cold water (Rathke, *A.* 161, 153; 167, 220).

NITRO-METHOXY- compounds *v. Methyl derivatives* of NITRO-OXY- compounds.

NITRO-DI-METHYL-AMIDO-BENZENE SULPHONIC ACID $C_8H_{10}N_2SO_5$ *i.e.* $C_6H_3(NMe_2)(NO_2).SO_3H$. Formed together with $C_6H_4(NO_2)NMe_2$, from $C_6H_4(NMe_2).SO_3H$ and aqueous $NaNO_2$ (Michler a. Walder, *B.* 14, 2176). Yellow crystals (from water).—BaA'_2.—CaA'_2.

NITRO-TETRA-METHYL-DI-AMIDO-BENZOPHENONE $C_{17}H_{19}N_3O_3$ *i.e.* $NMe_2.C_6H_3(NO_2).CO.C_6H_4.NMe_2$. [144°]. Formed from $CO(C_6H_4.NMe_2)_2$ by nitration (Nathansohn a. Müller, *B.* 22, 1883). Needles (from warm alcohol), sl. sol. ether.

Di-nitro-di-methyl-amido-benzophenone $C_{15}H_7(NO_2)_2(NMe_2)CO$. [142°]. Obtained from $C_6H_5.CO.C_6H_4NMe_2$ and fuming HNO_3 (Fischer *A.* 206, 88). Nodules (from dilute HOAc).

Tetra-nitro-di-methyl-di-amido-benzophenone $CO(C_6H_2(NO_2)_2.NMeH)_2$. [225°]. Formed by boiling its di-nitro- derivative with phenol (Van Romburgh, *R. T. C.* 6, 252, 365). Plates, v. sl. sol. alcohol.

Di-nitro-derivative $CO(C_6H_2(NO_2)_2.NMeNO_2)_2$. Formed by the action of conc. HNO_3 on $CO(C_6H_4NMe_2)_2$ or $CS(C_6H_4NMe_2)_2$ (R.; Baither, *B.* 20, 3296). Yellow crystals, decomposing at about 210°.

NITRO-DI-METHYL-AMIDO-PHENOL. *Anhydride of the methylo-hydroxide* $C_9H_{12}N_2O_3$ *i.e.* $C_6H_3(NO_2)<\genfrac{}{}{0pt}{}{O}{NMe_3}>$. Formed from nitro-amido-phenol, MeI and KOH (Griess, *B.* 13, 647). Yellow crystals.—B'HCl aq.—B'HI 2aq.—$B'_2H_2PtCl_6$ 6aq: yellow crystals.

Di-nitro-di-methyl-amido-phenol $C_8H_9N_3O_5$ *i.e.* $C_6H_2(NO_2)_2NMe_2(OH)$. [195°]. Formed from KCy and alcoholic $C_6H_3(NO_2)_2NMe_2$ at 50° (Lippmann a. Fleissner, *M.* 6, 808). Triclinic yellow crystals. Converted by boiling KOHAq into dimethylamine and di-nitro-resorcin [145°].—NH_4A'. [195°].—KA'.—BaA'_2 $1\frac{1}{2}$aq.—AgA': red crystalline pp.

Tri-nitro-methyl-amido-phenol. *Nitro-derivative* $C_6H(NO_2)_3(OH).NMe(NO_2)$. [188°]. Formed by boiling $C_6H(NO_2)_4.NMe(NO_2)$ with water (Van Romburgh, *R. T. C.* 8, 275). Yellow crystals (from water). Its *methyl ether* $C_6H(NO_2)_3(OMe).NMe(NO_2)$ [99°] is formed by dissolving $C_6H(NO_2)_4NMe(NO_2)$ in MeOH. The *ethyl ether* $C_6H(NO_2)_3(OEt).NMe(NO_2)$ [98°] is formed in like manner.

DI-NITRO-TETRA-METHYL-DI-*p*-AMIDO-DIPHENYL $C_6H_3(NO_2)(NMe_2).C_6H_3(NO_2)(NMe_2)$. [188°]. Obtained by nitration (Michler, *B.* 14, 2164; 17, 118). Red needles.

DI-NITRO-DI-METHYL-*p*-AMIDO-DI-PHENYLAMINE [4:2:1] $C_6H_3(NO_2)_2.NH.C_6H_4NMe_2$. [168°]. Formed from $C_6H_3Cl(NO_2)_2$ and $C_6H_4(NH_2)(NMe_2)$ (Lellmann a. Mack, *B.* 23, 2739).—Orange plates.

***p*-NITRO-DI-METHYL-AMIDO-DI-PHENYL-CARBINOL** $C_6H_4(NO_2).CH(OH).C_6H_4NMe_2$. [96°]. Formed by boiling *p*-nitro-benzoic aldehyde with di-methyl-aniline and HClAq (Albrecht, *B.* 21, 3294). Thin yellow needles.

Reactions.—1. *Dimethylaniline* and $ZnCl_2$ yield $C_6H_4(NO_2).CH(C_6H_4NMe_2)_2$ [177°].—2. Boiling *alcoholic potash* and *zinc-dust* form an azo- compound [199°].—3. *Zinc-dust* and HCl reduce it to di-methyl-di-amido-di-phenyl-carbinol [165°] and di-methyl-di-amido-di-phenyl-methane [93°].

Methylo-iodide B'MeI. [c. 175°].

o-Nitro-tetra-methyl-di-*p*-amido-tri-phenyl-carbinol $C_{23}H_{25}N_3O_3$ *i.e.* $C_6H_4(NO_2).C(OH)(C_6H_4NMe_2)_2$. o-*Nitro-malachite green.* [163°]. Formed by heating di-methyl-aniline ($3\frac{1}{2}$ pts.) with *o*-nitro-benzoic aldehyde (1 pt.) and $ZnCl_2$ (1 pt.) on the water-bath, and oxidising the resulting leuco-base with PbO_2 and dilute H_2SO_4 (O. Fischer a. Schmidt, *B.* 17, 1890). Small yellow crystals, sol. alcohol.

m-Nitro-tetra-methyl-di-*p*-amido-tri-phenyl-carbinol [3:1] $C_6H_4(NO_2).C(OH)(C_6H_4NMe_2)_2$. Formed by oxidation of *m*-nitro-tetra-methyl-di-amido-tri-phenyl-methane (E. a. O. Fischer, *B.* 12, 802).—Picrate: small green needles.

p-Nitro-tetra-methyl-di-amido-tri-phenyl-carbinol. Formed like the two preceding isomerides, and also by heating dimethylaniline with BzCl and ZnCl (E. a. O. Fischer, *B.* 12, 800; 14, 2528). Small golden prisms. Dyes a splendid green.—Picrate: minute needles.

NITRO-DI-METHYL-AMIDO-PHENYL-HEXYL KETONE $C_{15}H_{22}N_2O_3$ *i.e.* $C_6H_3(NO_2)(NMe_2).CO.C_6H_{13}$. [65°]. Obtained by nitrating $C_6H_4(NMe_2).CO.C_6H_{13}$ (Auger, *Bl.* [2] 47, 42). Yellow needles (from alcohol).

o-**NITRO-TETRA-METHYL-DI-*p*-AMIDO-TRI-PHENYL-METHANE** $C_6H_4(NO_2).CH(C_6H_4NMe_2)_2$. *o-Nitro-leuco-malachite-green.* [160°]. Prepared by heating o-nitro-benzoic aldehyde with dimethylaniline and $ZnCl_2$ (Fischer, *B.* 15, 682; 17, 1889. Yellow monoclinic prisms, sl. sol. alcohol.

m-Nitro-tetra-methyl-di-amido-tri-phenyl-methane $C_6H_4(NO_2).CH(C_6H_4NMe_2)_2$. [152°]. Obtained in the same way from *m*-nitro-benzoic aldehyde (E. a. O. Fischer, *B.* 12, 802). Yellow crystals, sl. sol. alcohol.

p-Nitro-tetra-methyl-di-amido-tri-phenyl-methane. [177°]. Obtained from *p*-nitro-benzoic aldehyde, dimethylaniline, and $ZnCl_2$ at 100° (Fischer, *B.* 14, 2526). Golden plates.

Methylo-iodide $B''Me_2I_2$ aq. [220°].

Tetra-nitro-di-methyl-di-amido-di-phenyl-methane $CH_2(C_6H_2(NO_2)_2.NMeH)_2$. [250°]. Formed by boiling its di-nitro-derivative with phenol (Van Romburgh, *R. T. C.* 7, 233). Orange crystals, sl. sol. hot alcohol.

Di-nitro-derivative $CH_2(C_6H_2(NO_2)_2.NMe.NO_2)_2$. Formed from $CH_2(C_6H_4.NMe_2)_2$, acetic acid, and HNO_3. Yellow crystalline substance, decomposing at 217°–220°.

Hexa-nitro-tetra-methyl-di-amido-tri-phenyl-methane. [200°]. Formed by nitrating $CH(C_6H_5)(C_6H_4NMe_2)_2$ (O. Fischer, *A.* 206, 122). Golden needles, sol. alcohol.

NITRO-DI-METHYL-*p*-AMIDO-PHENYL-OXAMIC ETHER $C_{12}H_{15}N_3O_5$ *i.e.* [1:3:4] $C_6H_3(NMe_2)(NO_2).NH.CO.CO_2Et$. [152°]. Formed from di-methyl-amido-phenyl-oxamic ether and nitrous acid (Wurster a. Sendtner, *B.* 12, 1804). Red needles. Gives $C_6H_3(NMe_2)(NH_2)_2$ on reduction by tin and HClAq.

NITRO-TETRA-METHYL-DI-AMIDO-PHENYL-DI-TOLYL-METHANE $C_6H_4(NO_2).CH(C_6H_3Me.NMe_2)_2$. [224°]. Formed from di-methyl-*m*-toluidine and *p*-nitro-benzoic aldehyde (Kock, *B.* 20, 1562). Yields a picrate [199°].

NITRO-METHYL-AMINE *v.* METHYL-NITRO-AMINE, p. 279.

Nitro-di-methyl-amine *v.* DI-METHYL-NITRO-AMINE, p. 280.

o-**NITRO-METHYL-ANILINE** $C_7H_8N_2O_2$ *i.e.* [1:2] $C_6H_4(NO_2).NHMe$. [28°]. Formed by heating *o*-nitro-phenol with alcoholic methylamine at 180° (Hempel, *J. pr.* [2] 41, 164).

Nitrosamine $C_6H_4(NO_2).N(NO)Me$. [36°].

m-Nitro-methyl-aniline [1:3] $C_6H_4(NO_2).NHMe$. [66°]. Formed by methylation of *m*-nitro-aniline (Nölting a. Stricker, *B.* 19, 548). Reddish-yellow needles, sol. hot Aq.

Acetyl derivative $C_6H_4(NO_2).NAcMe$. [95°]. Needles, sol. water (Meldola, *C. J.* 53, 777).

Benzoyl derivative $C_7H_7BzN_2O_2$. [105°].

Nitrosamine $C_6H_4(NO_2).N(NO)Me$. [70°].

p-Nitro-methyl-aniline [1:4] $C_6H_4(NO_2).NHMe$. [152°]. Formed by heating [1:4] $C_6H_4(NO_2).N_2.NMe.C_6H_4(NO_2)$ [4:1] with HClAq (Meldola a. Salmon, *C. J.* 53, 774). Short thick yellowish-brown prisms or tablets (from alcohol), sl. sol. hot water, v. sol. alcohol.

Acetyl derivative $C_6H_4(NO_2).NAcMe$. [153°].

Benzoyl derivative. [112°]. Prisms.

Nitrosamine $C_6H_4(NO_2).N(NO)Me$. [100°].

m-Nitro-di-methyl-aniline $C_6H_4(NO_2).NMe_2$ [1:3]. [61°]. (280°–285°). Large red prisms. Obtained by heating *m*-nitro-aniline hydrobromide (1 mol.) with MeOH (2 mols.) at 100° (S. a. B.). Prepared by nitration of dimethylaniline in presence of a large excess of H_2SO_4, *p*-nitro-dimethylaniline being formed in smaller quantity. A mixture of 193 g. of HNO_3 (S.G. 1·35) and 600 g. of ordinary H_2SO_4 is allowed to slowly drop into a solution of 200 g. of dimethylaniline in 4,000 g. of ordinary H_2SO_4, keeping the mixture cooled below 5°. After standing for 4 or 5 hours it is poured into about 10 litres of iced water and filtered from the ppd. *p*-nitro- derivative, more of which separates on partial neutralisation with Na_2CO_3 (50 or 60 g. on the whole). The filtrate neutralised with Na_2CO_3 deposits the *m*-nitro-di-methyl-aniline; the yield is 160 to 170 g. (Groll, *B.* 19, 198).

Methylo-bromide $C_6H_4(NO_2).NMe_3Br$. Crystalline (Städel a. Bauer, *B.* 19, 1941). Yields crystalline B'MeCl, $B'_2Me_2PtCl_6$, and unstable B'MeOH which is converted by *m*-nitro-phenol into $C_6H_4(NO_2).NMe_3.O.C_6H_4(NO_2)$ [62°].

p-Nitro-di-methyl-aniline $C_6H_4(NO_2).NMe_2$. [163°]. Formed by adding HNO_3 to a solution of dimethylaniline in HOAc (Weber, *B.* 10, 760). Formed also by oxidising *p*-nitroso-di-methyl-aniline with $KMnO_4$ (Wurster, *B.* 12, 528; *cf.* Schraube, *B.* 8, 616); by heating *p*-chloro-nitro-benzene with NMe_3 at 180° (Leymann, *B.* 15, 1234); and by the action of nitrous acid on $C_6H_4(NMe_2).SO_3H$ (Michler a. Walder, *B.* 14, 2176), on $C_6H_4(NMe_2).N_2.C_6H_4NMe_2$ (Lippmann a. Fleissner, *B.* 16, 1421); and on the base $C_6H_3(NO_2)(NH_2)NMe_2$ (Hewi, *B.* 21, 2309). Yellow needles. Does not form salts.

Di-nitro-methyl-aniline $C_7H_7N_3O_4$ *i.e.* $C_6H_3(NO_2)_2.NHMe$. [177°].

Formation.—1. From chloro-di-nitro-benzene and methylamine (Leymann, *B.* 15, 1234).—2. By heating $C_6H_3(NO_2)_2NMe_2$ [78°] in HOAc with bromine (L.), or CrO_3 (Van Romburgh, *R. T. C.* 8, 250).—3. By nitrating the formyl, acetyl, or oxalyl derivative of methyl-aniline (Norton a. Allen, *B.* 18, 1995; Norton a. Livermore, *B.* 20, 2273).

Properties.—Yellow crystals, v. sol. alcohol, sl. sol. hot water.

Di-nitro-di-methyl-aniline $C_6H_3(NO_2)_2.NMe_2$ [4:2:1]. [87°]. Formed from $C_6H_3Cl(NO_2)_2$ and NMe_3 (Leymann, *B.* 15, 1283). Prepared by slowly adding 500 g. of dimethyl-aniline to a mixture of 6 litres of ordinary conc.

HNO_3 and 6 litres of water, cooled to 0°; the yield being 116° (Mertens, *B.* 19, 2123; *cf.* Weber, *B.* 10, 763). Large yellow pointed crystals or prisms. V. sol. alcohol, chloroform, benzene, acetic acid, and HClAq. Heated with 10 p.c. KOH aq it readily decomposes into di-nitro-phenol [114°] and dimethylamine. Boiled with fuming HNO_3 it is converted into tri-nitro-phenyl-methyl-nitramide $C_6H_2(NO_2)_3.NMe(NO_2)$.

Salts.—B'HCl: unstable.—$B'_2H_2Cl_2PtCl_4$: granular pp., or large brownish-red pyramids.

Di-nitro-di-methyl-aniline $C_6H_3(NO_2)_2.NMe_2$[5:3:1 ?]. Formed by nitration of dimethylaniline with dilute HNO_3 (equal vols. of HNO_3 (S.G. 1·4) and water) without cooling, the yield being 15 p.c. (Mertens, *B.* 19, 2125). Golden-brown plates. Decomposes at 250°–272°. Soluble in phenol. It is attacked only by very strong KOH. Boiled with fuming HNO_3 it is converted into di-nitro-phenyl-methyl-nitramine $C_6H_3(NO_2)_2.NMe(NO_2)$, a crystalline body which explodes above 220°.

Tri-nitro-methyl-aniline $C_7H_6N_4O_6$ *i.e.* $C_6H_2(NO_2)_3NHMe$. [111°]. Formed from $C_6H_2Cl(NO_2)_3$ (picryl chloride) and methylamine in hot alcoholic solution (Van Romburgh, *R. T. C.* 2, 31, 105, 305). Yellow needles (from alcohol). Gives off $NMeH_2$ when heated with KOHAq.

Nitro- derivative $C_6H_2(NO_2)_3NMe(NO_2)$. [127°]. Obtained from dimethylaniline (10 pts.), H_2SO_4 (100 pts.), and HNO_3 (200 pts. of S.G. 1·48). Obtained also from methyl-aniline and HNO_3 (Romburgh), and by nitration of di-methyl-amido-phenyl naphthyl sulphone (Michler a. Schacht, *B.* 12, 1790). Pale-yellow crystals (from alcohol). Yields picric acid on boiling with aqueous Na_2CO_3. Reduced by tin and HClAq to tri-amido-phenol.

Tri-nitro-di-methyl-aniline $C_6H_2(NO_2)_3NMe_2$. [138°]. Formed from picryl chloride and alcoholic dimethylamine (Van Romburgh, *R. T. C.* 2, 105; 8, 250). Yellow crystals (from benzene). Forms with picric acid the crystalline compound $C_8H_8N_4O_6C_6H_2(NO_2)_3OH$ [114°].

Tetra-nitro-methyl-aniline. *Nitro- derivative* $C_6H(NO_2)_4.NMe(NO_2)$. [146°]. Formed from the preceding tri-nitro-di-methyl-aniline and HNO_3 (S.G. 1·5) (Van Romburgh, *R. T. C.* 8, 274). Yellowish-white needles. On dissolving in MeOH it yields $C_6H(NO_2)_3(OMe).NMe(NO_2)$ [99°]; alcohol forms $C_6H(NO_2)_3(OEt).NMe(NO_2)$ [98°] in like manner. Aqueous methylamine produces $C_6H(NO_2)_3(NMeH).NMe(NO_2)$ [192°] and $C_6H(NO_2)_3(NMeH)_2$ [235°]. If a few drops of aniline be poured upon the nitro- derivative it catches fire.

NITRO-METHYL-ANTHRAQUINONE $C_{14}H_6O_2(CH_3)(NO_2)$. [270°]. Prepared by nitration of methyl-anthraquinone by adding KNO_3 to its solution in H_2SO_4 (Römer a. Link, *B.* 16, 696). Sublimes in small white needles. Sl. sol. alcohol and ether, v. sol. nitrobenzene.

TRI-NITRO-TRI-METHYL-BENZENE $C_6Me_3(NO_2)_3$ [1:2:3:4:5:6]. [209°]. Got by nitration (Jacobsen, *B.* 19, 2517).

NITRO-METHYL-BENZOIC ACID *v.* NITRO-TOLUIC ACID.

Nitro-di-methyl-benzoic acid $C_9H_9NO_4$ *i.e* $C_6H_2Me_2(NO_2).CO_2H$. [195°]. Formed by oxidising nitro-ψ-cumene (Schaper, *Z.* 1867, 13). Slender needles.—$CaA'_2$6aq.—$BaA'_2$9aq.—EtA'.

p-**NITRO-METHYL-COUMARILIC ACID** $C_6H_3(NO_2)\Big\langle {}^{CMe:C.CO_2H}_{O} \Big/$. [178°]. Obtained by saponification of its ethyl-ether, which is formed by heating dry *p*-nitro-phenol sodium with chloro-acetoacetic ether and dissolving the product (probably *p*-nitro-phenoxy-acetic ether) in conc. H_2SO_4 (Nuth, *B.* 20, 1332). Short yellow needles. M. sol. hot water, alcohol, and ether; nearly insol. cold water. Most of the salts are sparingly soluble.—AgA'½aq: small needles.

Ethyl ether EtA': [74°]. White needles.

NITRO-METHYL-ETHYL-BENZENE *v.* NITRO-ETHYL-TOLUENE.

NITRO-(*B.* 2-*Py.* 2)-DIMETHYL-(*Py.* 3)-ETHYL-QUINOLINE $C_{13}H_{14}N(NO_2)$. [109°]. Formed by nitration of di-methyl-ethyl-quinoline (Harz, *B.* 18, 3391). Triclinic crystals. Easily soluble in chloroform, m. sol. ether.

Salts.—B'HCl×: easily soluble yellow crystals.—$B'_2H_2PtCl_6$2aq: short thick orange crystals, sol. hot water.

Nitro-(*B.* 2, 4; *Py.* 2)-tri-methyl-(*Py.* 3)-ethyl-quinoline $C_{14}H_{16}(NO_2)N$. [90°]. Formed by nitration of the base (*cf.* p. 326). Needles (from alcohol). It is accompanied by the *di-nitro- derivative* $C_{14}H_{15}(NO_2)_2N$ [152·5°] Waldbott, *B.* 23, 2272).

DI-NITRO-METHYLIC ACID (so-called) $CH_4N_2O_2$ *i.e.* $CH_3.NH.NO_2$? By passing NO into $ZnMe_2$ there is formed $CH_3(ZnMe)N_2O_2$, which is decomposed by water yielding $CH_3(ZnOH)N_2O_2$, whence CO_2 yields crystalline $(CH_3.N_2O_2)_2Zn$aq, which is converted, by adding Na_2CO_3 to its aqueous solution, into very soluble $CH_3NaN_2O_2$aq (Frankland, *C. J.* 11, 88).

DI-NITRO-METHYL-MESIDINE *Nitramine* $C_6Me_3(NO_2)_2NMe(NO_2)$. [138°]. Formed from $C_6Me_3H_2.NMe_2$, H_2SO_4, and HNO_3 (Klobbie, *R. T. C.* 6, 31). Crystals, sl. sol. ether.

NITRO-METHYL-NAPHTHALENE $C_{11}H_9NO_2$. [81°]. Formed, together with the di-nitro- derivative [206°], by nitration of (β)-methyl-naphthalene (Schulze, *B.* 17, 844). Thin yellowish needles.

DI-NITRO-(*Py.* 3)-METHYL-(β)-NAPHTHOQUINOLINE $C_{14}H_9(NO_2)_2N$. Four bodies of this constitution, melting at 227°, 230°, 205°–212°, and 250°, may be obtained, as well as a tetra-nitro- derivative [277°], by nitrating the (*Py.* 3)-methyl-(β)-naphthoquinoline which is formed by condensation of (β)-naphthylamine with paraldehyde (Seitz, *B.* 22, 256).

NITRO-DI-METHYL-PHENYL-ACETIC ACID [3:5:2:1] $C_6H_2(CH_3)_2(NO_2).CH_2.CO_2H$. *Nitro-mesityl-acetic acid.* [139°]. Formed by heating (5:3:1)-di-methyl-phenyl-acetic acid with dilute nitric acid (Wispek, *B.* 16, 1579). Long fine needles. Sol. alcohol, ether, and hot water, insol. cold water. On reduction it gives carbo-mesyl $(C_6H_2(CH_3)_2\Big\langle {}^{CH_2}_{NH} \Big\rangle CO)$.

Salts.—A'_2Ca4aq: thick needles.—A'_2Ba4½aq: fine needles.—A'Ag.

Di-nitro-methyl-phenyl-acetic acid *v.* DI-NITRO-TOLYL-ACETIC ACID.

(*B.* 4)-**NITRO-(*Py.* 3)-METHYL-QUINOLINE** $C_{10}H_8N_2O_2$ *i.e.* $\begin{matrix}\text{CH:CH. C.CH:CH}\\ \text{CH:CNO}_2\text{.C. N :CMe}\end{matrix}$ o-*Nitro-quinaldine.* [137°]. Formed, together with the isomeride [82°] by nitration of (*Py.* 3)-methyl-quinoline (Doebner a. Miller, *B.* 17, 1699; Gerdeissen, *B.* 22, 245). Formed also by the action of aldehyde on *m*-nitro-aniline. Long needles, sl. sol. cold water.—B'HCl: prisms.—$B'_2H_2PtCl_6$: small needles.

(*B.* 1 or 3)-**Nitro-(*Py.* 3)-methyl-quinoline** $C_9H_5Me(NO_2)N$. *m-Nitro-quinaldine.* Formed as above, and also by the action of aldehyde on *m*-nitro-aniline (D. a. M.). Slender needles, volatile with steam. — B'HCl : prisms. — $B'_2H_2PtCl_6$: needles.

(*B.* 1 or 3)-**Nitro-(*B.* 2)-methyl-quinoline.** [117°]. Formed by nitrating (*B.* 2)-methyl-quinoline (Noelting a. Trautmann, *B.* 23, 3655). Formed also from (2, 1, 4)-nitro-toluidine, glycerin, picric acid, and H_2SO_4. Needles. Yields a methylo-iodide. [190°].

(*B.* 4)-**Nitro-(*B.* 2)-methyl-quinoline** $\begin{matrix}\text{CMe:CH——C.CH:CH}\\ \text{CH :C(NO}_2\text{).C.N : CH}\end{matrix}$ [122°]. Formed from nitro-*p*-toluidine (N. a. T.). Yellow needles.

(*B.* 1)-**Nitro-(*B.* 4)-methyl-quinoline** $\begin{matrix}\text{CH:C(NO}_2\text{).C.CH:CH}\\ \text{CH:CMe .C.N :CH}\end{matrix}$ [93°]. Formed from (4, 2, 1)-nitro-o-toluidine and also by nitrating (*B.* 4)-methyl-quinoline.

Nitro-methyl-quinoline. [127°]. Got by nitrating lepidine (Busch a. Königs, *B.* 23, 2687).

Nitro-(*Py.* 3)-methyl-quinoline tetrahydride. *Nitroso-derivative* $C_{10}H_{11}(NO_2)N.NO$. [152°]. A product of the action of nitrous acid on (*Py.* 3)-methyl-quinoline tetrahydride (Möller, *A.* 242, 314). Golden plates (from alcohol-benzene).

Nitro-(*Py.* 4)-methyl-quinoline tetrahydride $C_6H_3(NO_2)<\begin{matrix}CH_2.CH_2\\ NMe.CH_2\end{matrix}$. *Nitro-kairoline.* [94°]. Formed by careful nitration of kairoline (Feer a. Königs, *B.* 18, 2390). Long red needles.

(*B.* 1)-**Nitro-(*B.* 2, 4)-di-methyl-quinoline** $\begin{matrix}\text{CMe:C(NO}_2\text{).C.CH:CH}\\ \text{CH :CMe .C.N :CH}\end{matrix}$ [108°]. Formed by nitrating di-methyl-quinoline, and also from nitro-*m*-xylidine [125°], glycerin, H_2SO_4, and picric acid (N. a. T.). Yellow needles.

Nitro-(*B.* 2, 4; *Py.* 3)-tri-methyl-quinoline $\begin{matrix}\text{CMe:CH. C.CH:CH}\\ \text{CH :CMeC.N :CMe}\end{matrix}$ [92°]. Formed by nitrating tri-methyl-quinoline (Panajotoff, *B.* 20, 35). Needles.—$B'_2H_2PtCl_6$3aq: crystalline.

Di-nitro-(*Py.* 4)-methyl-quinoline tetrahydride $C_6H_2(NO_2)_2<\begin{matrix}CH_2.CH_2\\ NMe.CH_2\end{matrix}$. *Di-nitro-kairoline.* [148°]. Formed from kairoline, HOAc, and HNO_3 (Feer a. Königs, *B.* 18, 2390). Golden-yellow plates, sol. alcohol.

DI-NITRO-DI-METHYL-SULPHAMIDE $C_2H_6N_4SO_6$ *i.e.* $SO_2(NMe.NO_2)_2$. [90°]. Formed from di-methyl-sulphamide and HNO_3 (Franchimont, *R. T. C.* 3, 419). Crystals (from benzene).

NITRO-METHYL-THIENYL METHYL KETONE $C_7H_7NSO_3$ *i.e.* $C_4MeH(NO_2)S.CO.CH_3$. [121°]. Obtained by nitrating $C_4MeH_2S.CO.CH_3$ (Demuth, *B.* 19, 1861). Needles (from ether).

NITRO-DI-METHYL-THIOPHENE $C_6H_7NSO_2$ *i.e.* $SC_4Me_2H(NO_2)$. *Nitro-thioxene.* Oil, formed from di-methyl-thiophene vapour, HOAc, and HNO_3 (Messinger, *B.* 18, 1638).

NITRO-METHYL-o-TOLUIDINE $C_8H_{10}N_2O_2$ *i.e.* $C_6H_3Me(NO_2).NHMe$ [2:4:1]. [134°]. Obtained by oxidation from nitroso-methyl-o-toluidine $C_6H_3Me(NO).NHMe$ (Kock, *A.* 243, 309). Greenish-yellow needles, sol. benzene.

Nitro-methyl-*p*-toluidine $C_6H_3Me(NO_2).NHMe$ [4:2:1]. [85°]. Formed from nitro-*p*-toluidine and MeI (Gattermann, *B.* 18, 1487; Niementowski, *B.* 20, 1874). Red needles (from alcohol) or tables (from benzene).

Acetyl derivative [64°]. (250–255° at 270 mm.). Plates.—$B'C_6H_2(NO_2)_3OH$. [212°].

Di-nitro-methyl-o-toluidine. *Nitro-derivative.* [2:4:6:1]$C_6H_2Me(NO_2)_2NMe.NO_2$. [120°]. Formed from di-methyl-o-toluidine and HNO_3 (Van Romburgh, *R. T. C.* 3, 395). Pale-yellow crystals. Potash converts it into methylamine and di-nitro-o-cresol.

Di-nitro-methyl-*p*-toluidine $C_6H_2Me(NO_2)_2NHMe$ [4:6:2:1]. [129°]. Obtained from $C_6H_4Me(NAcMe)$ and HNO_3 (A. L. Thomsen, *B.* 10, 1582; Gattermann, *B.* 18, 1487). Red needles (from dilute alcohol).

Nitrosamine $C_6H_2Me(NO_2)_2.NMe.NO$. [125°]. Yellow needles.

Nitro-derivative $C_6H_2Me(NO_2)_2.NMe.NO_2$. [139°]. Formed from di-methyl-*p*-toluidine (1 pt.), H_2SO_4 (2 pts.), and HNO_3 (10 pts.) (Van Romburgh, *R. T. C.* 3, 404). The same compound [130°] appears to be formed by the action of dilute HNO_3 on [1:4]$C_6H_4Me.NAcMe$ (Norton a. Livermore, *B.* 20, 2268). Nearly colourless crystals (from boiling alcohol). Yields di-nitro-*p*-cresol on boiling with potash.

Tri-nitro-methyl-*m*-toluidine. *Nitro-derivative* [3:6:4:2:1] $C_6HMe(NO_2)_3NMe.NO_2$. [102°]. Formed from di-methyl-*m*-toluidine and HNO_3 (S.G. 1·5) (Van Romburgh, *R. T. C.* 3, 413). Pale-yellow crystals.

Tri-nitro-methyl-*p*-toluidine $C_6HMe(NO_2)_3.NHMe$ [4:6:3:2:1]. [138°]. Formed by further nitration of nitro-methyl-*p*-toluidine (G.). Yellowish crystals.

Nitro-di-methyl-*m*-toluidine $C_6H_3Me(NO_2).NMe_2$. [84°]. Obtained by oxidising nitroso-di-methyl-*m*-toluidine with $KMnO_4$ (Wurster a. Riedel, *B.* 12, 1800). Yellow needles.

Di-nitro-di-methyl-*m*-toluidine $C_6H_2Me(NO_2)_2.NMe_2$. [107°]. Prepared by nitration of di-methyl-*m*-toluidine dissolved in HOAc (W. a. R.). Yellow needles.

Di-nitro-di-methyl-*m*-toluidine $C_6H_2Me(NO_2)_2.NMe_2$. [168°]. Formed from di-methyl-*m*-toluidine, HNO_3 and H_2SO_4 (W. a. R.). Less sol. alcohol than the isomeride [107°].

(α)-**NITRO-NAPHTHALENE** $C_{10}H_7NO_2$. Mol. w. 173. [56°] (Mills, *P. M.* [5] 14, 27); [61°] (D'Aguiar, *B.* 5, 370; Schiff). (304°) (De Coninck, *B.* 5, 12). S.V.S. 141 (Schiff, *A.* 223, 265). S.G. $\frac{4}{4}$ 1·331 (Schröder, *B.* 12, 1613). S. (88 p.c. alcohol) 2·8. Formed by nitration of naphthalene (Laurent, *A. Ch.* [2] 59, 378; Beilstein a. Kuhlberg, *A.* 169, 83; Guareschi, *B.* 10, 294). Formed also by elimination of NH_2 from (α)-nitro-(α)-naphthylamine (Liebermann, *A.* 183, 235).

Preparation.—By shaking naphthalene with nitric acid in the cold, and recrystallising from alcohol or ligroïn (B. a. K.; *cf.* Piria, *A.* 78, 32). Prepared also by stirring naphthalene (250 pts.)

with a mixture of HNO_3 (200 pts.) and H_2SO_4 (800 pts.) at 40°–50° (Witt, *Chem. Ind.* 10, 215).

Properties.—Pale-yellow prisms. A few milligrammes projected into a red-hot test-tube containing nitrogen detonates slightly with a white flame; a larger quantity gives a red flame; with a still larger quantity no flame is seen (Berthelot, *A. Ch.* [6] 16, 24).

Reactions.—1. Readily reduced to (α)-naphthylamine. Zinc-dust and HClAq yields chlorinated naphthylamines.—2. PCl_5 forms (α)-chloro-naphthalene.—3. *Chlorine* yields mono-, di-, tri-, and tetra-chloro-naphthalenes (Atterberg, *B.* 9, 316, 926).—4. *Bromine* forms bromo-nitro-naphthalene [122·5°], di-bromo-nitro-naphthalene [98°], and two tetrabromides.—5. HBrAq at 195° yields $C_{10}H_7Br$ and $C_{10}H_6Br_2$ (Baumhauer, *B.* 4, 926).—6. CrO_3 in HOAc forms *c*-nitro-phthalic acid (Beilstein a. Kurbatoff, *C. C.* 1881, 359).—7. Distillation over *zinc-dust* produces (αβ)-naphthazine (G. Schultz, *B.* 17, 478).

Tetrabromide $C_{10}H_7(NO_2)Br_4$. [131°]. S. (93·5 p.c. alcohol) ·26 at 15·2°. Formed from nitro-naphthalene and bromine (Guareschi, *A.* 222, 286). White needles. When kept at 137° in a current of air for some time it changes to an isomeride [143°] and $C_{10}H_6Br(NO_2)$ [122·5°]. When boiled with alcohol for a long time it changes to a second isomeride [173°], S. (93·5 p.c. alcohol) ·13 at 15·2°.

(β)-Nitro-naphthalene $C_{10}H_7NO_2$. [79°]. Formed by eliminating NH_2 from (2, 1)-nitro-(α)-naphthylamine (Lellmann, *B.* 19, 236; 20, 891). Formed also by the action of precipitated Cu_2O (2 mols.) upon a solution of (β)-diazo-naphthalene nitrite (1 mol.) obtained by adding a solution of 12 g. $NaNO_2$ in 40 g. water to a mixture of 7 g. of (β)-naphthylamine, 15 g. HNO_3, and 250 c.c. of water. The yield is small. (Sandmeyer, *B.* 20, 1496). Yellow needles, v. sol. alcohol. Volatile with steam. Reduced by zinc and HOAc to (β)-naphthylamine.

'α'-Di-nitro-naphthalene $C_{10}H_6(NO_2)_2$ [1:4']. Mol. w. 218. [212°]. Formed, together with the (1,1')-isomeride, by boiling naphthalene with fuming HNO_3 or by heating it with HNO_3 and H_2SO_4 at 100° (Darmstädter a. Wichelhaus, *B.* 5, 253; D'Aguiar, *B.* 5, 370; Beilstein a. Kurbatoff, *A.* 202, 219). Formed also by heating nitro-(α)-naphthoic acid [239°] with HNO_3 (S.G. 1·3) (Ekstrand, *B.* 18, 2881).

Properties.—Six-sided needles (from HOAc), v. sl. sol. HOAc. A few milligrammes thrown into a red-hot tube full of nitrogen detonate with reddish-white flame (Berthelot, *A. Ch.* [6] 16, 25).

Reactions.—1. *Oxidised* by HNO_3 (S.G. 1·15) at 150° to *c*-nitrophthalic, *s*-di-nitro-benzoic, and picric acids (Beilstein a. Kurbatoff, *Bl.* [2] 34, 327).—2. PCl_5 yields (γ)-di-chloro-naphthalene [107°].

'β'-Di-nitro-naphthalene $C_{10}H_6(NO_2)_2$ [1:1']. [172°]. S. (88 p.c. alcohol) ·187 at 19°. S. (benzene) ·72 at 19°. S. (chloroform) 1·1 at 19°. Formed, at the same time as the preceding, by nitrating naphthalene (Darmstädter a. Wichelhaus, *A.* 152, 301; Beilstein a. Kuhlberg, *A.* 169, 86). Formed also by heating nitro-(α)-naphthoic acid [215°] with HNO_3 (S.G. 1·3) (Ekstrand, *B.* 18, 2881), and by eliminating NH_2 from di-nitro-(β)-naphthylamine (Gaess, *J. pr.* [2] 43, 37). Tables, more soluble in HOAc, chloroform, benzene, and acetone than the (1,4')-isomeride.

Reactions.—1. Dilute HNO_3 at 150° yields di-nitro-phthalic acid [226°], *s*-di-nitro-benzoic acid, and picric acids.—2. PCl_5 forms ζ-di-chloro-naphthalene and δ-tri-chloro-naphthalene.

(γ)-Di-nitro-naphthalene $C_{10}H_6(NO_2)_2$[1:3']. [144°]. Obtained from di-nitro-(α)-naphthylamine [235°] by elimination of NH_2 (Liebermann a. Hammerschlag, *A.* 183, 272). Yellow needles.

(δ)-Di-nitro-naphthalene $C_{10}H_6(NO_2)_2$ [1:3' ?]. [162°]. Formed by eliminating NH_2 from di-nitro-(β)-naphthylamine [238°] (Graebe a. Drews, *B.* 17, 1172). Yellow needles, v. sol. alcohol.

'α'-Tri-nitro-naphthalene $C_{10}H_5(NO_2)_3$. Mol. w. 263. [122°]. Formed by further nitration of 'α'-di-nitro-naphthalene (D'Aguiar, *B.* 5, 372, 897). Monoclinic crystals, v. sol. HOAc.

'β'-Tri-nitro-naphthalene $C_{10}H_5(NO_2)_3$. [213°]. S. (88 p.c. alcohol) ·06 at 23°. Obtained by further nitration of 'β'-di-nitro-naphthalene (Laurent, *A.* 41, 98; D'Aguiar; Beilstein a. Kuhlberg, *A.* 169, 96). Formed also by eliminating NH_2 from tri-nitro-(α)- or (β)-naphthylamine (Staedel, *B.* 14, 901; *A.* 217, 174), and by the action of fuming HNO_3 and conc. H_2SO_4 on nitro-(α)-naphthoic acid (Ekstrand, *B.* 19, 1131). Prisms (from HOAc), v. sl. sol. HOAc and ether.

(γ)-Tri-nitro-naphthalene $C_{10}H_5(NO_2)_3$. [147°] (B. a. K.); [154°] (A.). S. (90 p.c. alcohol) ·11 at 18·5°. S. (ether) ·38. S. (benzene) 1·05 at 18·5°. Obtained by boiling 'α'-di-nitro-naphthalene for a few minutes with H_2SO_4 and fuming HNO_3 (Beilstein a. Kuhlberg, *B.* 6, 647). Yellow plates.

'α'-Tetra-nitro-naphthalene $C_{10}H_4(NO_2)_4$. [259°]. Formed by boiling 'α'-di-nitro-naphthalene with HNO_3 and H_2SO_4 for some hours (A.; B. a. K.). Crystals (from chloroform), almost insol. alcohol.

'β'-Tetra-nitro-naphthalene $C_{10}H_4(NO_2)_4$. [200°]. Formed by heating 'β'-di-nitro-naphthalene with fuming HNO_3 for 4 days at 100° (Lautemann a. D'Aguiar, *Bl.* 3, 261). Asbestos-like needles (from alcohol). Explodes when heated.

References.—Bromo-, Chloro-, and Iodo-, nitro-naphthalene.

NITRO-NAPHTHALENE DICARBOXYLIC ACID $C_{10}H_5(NO_2)(CO_2H)_2$. *Nitro-naphthalic acid.* Got by oxidising nitro-acenaphthene (Quincke, *B.* 21, 1454). Yellow needles. On heating it yields an anhydride [220°].—CaA″ aq.—$(NH_4)_2A''$ aq.

'α'-NITRO-NAPHTHALENE SULPHONIC ACID $C_{10}H_6(NO_2)(SO_3H)$ [1:4']. Formed from (α)-nitro-naphthalene and fuming H_2SO_4 or $ClSO_3H$ (Laurent, *C. R.* 31, 537; Armstrong a. Williamson, *C. J. Proc.* 2, 233; Erdmann, *A.* 247, 311). Formed also by nitrating naphthalene (α)-sulphonic acid (Cleve, *Bl.* [2] 24, 506). Straw-yellow prisms (containing 4aq), v. sol. water, sl. sol. dilute H_2SO_4. Tastes bitter. Its K salt distilled with $K_2Cr_2O_7$ and HCl gives chloro-nitro-naphthalene [111°] and di-chloro-nitro-naphthalene [85°]. Sodium-amalgam reduces it to (α)-naphthylamine and H_2SO_4 (Claus a. Graeff, *B.* 10, 1303).

Salts.—KA′ ½aq. S. 2·1 at 15°.—NH_4A′ 1½aq. —NaA′ ½aq.—MgA'_2 3aq.—CaA'_2 2aq.—BaA'_2 3aq.

— ZnA'_2 6aq. — PbA'_2 3aq. — MnA'_2 2aq. — CuA'_2 4aq.—AgA′: monoclinic prisms.

Ethyl ether EtA′. [101°].

Chloride $C_{10}H_6(NO_2)(SO_2Cl)$. [113°].

Amide $C_{10}H_6(NO_2)(SO_2NH_2)$. [225°].

Nitro-naphthalene-'β'-sulphonic acid $C_{10}H_6(NO_2)(SO_3H)$[1:3′]. Formed, together with two or more isomerides, by nitration of naphthalene (β)-sulphonic acid (Cleve, *Bl.* [2] 26, 444), and, together with a larger quantity of the 'α'-acid and some of the θ-acid by heating nitro-naphthalene with H_2SO_4 containing excess of SO_3 at 100° (Palmaer, *B.* 21, 3260). Yields $C_{10}H_6Cl_2$ [48°].

Salts.—KA′.—NH_4A'.—NaA′3aq.—BaA'_2 aq. S. ·115 at 22°.—MgA'_2 7aq.—CaA'_2 aq.—ZnA'_2 6aq. —PbA'_2 3aq.—MnA'_2 6aq.—CuA'_2 6aq.—AgA′.

Ethyl ether EtA′. [115°].

Chloride $C_{10}H_6(NO_2).SO_2Cl$. [126°]. Monoclinic crystals; $a:b:c = ·996:1:·831$; $\beta = 81° 28'$.

Amide. [184°]. Yellowish needles.

(γ)-Nitro-naphthalene sulphonic acid $C_{10}H_6(NO_2)(SO_3H)$[1:3]. Formed, together with the 'β' and (θ)-isomerides, by nitration of naphthalene (β)-sulphonic acid (Cleve, *B.* 19, 2170). Its chloride on heating with PCl_5 yields $C_{10}H_6Cl_2$ [61°].—KA′.—NaA′.—BaA'_2 3aq.—PbA'_2 3aq.

Ethyl ether EtA′. [115°].

Chloride $C_{10}H_6(NO_2).SO_2Cl$. [140°].

Amide [225°]. Long needles.

(θ)-Nitro-naphthalene sulphonic acid $C_{10}H_6(NO_2)(SO_3H)$ [1:2′]. The Ba salt is the most soluble of the Ba salts of the acids obtained by nitration of naphthalene (β)-sulphonic acid (Cleve, *Bl.* [2] 29, 415; *B.* 21, 3264). Occurs also among the products of sulphonation of (α)-nitro-naphthalene (Palmaer). Its chloride, heated with PCl_5, yields $C_{10}H_6Cl_2$ [62°].—KA′½aq. —NaA′½aq.—NH_4A'.—BaA'_2 3aq. S. (of BaA'_2) 11 at 100°; ·2 at 17°.—CaA'_2 2aq.—MgA'_2 9aq.— PbA'_2 3aq. — MnA'_2 10aq. — CuA'_2 8aq. — ZnA'_2 10aq.—AgA′.

Ethyl ether EtA′. [107°]. Needles.

Chloride [167°]. Yellow needles.

Amide [223°]. Needles.

Nitro-naphthalene sulphonic acid $C_{10}H_6(NO_2)(SO_3H)$[1:4]. Formed, together with the (1:1′) and 1:4′) isomerides by nitration of naphthalene (α)-sulphonic acid; the acids being separated by crystallisation of their chlorides from benzene (Cleve, *B.* 23, 958). Yellowish crystalline mass.—KA′.—NaA′aq.—CaA'_2 2aq. S. 2·7 at 17°; 7 at 100°.—BaA'_2 aq. S. 1·5 in the cold; 3 at 100°.—PbA'_2 6aq.—AgA′: needles.

Methyl ether MeA′. [117°].

Ethyl ether EtA′. [93°].

Chloride $C_{10}H_6(NO_2)SO_2Cl$. [99°].

Amide [188°]. Octahedra.

Nitro-naphthalene sulphonic acid $C_{10}H_6(NO_2)(SO_3H)$ [1:1′]. A product of the nitration of naphthalene (α)-sulphonic acid (Cleve, *B.* 23, 962).

Chloride [101°].

'α'-Nitro-naphthalene disulphonic acid $C_{10}H_5(NO_2)(SO_3H)_2$[4:2:2′]. Obtained from its chloride, which is formed by nitrating naphthalene 'α'-disulphonic chloride $C_{10}H_6(SO_2Cl)_2$ (Alén, *Bl.* [2] 39, 63; *Bn.* 2, 156). Needles, v. e. sol. water.—Na_2A''6aq.—K_2A''3aq.—CaA″5aq. —BaA″5aq.—PbA″4aq.—Ag_2A''3aq.

Chloride $C_{10}H_5(NO_2)(SO_2Cl)_2$. [141°]. With PCl_5 it yields θ-tri-chloro-naphthalene.

Amide. [287°].

'β'-Nitro-naphthalene disulphonic acid $C_{10}H_5(NO_2)(SO_3H)_2$[1:3:2′]. Formed by nitrating naphthalene 'β'-disulphonic acid (Alén). Scales. —Na_2A''2aq.—K_2A''.—CaA″2aq.—BaA″2aq.— PbA″2aq.—Ag_2A''2aq.

Chloride $C_{10}H_5(NO_2)(SO_2Cl)_2$. [186°]. With PCl_5 it gives (γ)-tri-chloro-naphthalene.

Amide [above 300°]. Needles.

Di-nitro-naphthalene 'α'-disulphonic acid $C_{10}H_4(NO_2)_2(SO_3H)_2$. Obtained from its chloride which is formed by nitrating naphthalene 'α'-disulphonic acid (Alén).—K_2A''.—K_2A''4aq. —BaA″5aq.—Ag_2A'' aq.

Chloride [219°]. Needles (from benzene).

Amide $C_{10}H_4(NO_2)_2(SO_2NH_2)_2$. [c. 306°].

***Peri*-NITRO-(α)-NAPHTHOIC ACID** $C_{10}H_6(NO_2)(CO_2H)$[1:1′]. [215°]. S. ·04 in the cold. S. (alcohol) 5. Formed, together with the (1,4′)-isomeride by nitrating (α)-napthtoic acid (Küchenmeister, *B.* 3, 739; Ekstrand, *B.* 12, 1393; 18, 73, 2881; 19, 1138; *J. pr.* [2] 38, 156, 276). Prisms, v. sol. alcohol. Yields on nitration di-nitro-naphthalene [170°].

Salts.—NaA′.—CaA'_2 3aq. S. 2 at 15°.— BaA'_2 6aq.—PbA'_2 aq: yellow prisms.

Ethyl ether EtA′. [69°]. Octahedra.

Amide $C_{10}H_6(NO_2)(CONH_2)$. [280°]. Needles, converted by conc. HClAq at 170 into $C_{10}H_4Cl_2<\begin{smallmatrix}NH\\CO\end{smallmatrix}>$ [261°].

Nitro-(α)-naphthoic acid $C_{10}H_6(NO_2)(CO_2H)$[1:4′]. [239°]. S. ·02 at 15°. S. (alcohol) ·5 at 15°. Formed as above, and also by saponifying its nitrile which is obtained by nitrating the nitrile of (α)-naphthoic acid (Graeff, *B.* 14, 1063; 16, 2250; Ekstrand, *J. pr.* [2] 38, 241). Needles. HNO_3 (S.G. 1·3) converts it into di-nitro-naphthalene [212°].—NaA′5aq. —CaA'_2 2aq. S. ·63 at 15°.—BaA'_2 3½aq: yellow needles.—PbA'_2 5½aq.

Methyl ether MeA′. [110°].

Ethyl ether EtA′. [93°].

Isopropyl ether PrA′. [101°].

Nitrile $C_{10}H_6(NO_2)CN$. [205°].

(γ)-Nitro-(α)-naphthoic acid [255°]. Formed by heating its nitrile with HClAq at 160° (Graeff, *B.* 16, 2252). Needles (by sublimation).

Nitrile [153°]. Formed, together with the isomeride [205°] by nitrating (α)-naphthonitrile.

'α'-Nitro-(β)-naphthoic acid [220°]. Formed, as well as the four following acids, by nitration of (β)-naphthoic acid (Ekstrand, *B.* 12, 1325). Needles.—CaA'_2. S. ·26 at 15°.

Ethyl ether EtA′. [82°]. Needles.

'β'-Nitro-(β)-naphthoic acid $C_{10}H_6(NO_2)(CO_2H)$[1′or4′:2]. [293°]. Formed as above (Ekstrand, *B.* 18, 1207; *J. pr.* [2] 42, 375). Obtained also by saponifying its nitrile (Graeff, *B.* 16, 2252). Needles, m. sol. hot alcohol.—KA′aq.—NaA′2aq.—CaA'_2 3aq. S. ·12 at 15°.—BaA'_2 4aq.

Methyl ether MeA′. [112°]. Needles.

Ethyl ether EtA′. [109°]. Needles.

Isopropyl ether PrA′. [76°]. Needles.

Nitrile $C_{10}H_6(NO_2)CN$. [173°]. Formed by nitration of (β)-naphthoic nitrile. Needles.

(γ)-Nitro-(β)-naphthoic acid [269°]. Formed as above. Needles, v. sol. alcohol.

Ethyl ether EtA′. [93°].

(δ)-Nitro-(β)-naphthoic acid $C_{10}H_6(NO_2)(CO_2H)$ [4′or1′:2]. [288°]. S. (alcohol) ·25 in the cold. Formed as above (Ekstrand, *J. pr.* [2] 42, 292). Needles. Yields di-nitro-naphthoic acid [226°] with fuming HNO_3. —NH_4A'.—NaA′ 2aq.—BaA'_2 8aq.—CaA'_2 4½aq. S. ·15 in the cold.

Ethyl ether EtA′. [121°]. Plates.

(ε)-Nitro-(β)-naphthoic acid. [285°]. One of the products of the action of HNO_3 (S.G. 1·42) on (β)-naphthoic acid (Ekstrand, *J. pr.* [2] 42, 304). Stellate needles (from alcohol).

Ethyl ether EtA′. [75°]. Needles.

Di-nitro-(α)-naphthoic acid $C_{10}H_5(NO_2)_2CO_2H$ [4:4′:1]. [265°]. Obtained by nitration of (α)-naphthoic acid and of (1,4′)-nitro-naphthoic acid (Ekstrand, *B.* 17, 1600; 19, 1984; 20, 219, 1353; *J. pr.* [2], 38, 259). Prisms or needles (from alcohol). Reduced by tin and HClAq to naphthylene-diamine [65°]. H_2S in alkaline solution forms $C_{10}H_5N_2.CO_2H$ (?), a bluish-violet pp.—NaA′ 6aq.—BaA'_2 2½aq.—CaA'_2 3aq: needles. S. ·7 in the cold.

Ethyl ether EtA′. [143°]. Needles.

Di-nitro-(α)-naphthoic acid $C_{10}H_5(NO_2)_2CO_2H$. [215°]. Formed, together with the preceding acid, by nitrating (α)-naphthoic acid (Ekstrand, *B.* 19, 1984; *J. pr.* [2] 38, 270). Needles or plates (from alcohol). Yields nitro-amido-naphthoic acid [c. 110°] on reduction by H_2S and NH_3.—CaA'_2.

Ethyl ether EtA′. [137°]. Needles.

Di-nitro-(α)-naphthoic acid $C_{10}H_5(NO_2)_2CO_2H$ [4′:1′:1]. [218°]. Formed by nitrating nitro-(α)-naphthoic acid [239°], and occurs among the products of the action of fuming HNO_3 on (α)-naphthoic acid (Ekstrand, *B.* 20, 220; *J. pr.* [2] 38, 267). Trimetric crystals (from alcohol); $a:b:c = \cdot973:1:1\cdot442$. Yields a lactam of di-amido-naphthoic acid on reduction. —CaA'_2 7aq: yellow needles, v. e. sol. water.

Ethyl ether EtA′. [129°]. Needles.

Di-nitro-(β)-naphthoic acid $C_{10}H_5(NO_2)_2CO_2H$. [226°]. S. (alcohol) 1·7 in the cold. Formed, together with the isomeride [148°] by dissolving (β)-naphthoic acid in fuming HNO_3. Formed also, in like manner, from nitro-(β)-naphthoic acid [288°] (Ekstrand, *B.* 17, 1602; *J. pr.* [2] 42, 300). Needles (from alcohol). Yields by reduction nitro-amido-naphthoic acid [235°] and di-amido-naphthoic acid [c. 230°].—NH_4A' aq. S. ·35 in the cold.—BaA'_2 6aq. —CaA'_2 4aq. S. ·06 in the cold.

Ethyl ether EtA′. [141°]. Needles.

Di-nitro-(β)-naphthoic acid $C_{10}H_5(NO_2)_2CO_2H$ [1:1′:2] or [4:4′:2]. [248°]. S. (alcohol) 1·6 in the cold. Formed as above, and also by nitrating nitro-(β)-naphthoic acid [293°] (Ekstrand, *B.* 17, 1602; *J. pr.* [2] 42, 286). Rectangular prisms. Reduced by $FeSO_4$ and NH_3 to di-amido-naphthoic acid [202°].—NH_4A' aq.—NaA′ 4aq.—BaA'_2 8aq.—CaA'_2 5aq.

Ethyl ether EtA′. [165°].

Tri-nitro-(α)-naphthoic acid $C_{10}H_4(NO_2)_3CO_2H$. [283°]. Formed in small quantity by the action of H_2SO_4 and HNO_3 on nitro-(α)-naphthoic acid [215°] (Ekstrand, *B.* 19, 1131; *J. pr.* [2] 38, 372). Wedge-shaped needles (from alcohol). Tastes very bitter.—CaA'_2 5aq.

Ethyl ether EtA′. [131°]. Prisms.

Tri-nitro-(α)-naphthoic acid $C_{10}H_4(NO_2)_3CO_2H$. [236°]. Formed from di-nitro-(α)-naphthoic acid [265°], H_2SO_4, and fuming HNO_3 (Ekstrand, *B.* 19, 1987). Needles.

Ethyl ether EtA′. [191°]. Needles.

Tri-nitro-(α)-naphthoic acid $C_{10}H_4(NO_2)_3CO_2H$. [293°]. A product of nitration of di-nitro-(α)-naphthoic acid [265°] (E.). Cubes, sl. sol. alcohol.

Ethyl ether EtA′. [150°]. Needles.

NITRO-(α)-NAPHTHOL $C_{10}H_6(NO_2)(OH)$ [2:1]. [128°]. Formed, together with the isomeride [164°], from acetyl- or benzoyl-naphthylamine by nitrating and boiling the product with NaOHAq (Andreoni a. Biedermann, *B.* 6, 342; Liebermann a. Dittler, *A.* 183, 245; Worms, *B.* 15, 1815; Lellmann, *B.* 19, 802). Obtained also by oxidising (β)-naphthoquinone (β)-oxim (Fuchs, *B.* 8, 629); and by the action of nitrous acid on (α)-naphthylamine at 100° (Deninger, *J. pr.* [2] 40, 300). Yellow needles, sl. sol. water, m. sol. alcohol; volatile with steam.—KA′ aq.—BaA'_2 3aq: red needles.

Nitro-(α)-naphthol $C_{10}H_6(NO_2)(OH)$ [4:1]. [164°]. Formed as above, and also by the action of (nascent) nitrous acid on (α)-naphthylamine in the cold (Deninger, *J. pr.* [2] 40, 300). Golden needles (from water), not volatile with steam; v. e. sol. alcohol. Yields di-nitro-naphthol [138°] on nitration. By successive reduction and oxidation it may be converted into (α)-naphthoquinone.—KA′.—NaA'_2 2aq: crimson needles, bluish-red when anhydrous.—BaA'_2 aq. —BaA'_2 3aq (Hübner, *A.* 208, 325).—CaA'_2 3aq. —PbA'_2: scarlet powder.—AgA′.

Nitro-(β)-naphthol. *Ethyl ether* $C_{10}H_6(NO_2)(OEt)$ [1:2′]. [73°]. Formed, together with the ethyl ethers of the two following isomerides, by nitrating $C_{10}H_7(OEt)$ dissolved in HOAc (Gaess, *J. pr.* [2] 43, 25). Needles.

Nitro-(β)-naphthol. *Ethyl ether* $C_{10}H_6(NO_2)(OEt)$ [2:2′]. [114°]. Needles. Yields on oxidation nitrophthalic acid [114°].

Nitro-(β)-naphthol $C_{10}H_6(NO_2)(OH)$ [1:2]. [103°]. Formed by oxidising the (α)-oxim of (β)-naphthoquinone (Stenhouse a. Groves, *C. J.* 32, 51), or by boiling the acetyl derivative of nitro-(β)-naphthylamine with NaOHAq (Liebermann a. Jacobson, *A.* 211, 46). Formed also by the action of (nascent) nitrous acid on (β)-naphthylamine (D.). Needles. By reduction followed by oxidation it may be converted into (β)-naphthoquinone.

Acetyl derivative $C_{10}H_6(NO_2)(OAc)$. [61°]. Yields $C_{10}H_6(NHAc)(OH)$ on reduction by zinc-dust and HOAc (Böttcher, *B.* 16, 1933).

Benzoyl derivative $C_{10}H_6(NO_2)(OBz)$. [142°]. Yields $C_{10}H_6(NHBz)(OH)$ on reduction.

Ethyl ether EtA′. [104°]. Yellow needles (Wittkamp, *B.* 17, 393; Gaess, *J. pr.* [2] 43, 22).

Di-nitro-(α)-naphthol $C_{10}H_5(NO_2)_2(OH)$[4:2:1]. *Martius yellow.* [138°]. Formed by the action of HNO_3 on (α)-naphthol, (α)-naphthol sulphonic acid, and (2,1)- or (4,1)-nitro-naphthol (Martius, *Z.* [2] 4, 80; Darmstädter a. Wichelhaus, *A.* 152, 299; Liebermann, *A.* 183, 249). Formed also by boiling diazonaphthalene chloride or sulphonate with dilute nitric acid (Martius; Nevile a. Winther, *C. J.* 37, 632). Sulphur-yellow crystals, nearly insol. boiling water, sl. sol. alcohol. Not volatile with steam.

Yields phthalic acid on oxidation. Its salts dye wool yellow. Poisonous: ·4 g. killed a dog (Weyl, *B.* 21, 2191).—NH_4A' aq.—Na_2A'' aq.—CaA'_2 6aq.—SrA'_2 3aq.—BaA'_2 3aq.—AgA'.

Ethyl ether EtA'. [88°]. Needles.

Di-nitro-(β)-naphthol $C_{10}H_5(NO_2)_2(OH)$ [1:2':2]. [194°]. Formed by heating (β)-naphthol with alcohol and HNO_3 (Wallach a. Wichelhaus, *B.* 3, 846). Prepared by boiling a solution of (β)-diazonaphthalene chloride with HNO_3 (Graebe a. Drews, *B.* 17, 1170). Yellow needles. Dyes deep yellow. On oxidation it yields nitro-phthalic acid [160°].—KA'2aq: yellow needles.—$Ba'A_2$ aq (Löwe, *B.* 23, 2542).—AgA': scarlet pp.

Ethyl ether EtA'. [138°] (Graebe); [144°] (Gaess). Formed by nitrating the compounds $C_{10}H_6(NO_2)(OEt)$ [114°] and [104°]. Yellow needles. Converted by NH_3 into di-nitro-naphthylamine [238°].

Di-nitro-(β)-naphthol $C_{10}H_5(NO_2)_2(OH)$ [1:1':2']. [198°]. Formed from its ether by saponifying with alcoholic potash (Gaess). Plates. Yields nitrophthalic acid [212° or 218°] on oxidation.

Ethyl ether EtA'. [215°]. Obtained by nitrating $C_{10}H_6(NO_2)(OEt)$ [1:2] (Gaess), and also from the [1:2'] isomeride. Needles. Possibly identical with the following isomeride.

Di-nitro-(β)-naphthol $C_{10}H_5(NO_2)_2(OH)$[4':1':2].

Ethyl ether EtA'. [215°]. Formed by nitrating $S(C_{10}H_6.OEt)_2$ (Onufrovitch, *B.* 23, 3356). Orange needles. Yields (6, 3, 2, 1)-di-nitro-phthalic acid on oxidation.

Tri-nitro-(α)-naphthol $C_{10}H_4(NO_2)_3(OH)$. [176°]. S. ·28 at 15°. Formed from di-nitro-(α)-naphthol, H_2SO_4, and HNO_3 (Ekstrand, *B.* 11, 161; Diehl a. Merz, *B.* 11, 1662). Small crystals. Yields di-nitro-phthalic acid [213°] on oxidation.—KA' aq. S. ·25 in the cold.—NaA' aq. S. 3 in the cold.—NH_4A'. S. ·15 in the cold.—BaA'_2 2½aq. S. ·09.—CaA'_2 3½aq. S. ·4.—AgA'.

Methyl ether MeA'. [128°]. Got by nitrating $C_{10}H_7OMe$ (Staedel, *B.* 14, 899; *A.* 217, 172). Yellow plates.

Ethyl ether EtA'. [148°].

Tri-nitro-(β)-naphthol $C_{10}H_4(NO_2)_3OH$.

Methyl ether MeA'. [213°]. Got by nitrating $C_{10}H_7OMe$ (Staedel).

Ethyl ether EtA'. [186°].

Tetra-nitro-(α)-naphthol $C_{10}H_3(NO_2)_4OH$. [180°]. S. (benzene) ·45 at 18°. Formed by boiling $C_{10}H_3Br(NO_2)_4$ [170·5°] with Na_2CO_3Aq (Merz a. Weith, *B.* 15, 2714). Yields di-nitro-phthalic acid [227°] on oxidation.—NaA' 2aq. S. ·1 at 19°.—CaA'_2 2aq.—BaA'_2 3aq.—AgA' 3aq: red needles.

DI-NITRO-(α)-NAPHTHOL SULPHONIC ACID $C_{10}H_6N_2SO_8$ *i.e.* $C_6H_3(SO_3H){<}\begin{matrix}C(OH):C(NO_2)\\C(NO_2):CH\end{matrix}$. *Naphthol yellow S.* Formed by warming (α)-naphthol trisulphonic acid with dilute nitric acid at 50° (Lauterbach, *B.* 14, 2028). Obtained also from mono- or di-sulphonic acids of (α)-naphthol in which one SO_3H is in a different ring to the hydroxyl. Long yellow needles. Very powerful dye, producing a very fast greenish-yellow shade.—K_2A'': v. sl. sol. cold water. Not poisonous (Weyl, *B.* 21, 2191).

Di-nitro-(α)-naphthol sulphonic acid $C_{10}H_4(NO_2)_2(OH)(SO_3H)$[4':x:2:4]. *Croceïn-yellow.* Formed by warming (β)-naphthol (α)-sulphonic acid with dilute HNO_3 (Nietzki a. Zübelen, *B.* 22, 454).—KA': golden scales.

NITRO-(β)-NAPHTHOQUINONE $C_{10}H_5(NO_2)O_2$. [158°]. Formed by nitrating (β)-naphthoquinone (Stenhouse a. Groves, *A.* 194, 203; *C. J.* 33, 416; 45, 299). Crimson plates (from HOAc), sl. sol. ether and water. With alcoholic aniline it forms the compound $C_{10}H_4(NO_2)(OH){<}\begin{matrix}O\\NPh\end{matrix}$ [253°] (Korn, *B.* 17, 908). *p*-Bromo-aniline forms the corresponding body $C_{10}H_4(NO_2)(OH){<}\begin{matrix}O\\N.C_6H_4Br\end{matrix}$ [245°] (Brauns, *B.* 17, 1133). The corresponding *o*-toluide melts at 240°, the *p*-toluide at 241°. Excess of aniline in benzene forms yellow needles of $C_{16}H_{14}N_2O_4$. [186°]. Hydroxylamine hydrochloride in presence of HOAc forms a salt $C_{10}H_5NO_4(NH_2OH)$ [141°], which on boiling with HOAc yields nitro-hydro-(β)-naphthoquinone (Zaertling, *B.* 23, 179).

Nitro-(γ)-naphthoquinone. [208°]. Formed by oxidising nitro-acenaphthene (Quincke, *B.* 21, 1460). Yellowish-red needles, yielding with aniline $C_{10}H_4O_2(NO_2)(NHPh)$ [1[illegible]8[illegible]]; and, with diphenylamine, $C_{10}H_4O_2(NO_2)(NPh_2)$.

NITRO-(αα)-DINAPHTHYL $C_{10}H_7.C_{10}H_6NO_2$. [188°]. Formed from dinaphthyl, HNO_3, and HOAc (Julius, *B.* 19, 2549). Orange plates.

Di-nitro-dinaphthyl $C_{10}H_6(NO_2).C_{10}H_6(NO_2)$. [280°]. Formed by nitrating dinaphthyl (J.). Yellow needles, insol. alcohol, v. sl. sol. C_6H_6.

Tetra-nitro-dinaphthyl $C_{20}H_{10}(NO_2)_4$. Formed from dinaphthyl and fuming HNO_3 (Lossen, *A.* 144, 77). Amorphous orange powder.

Tetra-nitro-(ββ)-dinaphthyl. [150°]. Formed from isodinaphthyl and HNO_3 (Staub a. Watson Smith, *C. J.* 47, 104). Amorphous yellow powder.

NITRO-(α)-NAPHTHYL-AMIDO-BENZOIC ACID $C_{10}H_7NH.C_6H_3(NO_2).CO_2H$[4:3:1]. Formed by heating (α)-naphthylamine with bromo-nitro-benzoic acid (Heidenleben, *B.* 23, 3458). Yields on reduction the amido- acid [90°].—NaA': reddish-brown powder.

Ethyl ether EtA'. [109°].

Nitro-(β)-naphthyl-amido-benzoic acid. Formed in like manner from (β)-naphthylamine (H.). Brick-red crystals, insol. water.—NaA'.

Ethyl ether EtA'. [127·5°].

NITRO-(α)-NAPHTHYLAMINE $C_{10}H_6(NO_2)(NH_2)$[2:1]. [144°]. Formed by saponifying its acetyl derivative, which is produced, together with that of the (4, 1)-isomeride [190°], by nitrating the acetyl derivative of (α)-naphthylamine (Lellmann a. Remy, *B.* 17, 109; 19, 236, 796). Red monoclinic prisms (from alcohol). Converted by boiling alcoholic potash into nitro-naphthol [128°].

Acetyl derivative $C_{10}H_6(NO_2)(NHAc)$. [199°]. With 1 mol. of the (4, 1)-isomeride it forms a compound [170°].

Di-acetyl derivative $C_{10}H_6(NO_2)(NAc_2)$. [115°]. Got by using Ac_2O at 140°.

Benzoyl derivative $C_{10}H_6(NO_2)(NHBz)$. [175°] (Worms, *B.* 15, 1814). Yields benzenyl-

naphthylene-diamine [210°] on reduction with tin and HCl (Hübner, *A.* 208, 324).

Nitro-(α)-naphthylamine $C_{10}H_6(NO_2)(NH_2)$[4:1]. [190°]. Formed as above (Liebermann, *A.* 183, 232; L. a. R.). Orange needles (from alcohol). Yields naphthylene-diamine [186°] on reduction.

Acetyl derivative [190°].

Di-acetyl derivative [144°].

Benzoyl derivative [224°]. Yields nitro-naphthol [164°] on boiling with potash.

Nitro-(α)-naphthylamine $C_{10}H_6(NO_2)(NH_2)$ [4':1]. [119°]. Formed by reduction of 'α'-di-nitro-naphthalene with alcoholic NH_3 and H_2S (Beilstein a. Kuhlberg, *A.* 169, 81). Small red needles (from water). On elimination of NH_2 it yields (α)-nitro-naphthalene.—$B'_2H_2SO_4$ 2aq: needles, sl. sol. cold water.

Sulphonic acid $C_{10}H_5(NO_2)(NH_2)(SO_3H)$ [4':1:4]. Formed from (1, 4)-naphthylamine sulphonic acid by acetylation, nitration, and subsequent saponification (Nietzki a. Zübelen, *B.* 22, 451). Colourless needles. Potash yields nitro-naphthylamine.

Nitro-(β)-naphthylamine $C_{10}H_6(NO_2)(NH_2)$[1:2]. [127°] (L. a. J.); [124°] (Meldola, *C. J.* 47, 520). Formed by saponifying its acetyl derivative, which is obtained by nitrating the acetyl derivative of (β)-naphthylamine (Liebermann a. Jacobson, *B.* 14, 806, 1792; *A.* 211, 42). Orange needles, sol. hot water.

Acetyl derivative $C_{10}H_6(NO_2)(NHAc)$. [124°]. Reduced by tin and HOAc to ethenyl-(αβ)-naphthylene-diamine (Fischer a. Hepp, *B.* 20, 2473).

Di-nitro-(α)-naphthylamine $C_{10}H_5(NO_2)_2(NH_2)$. [4:2:1] [239°] (Witt, *B.* 19, 2032). Obtained from its acetyl derivative, which is formed by nitrating $C_{10}H_7NHAc$. The saponification is effected by alcoholic NH_3 or by H_2SO_4 (Liebermann, *A.* 183, 274; Meldola, *B.* 19, 2683). Formed also by heating di-nitro-(α)-naphthol with alcoholic NH_3 (Witt). Lemon-yellow needles. Readily converted by potash into di-nitro-α-naphthol. On elimination of NH_2, it yields di-nitro-naphthalene [144°].

Acetyl derivative [250·5°] (Ebell, *A.* 208, 330); [247°] (L.). Needles.

Benzoyl derivative [252°]. Needles.

Di-nitro-(β)-naphthylamine $C_{10}H_5(NO_2)_2(NH_2)$. [242°]. Formed by heating $C_{10}H_5(NO_2)_2(OEt)$ [144°] with aqueous NH_3 at 140° (Graebe a. Drews, *B.* 17, 1172; Gaess, *J. pr.* [2] 43, 31). On elimination of NH_2 it yields di-nitro-naphthalene [161·5°] or [167°]. Two isomeric compounds $C_{10}H_5(NO_2)_2NHAc$ [185°] and [235°] are got by nitrating acetyl-(β)-naphthylamine (Maschke, *C. C.* 1886, 824).

Di-nitro-(β)-naphthylamine $C_{10}H_5(NO_2)_2(NH_2)$ [1:1':2']. [223°]. Formed from $C_{10}H_5(NO_2)_2(OEt)$ [215°] (Gaess). Yields di-nitro-naphthalene [172°].

Di-nitro-naphthylamine obtained from the $C_{10}H_5(NO_2)_2(OEt)$ [215°] of Onufrovitch (*B.* 23, 3362) carbonises at 235°–250°.

Tri-nitro-(α)-naphthylamine $C_{10}H_4(NO_2)_3(NH_2)$. [c. 264°]. Formed from $C_{10}H_4(NO_2)_3.OEt$ and alcoholic NH_3 at 50° (Staedel, *B.* 14, 901; *A.* 217, 173). Yellow prisms (from toluene). On elimination of NH_2 it yields tri-nitro-naphthalene [181°].

Tri-nitro-(β)-naphthylamine. Formed from $C_{10}H_4(NO_2)_3.OEt$ and NH_3 (S.). Yellow needles. Yields tri-nitro-naphthalene [181°] on elimination of NH_2.

Tetra-nitro-(α)-naphthylamine $C_{10}H_3(NO_2)_4NH_2$. [194°]. Formed from $C_{10}H_3Br(NO_2)_4$ and NH_3 (Merz a. Weith, *B.* 15, 2718). Yellow needles, sl. sol. alcohol.

Tetra-nitro-(β)-naphthylamine [202°]. Formed from (β)-bromo-tetra-nitro-naphthalene and NH_3 (M. a. W.). Yellow needles.

Nitro-di-(β)-naphthyl-amine. *Benzoyl derivative* $C_{10}H_7.NBz.C_{10}H_6NO_2$. [168°]. Got by nitrating $(C_{10}H_7)_2NBz$ (Ris, *B.* 20, 2625). Nodules (from alcohol) or prisms (containing C_6H_6) [95°] (from benzene). Yields, on reduction, benzenyl-naphthylene-naphthyl-diamine [163°].

Di-nitro-di-(β)-naphthyl-amine $C_{20}H_{12}(NO_2)_2NH$. [225°]. Formed from di-(β) naphthyl-amine, HOAc, and HNO_3 (Ris a. Weber, *B.* 17, 197).

Tetra-nitro-di-(β)-naphthyl-amine $C_{20}H_{10}(NO_2)_4NH$. [286°]. Formed by mixing di-(β)-naphthylamine, HOAc, and HNO_3 without cooling (R. a. W.). Granules. On further nitration it yields hexa-nitro-di-naphthyl-amine.

NITRO-NAPHTHYLENE-DIAMINE. *Di-acetyl derivative.* $C_{10}H_5(NO_2)(NHAc)_2$[2:4:1]. [c. 295°]. Formed by nitrating $C_{10}H_6(NHAc)_2$ (Kleemann, *B.* 19, 335). Yellow needles, yielding phthalic acid on oxidation.

DINITRO-(α)-DINAPHTHYLENE-OXIDE $C_{20}H_{10}(NO_2)_2O$. [270°]. Prepared by nitration of (α)-dinaphthylene-oxide (Knecht a. Unzeitig, *B.* 13, 1725). Yellow needles.

Dinitro-(β)-dinaphthylene-oxide $C_{20}H_{10}(NO_2)_2O$. [221°]. Prepared by nitration of (β)-dinaphthylene-oxide (K. a. U.). Orange-red needles.

TETRA-NITRO-DI-NAPHTHYL-METHANE $CH_2\{C_{10}H_5(NO_2)_2\}_2$. Formed from di-(α)-naphthyl-methane and HNO_3 (Grabowski, *B.* 7, 1605). Colourless crystals, decomposing at 260°–270°.

NITRO-(α)-NAPHTHYL-PIPERIDINE $C_{10}H_6(NO_2)NC_5H_{10}$. [77°]. Formed by heating (1, 4)-bromo-nitro-naphthalene with piperidine (Lellmann a. Büttner, *B.* 23, 1387). Yellow needles. Weak base.

DI-NITRO-DI-(α)-NAPHTHYL DISULPHIDE $S(C_{10}H_6.NO_2)_2$. [186°]. Formed from nitro-naphthalene sulphonic chloride and HI (Cleve, *B.* 23, 960). Greenish-yellow scales.

NITRO-NITROSO-ANTHRONE $C_{14}H_8N_2O_4$. [263°]. Formed by boiling hydroanthracene-nitrite (vol. i. p. 277) with alkalis (Liebermann a. Landshoff, *B.* 14, 470). Yellow needles, yielding anthraquinone on oxidation.

NITRO-OCTANE $C_8H_{17}NO_2$. (205°–212°). Formed by distilling octyl iodide with $AgNO_2$ (Eichler, *B.* 12, 1883).

NITRO-OCTOIC ACID $C_8H_{15}(NO_2)O_2$. S.G. $\frac{18}{}$ 1·093. Formed by boiling the non-volatile acids of cocoa-nut oil for a long time with HNO_3 (Wirz, *A.* 104, 289). Oil.—AgA'.—EtA'. S.G. $\frac{18}{}$ 1·031. Oil.

NITRO-OCTYL-BENZENE $C_6H_4(NO_2)C_8H_{17}$. The three isomerides may be got by nitrating octyl-benzene (Ahrens, *B.* 19, 2721). o-Nitro-octyl-benzene carbonises at 130°; the *m*-isomeride melts at 124°; the *p*- variety melts at

204°. They yield the corresponding nitro-benzoic acids on oxidation by $KMnO_4$.

Di-nitro-octyl-benzene $C_6H_3(NO_2)_2C_8H_{17}$. [226°]. Formed by nitration of octyl-benzene.

NITRO-OPIANIC ACID *v.* OPIANIC ACID.

NITRO-ORCIN $C_7H_7NO_4$ *i.e.* $C_6H_2Me(NO_2)(OH)_2$. Two nitro-orcins [120°] and [115°] are formed, together with an azo-compound, by the action of a cold mixture of nitrous and nitric acids on an ethereal solution of orcin (Weselsky, *B.* 7, 439). They may be separated by steam-distillation, the compound melting at 120° being volatile. The nitro-orcin [120°] forms $Ba(HA'')_2$; the isomeride [115°] yields $Ba(HA'')_2 8aq$ and $BaA'' 3aq$. By the action of HNO_2 and HNO_3 on the ethyl derivative of orcin there are formed two compounds $C_6H_2Me(NO_2)(OH)(OEt)$, melting at 54° and 103° respectively (Weselsky a. Benedikt, *M.* 2, 371).

Di-nitro-orcin $C_6HMe(NO_2)_2(OH)_2$. [164·5°]. S. (alcohol) 5·5 at 15°. Formed from di-nitroso-orcin and cold dilute HNO_3 (S.G. 1·3) (Stenhouse a. Groves, *A.* 188, 358). Yellow plates, m. sol. boiling water. May be sublimed.—$Ba(HA'')_2$ aq.

Di-nitro-orcin [110°]. Obtained by saturating toluene with NO_2 (Leeds, *A. C. J.* 2, 416; *B.* 14, 483). Golden needles (from alcohol). Dyes silk yellow.

Tri-nitro-orcin $C_6Me(NO_2)_3(OH)_2$. [163°]. Formed from orcin, H_2SO_4, and HNO_3 (Stenhouse, *Pr.* 19, 410; Merz a. Zetter, *B.* 12, 681). Yellow needles, v. sol. hot water. Explodes above 163°. Dyes the skin yellow.—K_2A'': orange needles.—BaA'' 3aq.—PbA''.—Ag_2A'': amorphous orange-red pp.

Methyl ether Me_2A''. [69·5°].

Ethyl ether Et_2A''. [61·5°].

NITRO-OXINDOL $C_8H_6ON(NO_2)$. Prepared by adding powdered KNO_3 to a solution of oxindol in H_2SO_4 (Baeyer, *B.* 12, 1313). Yellow needles, sol. alcohol. Begins to decompose at 175°.

p-**NITRO-ω-OXY-ACETOPHENONE** $C_6H_4(NO_2).CO.CH_2OH$. [121°]. Formed by boiling bromo-nitro-acetophenone with NaOAc and HOAc, diluting with water, and boiling again (Engler a. Zulke, *B.* 22, 204). Sol. hot alkalis.

Nitro-di-oxy-acetophenone $C_6H_2(NO_2)(OH)_2.CO.CH_3$. [142°]. Formed by nitration (Nencki a. Sieber, *J. pr.* [2] 23, 537).

TETRA-NITRO-OXY-AMIDO-ANTHRAQUINONE $C_{14}H_5N_5O_{11}$ *i.e.* $C_{14}H_2(NO_2)_4(NH_2)(OH)O_2$. *Chrysammidic acid.* Formed by boiling chrysammic acid $C_{14}H_2(NO_2)_4(OH)_2O_2$ with ammonia (Schunck, *A.* 65, 236; Graebe a. Liebermann, *A. Suppl.* 7, 310). Olive-green needles, forming a dark-purple aqueous solution. Its salts explode when heated.

NITRO-OXY-AMIDO-BENZOIC ACID $C_7H_6N_2O_5$ *i.e.* $C_6H_2(NO_2)(OH)(NH_2)CO_2H$ [5:2:3:1]. [220°]. Got by reducing di-nitro-o-oxy-benzoic acid (Hübner a. Babcock, *B.* 12, 1345). Crystals.

NITRO-OXY-AMIDO-DIPHENYL. *Acetyl derivative* $C_6H_4(NHAc).C_6H_3(NO_2)(OH)$. [264°] (Schmidt a. Schultz, *A.* 207, 347). Yellow needles.

NITRO-DI-OXY-DI AMIDO-TRI-PHENYL-METHANE *Di-methyl-ether* $C_6H_4(NO_2)CH(C_6H_3(OMe)NH_2)_2$. [108°]. Formed by heating *p*-nitro-benzoic aldehyde with anisidine sulphate and H_2SO_4 (Fischer, *B.* 15, 680). Golden needles (containing C_6H_6). *m*-Anisidine yields an isomeric body [189°] (Kock, *B.* 20, 1562).

NITRO-DI-OXY-AMIDO-QUINONE $C_6H_4N_2O_6$ *i.e.* $C_6(NO_2)(OH)_2(NH_2)O_2$. The salt $C_6H_2K_2N_2O_6$ is precipitated on exposing a solution of $C_6(NO_2)(NH_2)(OH)_4$ in aqueous K_2CO_3 to the air (Nietzki a. Benckiser, *B.* 18, 499). It forms coppery needles.

NITRO-OXY-ANTHRAQUINONE. *Ethyl ether* $C_6H_4<^{CO}_{CO}>C_6H_2(NO_2)(OEt)$ $\left[{}^{1}_{6}:2:3\right]$. [243°]. Formed by oxidation of the nitroso-anthrone of the ethyl ether of nitro-anthrol (Liebermann a. Hagen, *B.* 15, 1795). Colourless needles, sl. sol. alcohol.

Nitro-di-oxy-anthraquinone $C_{14}H_7(NO_2)O_4$. (α)-*Nitro-alizarin.* [196°]. Prepared by nitration of the di-acetyl derivative of alizarin (Schunck a. Römer, *B.* 12, 587). Less soluble in alcohol and HOAc than the (β)-isomeride. Oxidised by HNO_3 to phthalic acid. Yields purpurin on warming with H_2SO_4.

Nitro-di-oxy-anthraquinone. (β)-*Nitro-alizarin. Alizarin orange.* [244°]. Formed by nitration of alizarin dissolved in HOAc (S. a. R.; Rosenstiehl, *Bl.* [2] 26, 63). Formed also by boiling di-nitro-oxy-anthraquinone with dilute (20 p.c.) NaOH (Simon, *B.* 15, 692). Orange needles (from benzene), sl. sol. KOHAq. Dyes alumina mordants red and iron mordants reddish-violet.

Di-acetyl derivative [218°]. Needles.

Nitro-tri-oxy-anthraquinone $C_{14}H_7(NO_2)O_5$. Formed from alizarin and fuming HNO_3 (Strecker, *Z.* 1868, 264). Red crystalline powder.—K_2A''.

Di-nitro-oxy-anthraquinone $C_6H_4:C_2O_2:C_6H(NO_2)_2(OH)$[1:3:2]. [270°]. Formed from oxy-anthraquinone and fuming HNO_3 (Simon, *B.* 14, 464; 15, 694). Yellow needles. Dyes wool and silk orange.—KA'.—CuA'_2 2aq.—MgA'_2 5aq.—AgA'.

Ethyl ether EtA'. [158°].

Di-nitro-di-oxy-anthraquinone $C_{14}H_6(NO_2)_2O_4$. *Di-nitro-purpuroxanthin.* [250°]. Formed from purpuroxanthin and cold HNO_3 (S.G. 1·48) (Plath, *B.* 9, 1205). Red needles (from HOAc).—NH_4HA''.—BaA'': red needles.

Tetra-nitro-di-oxy-anthraquinone $C_{14}H_4(NO_2)_4O_4$. *Tetra-nitro-anthraflavic acid. Tetra-nitro-anthraflavone.* Formed by boiling anthraflavic acid with HNO_3 (S.G. 1·4) (Schardinger, *B.* 8, 1487). Yellow needles, melting with explosion at 307·6° cor.—Salts.—$(NH_4)_2A''$.—$(NH_4)_2A''NH_3$.—$(NH_4)_2A''2NH_3$.—Ag_2A'': brownish needles.

Tetra-nitro-di-oxy-anthraquinone $C_{14}H_4(NO_2)_4O_4$. *Tetra-nitro-isoanthraflavic acid.* Formed by nitrating isoanthraflavic acid (Roemer a. Schwarzer, *B.* 15, 1045). Yellow plates (from dilute HNO_3). Its alkaline solution is red. Dyes wool and silk orange-yellow, but does not combine with mordants.—K_2A''2aq: silky-red needles.

Tetra-nitro-di-oxy-anthraquinone $C_{14}H_4(NO_2)_4O_4$. *Tetra-nitro-anthrarufin.* Formed by nitration of anthrarufin (Liebermann, *B.* 12, 188). Small yellow plates (from fuming HNO_3).—Na_2A'' 4aq.—K_2A'' aq: bronze-coloured prisms. MgA'' 6aq.

Tetra-nitro-di-oxy-anthraquinone $C_{14}H_4(NO_2)_4O_4$. *Chrysammic acid.* Formed by heating aloes with HNO_3 (S.G. 1·37) (Schunck, *A.* 39, 1; 65, 235; Stenhouse a. Müller, *C. J.* 19, 319; Tilden, *Ph.* [3] 2, 845). Formed also by nitration of chrysazin (di-oxy-anthraquinone) (Liebermann a. Giesel, *B.* 8, 1643; 9, 329; *A.* 183, 193). Golden plates or monoclinic prisms. Explodes when quickly heated. Aqueous potassium cyanide at 60° forms *chrysocyammic acid* $C_{18}H_6N_6O_{12}$ 6aq, which forms the dark-red salts $(NH_4)_2A''$ 3aq, K_2A'' 3aq, and CaA'' 3aq.

Salts.—Na_2A'' 3aq (Mulder, *A.* 68, 339; 72, 285).—K_2A''. S. ·08 in the cold. Flat rhomboidal plates; polarises light, the two rays being differently coloured (Brewster, *P.* 69, 552; Hirschwald, *A.* 183, 198).—BaA'' 2aq.—BaA'' 4aq. — MgA'' 5aq. — PbA'' 5aq. — $Pb_2A''(OH)_2$. — PbA'' 4aq.—MnA'' 5aq.—CuA'' 4aq.

Ethyl ether Et_2A''. Pale-red needles or yellow prisms (Stenhouse).

Benzoyl derivative $C_{14}H_2Bz_2N_4O_{12}$. Yellow, almost insoluble, prisms.

NITRO-OXY-BENZENE *v.* NITRO-PHENOL.

Nitro-tri-oxy-benzene. *Tri-methyl derivative* $C_6H_2(NO_2)(OMe)_3$ [*x*:1:2:3]. [100°]. Formed from $C_6H_3(OMe)_3$ and conc. HNO_3 (Will, *B.* 21, 612). Thick prisms. With HNO_3 it yields $C_6H(NO_2)_2(OMe)_3$ [126°], sl. sol. alcohol.

Di-nitro-tetra-oxy-benzene. *Methylene-di-methyl derivative. Di-nitro-apione.* $C_6(NO_2)_2(OMe)_2{<}^{O}_{O}{>}CH_2$. [118°]. Formed from apiolic acid (4 g.), HOAc (50 c.c.), and HNO_3 (100 c.c. of S.G. 1·4) (Ciamician a. Silber, *B.* 22, 2489; 23, 2290). Yellow needles, insol. water. Yields on reduction $C_9H_8O_4(NH_2)_2$ [119°]. With diacetyl it condenses to $C_{13}H_{14}N_2O_4$ [176°], and with benzil to $C_9H_8O_4{<}^{N.CPh}_{N.CPh}$ [222°], both crystallising in needles.

NITRO-o-OXY-BENZOIC ACID $C_6H_3(NO_2)(OH)(CO_2H)$ [5:2:1]. *Nitro-salicylic acid. Anilotic acid.* [228°]. Mol. w. 183. S. ·176 at 22° (Hübner); ·07 at 15·5° (Schiff). Formed, together with the isomeride [144°], by the action of nitric acid on salicylic acid and on indigo (Chevreul, *A. Ch.* [1] 72, 131; Buff, *A. Ch.* [2] 37, 160; Dumas, *A. Ch.* [2] 63, 205; [3] 2, 227; Gerhardt, *A. Ch.* [3] 7, 325; Marchand, *J. pr.* 26, 385; Piria, *A.* 56, 35; Stenhouse, *A.* 70, 253; Schiff, *A.* 154, 14; Schiff a. Masino, *G.* 9, 318; *A.* 198, 258; Hübner, *A.* 195, 6). Formed also by the action of aqueous $NaNO_2$ and H_2SO_4 on salicylic acid at 50° (Deninger, *J. pr.* [2] 42, 550); by boiling (ε)-nitro-amido-benzoic acid [263°] with potash (Griess, *B.* 11, 1730); and by heating *p*-nitro-phenol with CCl_4 and alcoholic potash at 100° (Hasse, *B.* 10, 2188). White needles, v. sol. alcohol. Its aqueous solution is coloured red by $FeCl_3$. Distillation with CaO yields *p*-nitro-phenol [114°].

Salts. — KA'. — NH_4A'. — BaA'_2 6aq. — $BaC_7H_3NO_5$ 2aq. — CaA'_2 6aq. — SrA'_2 5½aq. — MgA'_2 4aq.—ZnA'_2 5aq.—AgA'.

Methyl ether MeA'. [88°]. Formed from methyl salicylate and nitrous acid (Deninger, *J. pr.* [2] 40, 302).

Ethyl ether EtA'. [94°]. Needles.

Methyl derivative $C_6H_3(NO_2)(OMe)(CO_2H)$. [149°]. Formed from $C_6H_4(OMe)(CO_2H)$ and HNO_3 (Kraut, *A.* 150, 6; Salkowski, *A.* 173, 41). Needles. Gives no colour with $FeCl_3$.

Ethyl derivative $C_6H_3(NO_2)(OEt).CO_2H$. [163°] (P.); [161°] (K.). Formed from ethoxy-benzoic aldehyde $C_6H_4(OEt)CHO$ and conc. HNO_3 (Perkin, *A.* 145, 311). Formed also from $C_6H_3(NO_2)(OH).CO_2Me$, EtI, and KOH, the resulting $C_6H_3(NO_2)(OEt).CO_2Me$ being saponified (Kraut). Plates (from boiling water).—BaA'_2 2aq —EtA'. [98°] (Hübner).

Amide $C_6H_3(NO_2)(OH).CONH_2$. [225°]. Needles. Behaves as an acid, decomposing carbonates, and forming the salts $C_7H_5KN_2O_4$ aq. —CaA'_2 4aq.—BaA'_2 4aq.—PbA'_2 4aq.

Anilide $C_6H_3(NO_2)(OH).CO.NHPh$. [224°]. Formed by nitrating $C_6H_4(OH).CONHPh$ (Mensching, *A.* 210, 343). Needles.

Nitro-o-oxy-benzoic acid $C_6H_3(NO_2)(OH)CO_2H$ [3:2:1]. [144°]. S. ·13 at 15·5° (Schiff). Formed as above, and also by adding H_2SO_4 to a solution of salicylic acid and $NaNO_2$ at 100° (Deninger, *J. pr.* [2] 42, 551), and by the action of nitrous acid on oil of wintergreen (Smith a. Knerr, *Am.* 8, 100). Obtained also by heating *o*-nitro-phenol with CCl_4 and alcoholic potash at 100° (Hasse). Needles (containing aq). Melts at 125° when hydrated, 144° when anhydrous. $FeCl_3$ colours its solution red. Yields o-nitro-phenol on heating with dilute H_2SO_4 at 150°.

Salts.—NaA'.—KA'.—BaA'_2. Needles.— $BaC_7H_3NO_5$ 1½aq. — MgA' 2aq. — $PbC_7H_3NO_5$. — AgA'.

Ethyl ether EtA'. [118°].

Amide $C_6H_3(NO_2)(OH).CONH_2$. [146°]. Needles. Yields the salts $Ca(C_7H_5N_2O_4)_2$ 4aq.— BaA'_2 2aq.—Pb(OH)A' 2aq.

Nitro-o-oxy-benzoic acid $C_7H_5NO_5$ *i.e.* $C_6H_3(NO_2)(OH)(CO_2H)$[6:2:1]. *Amide of the methyl derivative* $C_6H_3(NO_2)(OMe)CONH_2$. [195°]. Formed by boiling its nitrile with baryta-water (Lobry de Bruyn, *R. T. C.* 2, 217). Yellowish needles, m. sol. acetone.

Nitrile of the methyl derivative $C_6H_3(NO_2)(OMe)CN$. [171°]. Formed by boiling *m*-di-nitro-benzene with KCy and MeOH (Lobry de Bruyn, *R. T. C.* 2, 212). Needles (from alcohol). Boiling alcoholic potash converts it into $C_6H_3(OH)_2CO_2H$.

Amide of the ethyl derivative $C_6H_3(NO_2)(OEt).CONH_2$. [197°]. Needles.

Nitrile of the ethyl derivative $C_6H_3(NO_2)(OEt)CN$. [137°]. Formed from *m*-di-nitro-benzene and alcoholic KCy. Tables.

α-Nitro-*m*-oxy-benzoic acid $C_6H_3(NO_2)(OH)CO_2H$[6:3:1]. [169°]. Formed by boiling (α)-nitro-amido-benzoic acid with potash (Griess, *B.* 11, 1733). Light-yellow crystals containing aq), v. sol. water.—$BaC_7H_3NO_5$ 6aq: orange prisms.

Methyl derivative $C_6H_3(NO_2)(OMe)(CO_2H)$. [133°]. Formed by oxidising $C_6H_3(NO_2)(OMe)CHO$ with $KMnO_4$ (Riecho, *B.* 22, 2354).

β-Nitro-*m*-oxy-benzoic acid $C_6H_3(NO_2)(OH)CO_2H$[4:3:1]. [230°]. Formed by boiling the corresponding nitro-amido-benzoic acid with KOHAq and, together with the (2,3,1)- and (5,3,1)-isomerides, by nitration of a boiling aqueous solution of *m*-oxy-benzoic acid by HNO_3

(Griess, *B.* 5, 856; 20, 403). Yellow plates (from hot water).—$BaC_7H_3NO_5$ aq.

Nitrile $C_6H_3(NO_2)(OH).CN$. [183°]. From *m*-oxy-benzoic nitrile and HNO_3 (Smith, *J. pr.* [2] 16, 227). Coloured dark red by aqueous $FeCl_3$. Belongs perhaps to one of the isomeric nitro-*m*-oxy-benzoic acids.

(γ)-Nitro-*m*-oxy-benzoic acid $C_6H_3(NO_2)(OH)CO_2H$[2:3:1]. [178°]. Formed by boiling (2,3,1)-nitro-amido-benzoic acid with potash, and also by nitrating *m*-oxy-benzoic acid (Griess, *B.* 11, 1734; 20, 403). Yellow plates or prisms (containing aq). Tastes sweet. —BaA'_2 $1\frac{1}{2}$aq.

Methyl derivative $C_6H_3(NO_2)(OMe)CO_2H$. [251°]. Formed from its aldehyde and Ag_2O (Rieche, *B.* 22, 2352). White plates.—AgA′.

(ζ)-Nitro-*m*-oxy-benzoic acid $C_6H_3(NO_2)(OH)CO_2H$[5:3:1]. [167°]. Formed by nitrating *m*-oxy-benzoic acid (*v. supra*). Crystals (containing aq).—BaA'_2 6aq: prisms.

Methyl derivative $C_6H_3(NO_2)(OMe)CO_2H$. [233°]. Long white needles (Rieche, *B.* 22, 2356).

δ-Nitro-*p*-oxy-benzoic acid $C_6H_3(NO_2)(OH).CO_2H$[3:4:1]. [185°].

Formation.—1. By dissolving *p*-oxy-benzoic acid in dilute nitric acid (Barth, *Z.* 1866, 647; Griess, *B.* 20, 408).—2. By boiling (3,4,1)-nitro-amido-benzoic acid with potash (Griess, *B.* 5, 856).—3. By the action of aqueous $NaNO_2$ and H_2SO_4 on *p*-oxy-benzoic acid at 40° (Deninger, *J. pr.* [2] 42, 552).—4. In small quantity in the action of CCl_4 and alcoholic potash on *o*-nitro-phenol (H.)

Properties.—Needles, sl. sol. hot water. Gives no colour with $FeCl_3$.

Salt.—$BaC_7H_3NO_5$ aq: red nodules.

Methyl derivative $C_6H_3(NO_2)(OMe)CO_2H$. *Nitranisic acid.* [187°]. Formed by boiling anisic acid or oil of anise with nitric acid (Laurent, *B. J.* 23, 416; Cahours, *A.* 41, 71; Engelhardt, *A.* 108, 243; Salkowski, *A.* 163, 6; *B.* 10, 1254). Also from $C_6H_3(NO_2)(OMe).CH_2NHAc$ by oxidation with $K_2Cr_2O_7$ (Goldschmidt a. Polonowska, *B.* 20, 2410). Small needles (from water). Yields *o*-nitro-phenol on heating with water at 220°.—NaA′aq.—KA′aq.—CaA'_2 4aq.—SrA'_2 4aq.—BaA'_2: flocculent pp.—PbA'_2.—AgA′.

Methyl ether of the methyl derivative $C_6H_3(NO_2)(OMe)CO_2Me$. [108°]. Plates.

Ethyl ether of the methyl derivative $C_6H_3(NO_2)(OMe)CO_2Et$. [100°]. Tables.

Nitrile of the methyl derivative $C_6H_3(NO_2)(OMe).CN$. [150°]. Formed from $C_6H_4(OMe)CN$ and HNO_3 (Henry, *B.* 2, 668). Small needles (from alcohol).

Nitro-di-oxy-benzoic acid. *Di-methyl derivative* $C_6H_2(NO_2)(OMe)_2CO_2H$[4:5:3:1]. [225°]. Formed from $C_6H_3(OMe)_2CO_2H$ and dilute HNO_3 (H. Meyer, *M.* 8, 431). Needles (from water). Yields on reduction, $C_6H_2(NH_2)(OMe)_2CO_2H$ [182°].—CuA'_2 $2\frac{1}{2}$aq.—PbA'_2.—AgA′: needles.

Nitro-di-oxy-benzoic acid. *Methyl derivative* $C_6H_2(NO_2)(OH)(OMe)CO_2H$[*x*:4:3:1]. *Nitro-vanillic acid.* White needles (Matsmoto, *B.* 11, 122).

Acetyl derivative $C_6H_2(NO_2)(OAc)(OMe)CO_2H$. [182°]. Needles.

Di-methyl derivative $C_6H_2(NO_2)(OMe)_2CO_2H$. *Nitro-veratric acid.* Yellow needles (containing $\frac{1}{2}$aq). Its methyl ether melts at 144° and its ethyl ether at 100°.

Di-nitro-oxy-benzoic acid $C_6H_2(NO_2)_2(OH)CO_2H$[5:3:2:1]. *Di-nitro-salicylic acid.* [173°]. Formed by nitration of salicylic acid (Cahours, *A. Ch.* [3] 25, 11; Stenhouse, *A.* 78, 1; Hübner, *A.* 195, 45). Tables or needles (containing aq). After fusion it melts at 158°. $FeCl_3$ colours its solution red.—NH_4A'.—KA′: sl. sol. water.—$K_2C_7H_2N_2O_7$ aq: m. sol. water.—NaA′.—BaA'_2.—$BaC_7H_2N_2O_7$ 3aq: needles.—CaA'_2 2aq.—$PbC_7H_2N_2O_7$ 3aq.—AgA′: sparingly soluble granules.

Methyl ether MeA′. [127°]. Yellowish scales. Yields $NH_4C_8H_5N_2O_7$ and $AgC_8H_5N_2O_7$.

Ethyl ether EtA′. [99°]. Yields the salts $NH_4C_9H_7N_2O_7$ and $AgC_9H_7N_2O_7$.

Methyl derivative of the methyl ether $C_6H_2(NO_2)_2(OMe).CO_2Me$. [69°]. Prisms. (Salkowski, *A.* 173, 43).

Methyl derivative of the ethyl ether $C_6H_2(NO_2)_2(OMe).CO_2Et$. [47°]. Tables.

Ethyl derivative of the methyl ether $C_6H_2(NO_2)_2(OEt)CO_2Me$. [80°]. Prisms.

Ethyl derivative of the ethyl ether $C_6H_2(NO_2)_2(OEt)CO_2Et$. [49°]. Prisms.

Di-nitro-*p*-oxy-benzoic acid $C_6H_2(NO_2)_2(OH)(CO_2H)$ [5:3:4:1]. [237°]. Formed by boiling di-nitro-*p*-amido-benzoic acid with potash (Salkowski, *A.* 173, 36). Thin tables.—KA′. S. ·7 at 16·5°.—$K_2C_7H_2N_2O_7$ 2aq. S. 32 at 16·5°.—$BaC_7H_2N_2O_7$ 5aq.—$BaC_7H_2N_2O_7$ $3\frac{1}{2}$aq.—Ag′A.—$Ag_2C_7H_2N_2O_7$.

Ethyl ether EtA′. [87°]. Yields $KC_9H_7N_2O_7$, S. ·9, and $AgC_9H_7N_2O_7$.

Methyl derivative $C_6H_2(NO_2)_2(OMe)CO_2H$. *Dinitranisic acid.* [182°]. Formed by nitration of nitro-anisic acid (Salkowski a. Rudolph, *B.* 10, 1254; Stöhr, *A.* 225, 86).—KA′aq.—AgA′.

Ethyl ether EtA′. [79°].

Ethyl derivative of the ethyl ether $C_6H_2(NO_2)_2(OEt).CO_2Et$. [59°]. Needles.

Tri-nitro-*m*-oxy-benzoic acid $C_6H(NO_2)_3(OH).CO_2H$. Formed by warming *m*-diazoamido-benzoic acid with HNO_3 (Griess, *A.* 117, 28), and by the action of fuming HNO_3 on *m*-amido-benzoic acid (Beilstein a. Geitner, *A.* 139, 11). Large crystals (from conc. HNO_3). Explodes when heated.—$(NH_4)_2C_7HN_3O_9$ 2aq.—$BaC_7HN_3O_9$ 3aq.—$Ag_2C_7HN_3O_9$.

Tri-nitro-oxy-benzoic acid [105°]. Formed from *m*-oxybenzoic acid by successive treatment with dilute H_2SO_4 and HNO_3 (Schardinger, *B.* 8, 1490). Tables and prisms (containing aq).—$BaC_7HN_3O_9$ 2aq.—$CaC_7HN_3O_9$ 5aq: green needles, exploding at 237°.

NITRO-*o*-OXY-BENZOIC ALDEHYDE $C_6H_3(NO_2)(OH)CHO$. [3:2:1]. [109°]. Formed together with the (5,2,1)-isomeride, by nitrating salicylic aldehyde (Mazzara, *G.* 6, 460; Von Miller, *B.* 20, 1927; 22, 1709; Taege, *B.* 20, 2109). Its compound with $NaHSO_3$ does not crystallise. Sodium-amalgam forms brown amorphous $\{C_6H_3(OH)(CHO)\}_2N_2H_2$ (Brigel, *A.* 135, 169).—$NaC_7H_4NO_4$.—$Ba(C_7H_4NO_4)_2$ 2aq: orange crystals.

Acetyl derivative [110°].

Phenyl-hydrazide [165°].

Methyl derivative $C_8H_7NO_4$. [102°].

Nitro-*o*-oxy-benzoic aldehyde $C_6H_3(NO_2)(OH)CHO$ [5:2:1]. [125°]. Formed as

above. Forms a solid compound with $NaHSO_3$.—$NaA'2aq$: needles.—$BaA'_2 6aq$.—$BaA'_2 3aq$.

Acetyl derivative [112°].

Phenyl-hydrazide [186°].

Methyl derivative $C_6H_3(NO_2)(OMe)CHO$. [90°]. Formed by nitrating $C_6H_4(OMe)CHO$ (Schnell, *B.* 17, 1382; *cf.* Voswinckel, *B.* 15, 2027). Needles (from water).

Nitro-*m*-oxy-benzoic aldehyde $C_6H_3(NO_2)(OH)(CHO)$ [2:3:1]. [128°]. Formed, together with the isomeride [166°], by nitration of *m*-oxy-benzoic aldehyde (Tiemann a. Ludwig, *B.* 15, 2052, 3052). Yellow plates, sol. benzene.

Methyl derivative $C_6H_3(NO_2)(OMe)CHO$. [107°] (T. a. L.); [102°] (R.). Formed from the aldehyde, KOH, and MeI (T. a. L.). Formed also, together with the (6, 3, 1)- and (5, 3, 1)-isomerides from $C_6H_4(OMe)CHO$ and HNO_3 at 0° (Rieche, *B.* 22, 2350). Forms a very soluble compound with $NaHSO_3$. With acetone and NaOH it condenses to di-methoxy-indigo. $C_6H_3(NO_2)(OMe)CH:NOH$, its oxim, melts at 170°; and its phenyl-hydrazide $C_6H_3(NO_2)(OMe)CH:N_2HPh$ at 134°.

Nitro-*m*-oxy-benzoic aldehyde $C_6H_3(NO_2)(OH)CHO$ [6:3:1]. [166°]. Formed by nitrating *m*-oxy-benzoic aldehyde (T. a. L.). Needles, v. sl. sol. benzene.

Methyl derivative [83°]. Plates, volatile with steam. Its compound with $NaHSO_3$ is m. sol. water. With acetone and KOH it yields a substance resembling indigo. Its oxim $C_6H_3(NO_2)(OH)CH:NOH$ melts at 152°, and the corresponding phenyl-hydrazide at 154°.

Nitro-*m*-oxy-benzoic aldehyde. *Methyl derivative* $C_6H_3(NO_2)(OMe)(CHO)$ [5:3:1]. [97°] (U.); [104°] (R.). A product of the nitration of [3:1] $C_6H_4(OMe)CHO$ (Ulrich, *B.* 18, 2572; Rieche, *B.* 22, 2354). Does not give the indigo reaction. Forms an oxim [148°], and a phenyl-hydrazide [126°].

Nitro-*p*-oxy-benzoic aldehyde $C_6H_3(NO_2)(OH)CHO$ [3:4:1]. [140°]. Formed by nitrating *p*-oxy-benzoic aldehyde (Mazzara, *G.* 7, 285; Herzfeld, *B.* 10, 1269). Needles, slightly volatile with steam.—$C_6H_3(NO_2)(OK)CHO aq$.—AgA': canary yellow pp.

Methyl derivative. Nitro-anisic aldehyde. [84°]. Formed from anisic aldehyde, HNO_3, and H_2SO_4 (Einhorn a. Grabfield, *A.* 243, 370). Yellow needles. Forms a phenyl hydrazide [131°].

Di-nitro-*m*-oxy-benzoic aldehyde. *Methyl-derivative* $C_6H_2(NO_2)_2(OMe)CHO$. [110°]. Formed, together with an isomeride [155°], by treating [3:1] $C_6H_4(OMe)CHO$ with H_2SO_4 and KNO_3 (Tiemann a. Ludwig, *B.* 15, 2055).

Nitro-di-oxy-benzoic aldehyde. *Ethyl derivative* $C_6H_2(NO_2)(OEt)(OH)CHO$ [x:5:2:1]. [130°]. Formed from $C_6H_3(OEt)(OH)CHO$ and dilute HNO_3 (Hantzsch, *J. pr.* [2] 22, 472). Scarcely volatile with steam.

TETRA-NITRO-*o*-OXY-BENZYL-ANILINE $C_{13}H_8(OH)(NO_2)_4N$. [66°]. Formed from *o*-oxy-benzyl-aniline, HNO_3, and H_2SO_4 (Emmerich, *A.* 241, 345). Yellow needles (from benzene).

DI-NITRO-DI-OXY-DI-BENZYL UREA. *Di-ethyl derivative* $CO(NH.CH(OEt).C_6H_4NO_2)_2$. [170°]. Formed from urea, nitro-benzoic aldehyde, alcohol, and H_2SO_4 (Lüdy, *M.* 10, 305).

NITRO-OXY-CINNAMIC ACID *v.* NITRO COUMARIC ACID.

NITRO-OXY-CUMINIC ACID. *Methyl derivative* $C_6H_2(C_3H_7)(NO_2)(OMe)CO_2H$. [146°]. Formed from the methyl derivative of cymophenol and dilute HNO_3 (Paterno a. Canzoneri, *G.* 10, 233). Yellowish crystals.—$BaA'_2 2\frac{1}{2}aq$.

Isomeride *v.* NITRO-OXY-ISOPROPYL BENZOIC ACID.

NITRO-DI-OXY-ETHYL-PYRIMIDINE $CO{<}^{NEt.CH}_{NH\,.CO}{>}C(NO_2)aq$. *Nitro-ethyl-uracil* [194·5°]. Formed from potassium nitro-uracil and EtBr at 150° (Lehmann, *A.* 253, 84). White needles.—KA'.—AgA': needles, v. sl. sol. cold Aq.

DI-NITRO-OXY-ETHYL-QUINOLINE TETRAHYDRIDE. *Ethyl derivative* $C_{13}H_{17}N_3O_5$ *i.e.* $C_9H_7Et(OEt)(NO_2)_2N$. [77°]. Formed by nitrating $C_9H_9Et(OEt)N$ (Kohn, *C. J.* 49, 509; *B.* 19, 1048). Yellow prisms (from alcohol), with basic properties.

NITRO-OXY-MALEÏC IMIDE $C_4H_2N_2O_4$. The salt $NH{<}^{CO.C.NO_2}_{CO.C.OK}$ separates as light-yellow crystals when a solution of di-chloro-maleïc imide is warmed with KNO_2 (Ciamician a. Silber, *Rend. Accad. Linc.* [4] 4, 447; *B.* 22, 33, 2490). It is almost insol. water.

TETRA-NITRO-DI-OXY-METHYL-ANTHRA-QUINONE $C_{14}H_3Me(OH)_2(NO_2)_4O_2$. *Tetra-nitro-chrysophanic acid.* Formed by heating chrysophanic acid with fuming HNO_3 (Liebermann a. Giesel, *A.* 183, 175). Yellow plates or needles.

NITRO-DI-OXY-METHYL-ETHYL-PYRIMIDINE $CO{<}^{NMe.CH}_{NEt\,.CO}{>}C(NO_2)$. [73°]. *Nitro-methyl-ethyl-uracil.* Formed from silver nitro-ethyl-uracil and MeI at 130° (Lehmann, *A.* 253, 86). Pearly rhombohedra (containing aq).

Nitro-di-oxy-methyl-ethyl-pyrimidine $CO{<}^{NEt\,.CH}_{NMe.CO}{>}C(NO_2)$. [109°]. Formed from silver nitro-methyl-uracil and EtBr at 150° (L.). Needles (containing aq).

NITRO-OXY-TRI-METHYL-PYRIDINE $C_8H_{10}(NO_2)NO$. *Nitro-methyl-ψ-lutidostyril.* [161°]. Formed by nitrating oxy-tri-methyl-pyridine (Hantzsch, *B.* 17, 1032). Yellow needles or prisms, sol. hot alcohol.

NITRO-DI-OXY-METHYL-PYRIMIDINE $C_5H_5N_3O_4$ *i.e.* $CO{<}^{NH\,.CH}_{NMe.CO}{>}C.NO_2$. *Nitro-methyl-uracil.* [255°]. S. ·714 at 20°. Formed from potassium nitro-uracil and MeI at 140° (Hoffmann, *A.* 253, 77). Needles (containing aq), v. sol. hot water. Baryta-water at 160° liberates methylamine and NH_3.—KA': needles.—BaA'_2.—AgA': minute white needles (from hot water).

Nitro-di-oxy-di-methyl-pyrimidine $CO{<}^{NMe.CH}_{NMe.CO}{>}C(NO_2)$. [154·5°]. From the silver salt of nitro-di-oxy-methyl-pyrimidine and MeI at 120° (Lehmann, *A.* 253, 82). Needles (containing aq). Yields $NMeH_2$ when heated with baryta at 130°.

NITRO-OXY-METHYL-QUINAZOLINE $C_6H_3(NO_2){<}^{C(OH):N}_{N=\!=\!=CMe}$. Formed from oxy-methyl-quinazoline [233°] and conc. HNO_3 (De-

hoff, *J. pr.* [2] 42, 348). Yellow crystalline powder, sol. alcohol. Does not melt below 280°.

Methyl derivative [165°]. Needles.

(*Py*.2)-**NITRO**-(*Py*.1)-**OXY**-(*Py*.3)-**METHYL-QUINOLINE** $C_6H_4<\begin{matrix}C(OH):C(NO_2)\\N{=\!=\!=}CMe\end{matrix}$. Formed by nitrating oxy-(*Py*. 3)-methyl-quinoline (Conrad a. Limpach, *B.* 20, 950). Needles, v. sl. sol. boiling alcohol. Does not melt at 270°.

(*B*. 3)-**Nitro**-(*B*. 4)-**oxy**-(*B*. 1)-**methyl-quinoline** $\begin{matrix}CH:CMe\ \text{———}\ C.CH:CH\\C(NO_2):C(OH).C.\ N\ :CH\end{matrix}$ [206°]. This body is formed by oxidising the corresponding nitroso-oxy-methyl-quinoline with alkaline K_3FeCy_6 (Noelting a. Trautmann, *B.* 23, 3667). In the same way may be formed (*B*. 4)-nitro-(*B*. 1)-oxy-(*B*. 2)-methyl-quinoline; (*B*. 1)-nitro-(*B*. 4)-oxy-(*B*. 3)-methyl-quinoline [193°]; and (*B*. 2)-nitro-(*B*. 1)-oxy-(*B*. 4)-methyl-quinoline [182°].

NITRO-OXY-TRI-METHYL-QUINOLINE CARBOXYLIC ACID $C_{13}H_{12}N_2O_5$ *i.e.* $C_9HMe_3(NO_2)(CO_2H)(OH)N$. Formed by warming (*Py*. 1)-oxy-(*B*. 1, 2, 4; *Py*. 3)-tetra-methyl-quinoline with HNO_3 (S.G. 1·4) (Conrad a. Limpach, *B.* 21, 529). White insoluble powder. —NaA′ aq: yellowish needles.

NITRO-DI-OXY-NAPHTHALENE *v.* NITRO-HYDRONAPHTHOQUINONE.

Di-nitro-di-oxy-naphthalene. *Di-ethyl-derivative* $C_{10}H_4(NO_2)_2(OEt)_2$. [229°]. Formed from (ε)-di-chloro-di-nitro-naphthalene and alcoholic potash (Alén, *Bl.* [2] 36, 435). Yellow needles.

NITRO-OXY-NAPHTHOIC ACID $C_{10}H_5(NO_2)(OH).CO_2H$. [242°]. Formed by dissolving its anhydride in alkalis (Ekstrand, *J. pr.* [2] 38, 282). Plates.—$CaC_{11}H_5NO_5\,5\frac{1}{2}aq$: yellowish-red needles.

Anhydride $C_{10}H_5(NO_2)<\begin{matrix}O\\CO\end{matrix}$. [242°]. Formed by nitrating *peri*-oxy-naphthoic acid. Yellow needles (from HOAc).

Nitro-oxy-naphthoic acid [202°] (Schmidt a. Burkard, *B.* 20, 2700). Yields (β)-nitro-(α)-naphthol on distillation with lime.

NITRO-OXY-(α)-NAPHTHOQUINONE $C_{10}H_5NO_5$ *i.e.* $C_6H_4<\begin{matrix}CO.C.NO_2\\CO.C.OH\end{matrix}$. *Nitronaphthalic acid.* [157°]. Formed from oxy-(α)-naphthoquinone, H_2SO_4, and HNO_3; the yield being 85 p.c. of the theoretical (Diehl a. Merz, *B.* 11, 1317). Formed also from di-chloro-(α)-naphthoquinone and alcoholic $NaNO_2$ at 100° (Kehrmann, *B.* 21, 1780; *J. pr.* [2] 40, 180). Yellow leaflets or tables.—NH_4A'.—NaA′aq.—KA′aq.—BaA'_2.—PbA'_2 aq.—$PbA'_2\,4\frac{1}{2}aq$.—AgA′.

Sulphonic acid $C_{10}H_3(SO_3H)(NO_2)(OH)O_2$ [2′:3:2:4:1]. Formed from di-chloro-(α)-naphthoquinone sulphonic acid [229°] and $NaNO_2$ (K.).—$K_2C_{10}H_3NSO_8$ (dried at 100°): slender yellow needles.

DI-NITRO-DI-OXY-(ββ)-DINAPHTHYL DI-SULPHONIC ACID $C_{20}H_6(NO_2)_2(OH)_2(SO_3H)_2$. Got by nitrating $C_{20}H_8(OH)_2(SO_3)_2Ba$ (Julius, *Chem. Ind.* 10, 97). Yellow needles (containing 3aq).

o-**NITRO**-*p*-**OXY-DIPHENYL** [4:1] $C_6H_4(OH).C_6H_4.NO_2$ [1:2]. [138°]. Formed by the action of nitrous acid on the corresponding nitro-amido-diphenyl (Schultz a. Strasser, *B.* 14, 614; *A.* 207, 351). Yellow needles.

p-**Nitro**-*p*-**oxy-diphenyl** [4:1] $C_6H_4(OH).C_6H_4.NO_2$[1:4]. [170°]. Formed from *p*-nitro-*p*-amido-diphenyl (S. a. S.).

Nitro-oxy-diphenyl $C_{12}H_8(NO_2)(OH)$. [67°]. Formed by nitration of oxydiphenyl (Latschinoff, *J. R.* 5, 52). Lemon-yellow prisms (from ether).

Di-nitro-oxy-diphenyl $C_{12}H_7(NO_2)_2(OH)$. [154°]. Formed at the same time as the preceding (L.). Golden plates (from alcohol).—$KA'_2\,2aq$: sparingly soluble plates.

Di-nitro-di-oxy-diphenyl [3:4:1] $C_6H_3(NO_2)(OH).C_6H_3(NO_2)(OH)$ [1:3:4]. [272°] (K.); [280°] (S.). Formed from *pp*-di-oxy-diphenyl and HNO_3 (S.G. 1·45) (Kunze, *B.* 21, 3331; Schütz, *B.* 21, 3531). Yellow needles, insol. alcohol.

Di-acetyl derivative [215°]. Needles.

Di-benzoyl derivative [206°]. Plates.

Ethyl ether [193°]. Formed by nitrating the ethyl ether of di-oxy-diphenyl (Hirsch, *B.* 22, 336).

Di-nitro-di-oxy-diphenyl $C_{12}H_8N_2O_6$. [184°]. Formed by oxidising o-nitro-phenol with aqueous $KMnO_4$ (Goldstein, *J. R.* 6, 193; 10, 318). Yellow needles (from benzene).

Di-benzoyl derivative. [191°]. Needles.

Tetra-nitro-di-oxy-diphenyl [4:3:5:1] $C_6H_2(OH)(NO_2)_2.C_6H_2(NO_2)_2(OH)$ [1:3:5:4]. [220°] (K.); [225°] (S.). From di-oxy-diphenyl, HOAc, and HNO_3 (Kunze, *B.* 21, 3333; Schütz, *B.* 21, 3532). Yellow needles.—Na_2A''.—NaHA″: brownish-red needles.

Di-acetyl derivative. [236°]. Needles.

Hexa-nitro-tetra-oxy-diphenyl $C_{12}H_4N_6O_{16}$. *Hexa-nitro-diresorcin.* Formed by warming tetra-acetyl-diresorcin with fuming HNO_3 (Benedikt a. Julius, *M.* 5, 178). Yellow crystals, exploding at 230°; v. e. sol. water.

m-**NITRO-α-OXY-PHENYL-ACETIC ACID** *v.* NITRO-MANDELIC ACID.

NITRO-OXY-PHENYL-AMIDO-BENZOIC ACID $C_6H_4(OH).NH.C_6H_3(NO_2).CO_2H$[4:3:1]. [261°]. Formed from bromo-nitro-benzoic acid, alcohol, and amido-phenol at 120° (Schöpff, *B.* 22, 3288). Small needles, m. sol. water.

DI-NITRO-o-OXY-DIPHENYLAMINE [2:1] $C_6H_4(OH).NH.C_6H_3(NO_2)_2$[1:2:4]. [199°]. Got from $C_6H_3Br(NO_2)_2$ and o-amido-phenol (Schöpff, *B.* 22, 900). Orange crystals (from alcohol).

Acetyl derivative [150°]. Needles.

Ethyl derivative [164°]. Red needles.

Methyl derivative [151°]. Needles.

Di-nitro-*p*-oxy-diphenylamine. *Di-benzoyl derivative* $C_{12}H_7(NO_2)_2(OBz)NBz$. [195°]. Got by nitrating $C_{12}H_9(OBz)NBz$ (Philip a. Calm, *B.* 17, 2437). Small crystals, sl. sol. alcohol.

Di-nitro-di-oxy-diphenylamine. *Diethyl derivative* $C_6H_5NHC_6H(NO_2)_2(OEt)_2$. [133°]. Formed by heating aniline with the diethyl derivative of di-nitro-hydroquinone (Nietzki, *A.* 215, 157). Red needles (from alcohol).

NITRO-OXY-PHENYL-ANGELIC-(β)-LACTONE [4:1] $C_6H_4(NO_2).CH:CH.CH<\begin{matrix}CH_2\\O\end{matrix}>CO$. [111°]. Formed by adding soda to a cold solution of $C_6H_4(NO_2).C_2H_3Br.CH<\begin{matrix}CH_2\\O\end{matrix}>CO$ (Einhorn a. Gehrenbeck, *B.* 22, 47; *A.* 253, 370).

o-**NITRO-β-OXY-PHENYL-BUTYLENE DI-CARBOXYLIC ACID** [1:2] $C_6H_4(NO_2).CH:CH.CH(OH).CH(CO_2H)_2$.

[269°]. Formed by heating malonic acid (10 g.) with *o*-nitro-cinnamic aldehyde (15 g.) at 125° (Einhorn, *A.* 253, 375). Stellate needles.

NITRO-OXY-PHENYL-CARBAMIC ETHER. *Ethyl derivative* $C_6H_3(NO_2)(OEt).NH.CO_2Et$. [71°]. Formed, as well as two di-nitro- derivatives [141°] and [121°] and a tri-nitro- derivative [212°] by the action of nitric acid on [4:1]$C_6H_4(OEt).NH.CO_2Et$ (Köhler, *J. pr.* [2] 29, 261). All four compounds crystallise from alcohol in needles.

NITRO-DI-OXY-PHENYL-CROTONIC ACID. *Anhydride* $C_6H_2(NO_2)(OH)<\begin{matrix}CMe:CH\\O—CO\end{matrix}$. *Nitro-(β)-methyl-umbelliferone.* Formed, as well as the di-nitro- derivative [220°] by nitration of (β)-methyl-umbelliferone dissolved in HOAc (Pechmann a. Cohen, *B.* 17, 2136). Both compounds crystallise in yellow needles, sol. alcohol.

NITRO - OXY - PHENYL - ETHYLENE *v.* NITRO-OXY-STYRENE.

***o*-NITRO-β-OXY-PHENYL-ETHYL METHYL KETONE** $C_{10}H_{11}NO_4$ *i.e.* $C_6H_4(NO_2).CH(OH).CH_2.CO.CH_3$. [69°]. Formed from *o*-nitro-benzoic aldehyde, acetone, and dilute aqueous NaOH (Baeyer a. Drewsen, *B.* 15, 2857). Prisms.

p-**Nitro-β-oxy-phenyl-ethyl methyl ketone** [58°]. Formed in like manner from *p*-nitro-benzoic aldehyde (Baeyer a. Becker, *B.* 16, 1969). Crystals. Yields nitro-styryl methyl ketone on boiling with Ac_2O. Boiling potash forms a compound $(C_{10}H_9NO_3)_n$ [254°].

***p*-NITRO-β-OXY-PHENYL-(*Py.* 3)-ETHYL-QUINOLINE** $C_6H_4(NO_2).CH(OH).CH_2(NC_9H_6)$. [160°]. Formed by heating (*Py.* 3)-methyl-quinoline with *p*-nitro-benzoic aldehyde at 120° (Bulach, *B.* 20, 2046). Silky needles (from alcohol).—$B'_2H_2PtCl_6$.—$B'HNO_3$: white needles.

DI - NITRO - DI-*o*- OXY - DI - PHENYL - HYDRAZINE. *Di-ethyl derivative* $\{C_6H_3(NO_2)(OEt)\}_2N_2H_2$. [202°]. Formed by reduction of the corresponding azo- compound [285°] by alcoholic ammonium sulphide (Andreæ, *J. pr.* [2] 21, 325). Yellow prisms, insol. cold alcohol. Hot HClAq converts it into nitro-amido-phenol and $\{C_6H_3(NO_2)(OEt)\}_2N_2$.

NITRO-OXY-PHENYL-METHYL-PYRAZOLE $C_{10}H_9N_3O_3$ *i.e.* $C_6H_5.N<\begin{matrix}CO.CH(NO_2)\\N\ :CMe\end{matrix}$. [127°–130°]. Formed by the action of nitrous acid on oxy-phenyl-methyl-pyrazole, and of nitric acid on the oxim thereof (Knorr, *A.* 238, 187). Prisms (from alcohol), insol. acids.

NITRO-OXY-PHENYL-PROPIOLIC ACID. *Methyl derivative* $C_6H_3(NO_2)(OMe).C{:}C.CO_2H$. [135°]. Formed from $C_6H_3(NO_2)(OMe).CHBr.CHBr.CO_2H$ and alcoholic potash (Einhorn a. Grabfield, *A.* 243, 377). White needles, sol. water.

NITRO-OXY-PHENYL-PROPIONIC ACID [3:4:1]$C_6H_3(NO_2)(OH).CH_2.CH_2.CO_2H$. *Nitro-hydro-p-coumaric acid.* [91°]. Formed by nitrating *p*-oxy-phenyl-propionic acid (Stöhr, *A.* 225, 57). Orange needles (from water).

Methyl ether MeA'. [64°]. Needles.

Ethyl ether EtA'. [38°]. Needles.

Nitro-α-oxy-phenyl-propionic acid $C_6H_4(NO_2).CH_2.CH(OH).CO_2H$. A mixture of the *o*- and *p*- isomerides is formed by the action of fuming HNO_3 at −5° on α-oxy-phenyl-propionic acid (Erlenmeyer a. Lipp, *A.* 219, 228). The nitrate $C_6H_4(NO_2).CH_2.CH(ONO_2).CO_2H$ of the *p*- isomeride crystallises from hot water in needles, leaving that of the o- compound in solution.

o-Nitro-β-oxy-phenyl-propionic acid $C_9H_9NO_5$ *i.e.* [2:1] $C_6H_4(NO_2).CH(OH).CH_2.CO_2H$. [126°]. Formed by oxidation of the product of condensation of o-nitro-benzoic aldehyde with acetic aldehyde (Baeyer a. Drewson, *B.* 16, 2206). Formed also from β-bromo-*o*-nitro-phenyl-propionic acid and hot Na_2CO_3Aq (Einhorn, *B.* 16, 2214; 17, 1660, 2013). Monoclinic prisms (from water). Dilute H_2SO_4 at 190° converts it into o-nitro-cinnamic acid.—BaA'_2 2aq: needles.

Methyl ether MeA'. [51°].

β-Lactone $C_6H_4(NO_2).CH<\begin{matrix}CH_2\\O\end{matrix}>CO$. [124°]. Formed from $C_6H_4(NO_2).CHBr.CH_2.CO_2H$ and cold aqueous Na_2CO_3. Yellow monoclinic crystals (from chloroform). Split up by boiling with water into o-nitro-styrene and CO_2. Boiling HOAc yields indigo.

Amide $C_9H_{10}N_2O_4$. [197°]. Formed from β-bromo-*o*-nitro-phenyl-propionic acid and ammonia. Formed also from the lactone and NH_3 (Einhorn, *B.* 16, 2646; Basler, *B.* 17, 1494). Needles, v. sol. water. Yields with Ac_2O an acetyl derivative $C_9H_9AcN_2O_4$ [142°], a compound $C_9H_8N_2O_3$ [c. 80°], and the acetyl derivative thereof $C_9H_7AcN_2O_3$ [172°].

m-**Nitro-β-oxy-phenyl-propionic acid** [3:1] $C_6H_4(NO_2).CH(OH).CH_2.CO_2H$. [105°]. Formed by boiling β-bromo-*m*-nitro-phenyl-propionic acid with water (Prausnitz, *B.* 17, 596; 1660). Plates (from water).

Ethyl ether EtA'. [56°]. Crystals.

Lactone $C_9H_7NO_4$. [98°]. Deposited from a cold solution of the sodium salt. Yields *m*-nitro-styrene on boiling with water.

p-**Nitro-β-oxy-phenyl-propionic acid** $C_9H_9NO_5$. [132°]. Formed by the action of alkalis on β-bromo-*p*-nitro-phenyl-propionic acid, its lactone being the intermediate product (Basler, *B.* 16, 3004; 17, 1494). Needles, m. sol. cold Aq.

Methyl ether MeA'. [74°]. Prisms.

Ethyl ether EtA'. [46°]. Crystalline.

Lactone $C_9H_7NO_4$. [92°]. Yields *p*-nitro-styrene when boiled with HOAc.

Amide $C_9H_{10}N_2O_4$. [166°]. Prisms (from alcohol). Forms with Ac_2O an acetyl derivative [146°–150°].

Anilide $C_{15}H_{14}N_2O_4$. [176°]. Plates.

p-**Nitro-αβ-di-oxy-phenyl-propionic acid** $C_9H_9NO_6$ *i.e.* $C_6H_4(NO_2).CH(OH).CH(OH).CO_2H$. [168°]. Formed from *p*-nitro-phenyl-glycidic acid and diluted H_2SO_4 (Lipp, *B.* 19, 2645). Plates, sl. sol. cold water.

o-Nitro-*m*β-di-oxy-phenyl-propionic acid. *Methyl derivative* [2:5:1] $C_6H_3(NO_2)(OMe).CH(OH).CH_2.CO_2H$. [106°]. Got from $C_6H_3Cl(NO_2).CH(OH).CH_2.CO_2H$ and NaOMe (Eichengrün a. Einhorn, *B.* 23, 1491). Colourless plates (from water).

ap-**Di-nitro-β-oxy-phenyl-propionic acid.** *Methyl derivative* $C_6H_4(NO_2).CH(OMe).CH(NO_2).CO_2H$. *Methyl ether* MeA'. [118°]. Formed from methyl *ap*-di-nitro-cinnamate by boiling with MeOH (Friedländer a. Mähly, *B.* 16, 851; *A.* 229, 210).

Ethyl ether EtA′. [77°]. Formed in like manner, using EtOH.

Ethyl derivative $C_6H_4(NO_2).CH(OEt).CH(NO_2).CO_2H$. Methyl ether MeA′. [110°]. Formed by boiling *ap*-di-nitro-cinnamic ether with alcohol. Monoclinic prisms $a:b:c = \cdot849:1:\cdot517$; $\beta = 87° 25'$. Sol. potash. Yields the salts $Ba(C_{12}H_{13}N_2O_7)_2$ and $AgC_{12}H_{13}N_2O_7$. Ethyl ether EtA′. [52°]. Monoclinic crystals.

Di-nitro-oxy-phenyl-propionic acid $C_9H_8N_2O_7$ *i.e.* [5:3:4:1] $C_6H_2(NO_2)_2(OH).CH_2.CH_2.CO_2H$. *Di-nitro-hydro-p-coumaric acid.* [138°]. Formed by nitrating oxy-phenyl-propionic acid (Stöhr, *A.* 225, 68). Trimetric prisms (from HOAc).—NH_4HA''. [230°].—$(NH_4)_2A''$.—AgHA″.—Ag_2A'': dark-red needles.

Methyl ether MeA′. [87°]. Needles. Yields AgMeA″ on adding Ag_2CO_3 to its ethereal solution.

Ethyl ether EtA′. [175°]. Yields red needles of AgEtA″.

Methyl derivative $C_6H_2(NO_2)_2(OMe).CH_2.CH_2.CO_2H$. [124°]. Got by saponifying its methyl ether with H_2SO_4 and HOAc. Needles or plates (from dilute alcohol). Methyl ether $C_6H_2(NO_2)_2(OMe).C_2H_4.CO_2Me$. [53°]. From the basic silver salt and MeI. Ethyl ether EtA′. [71°]. Needles, v. sl. sol. Aq.

Ethyl derivative $C_6H_2(NO_2)_2(OEt).CH_2.CH_2.CO_2H$. [126°]. Needles. Methyl ether MeA′. [36°]. Ethyl ether EtA′. [50°]. Needles or plates.

Di-nitro-oxy-phenyl-propionic acid $C_9H_8N_2O_7$. *Dinitromelilotic acid.* [155°]. Formed by nitrating melilotic acid (Zwenger, *A. Suppl.* 5, 118). Prisms (from alcohol).—BaA″ aq.—Ag_2A''.

Two isomeric acids are obtained by nitration of phloretic acid (Hlasiwetz, *A.* 102, 155). Both form yellow crystals.

o-NITRO-β-OXY-PHENYL PROPIONIC ALDEHYDE $C_9H_9NO_4$ *i.e.* [1:2] $C_6H_4(NO_2).CH(OH).CH_2.CHO$. Formed from o-nitro-benzoic aldehyde, acetic aldehyde, and 2 p.c. aqueous NaOH (Baeyer a. Drewsen, *B.* 16, 2205). Crystalline. Forms a compound with aldehyde $C_9H_9NO_4(C_2H_4O)$ [125°], which yields indigo on treatment with alkalis. Similar compounds of the formula $C_9H_9NO_4(C_2H_4O)$ are formed by the action of *m*- and *p*-nitro-benzoic aldehydes on aldehyde and NaOHAq. The *m*- compound gives off aldehyde at 100°, the *p*- compound melts at about 115° (Göhring, *B.* 18, 372, 720).

***m*-NITRO-β-OXY-PHENYL-PYROTARTARIC ACID.** *Lactone* $C_{11}H_9NO_6$ *i.e.*

$C_6H_4(NO_2).CH{<}{\begin{matrix}O\text{——}CO\\CH(CO_2H)\end{matrix}}{>}CH_2$. *Nitro-phenyl-paraconic acid.* [171°]. Formed by heating *m*-nitro-benzoic aldehyde with sodium succinate and Ac_2O at 125° (Salomonson, *R. T. C.* 6, 1). Crystalline. Boiling with NH_3Aq and $BaCl_2$ ppts. $C_{11}H_9BaNO_7$. Phenylhydrazine at 130° forms $C_{11}H_9NO_5(N_2HPh)$ [132°]. — $Cu(C_{11}H_8NO_6)_2$. — PbA'_2: needles (from hot water).

Methyl ether $MeC_{11}H_8NO_6$. Oil.

p-Nitro-β-oxy-phenyl-pyrotartaric acid. *Lactone* [163°] (S.); [155°] (Erdmann, *B.* 18, 2742). Formed in like manner from *p*-nitro-benzoic aldehyde. Boiling with NH_3Aq and $BaCl_2$ ppts. $BaC_{11}H_9NO_7$.—CuA'_2.—AgA′.

NITRO-*p*-OXY-PHENYL-QUINOLINE $C_{15}H_{10}N_2O_3$. [151°]. Formed in small quantities when *p*-amido-(*Py.* 3)-phenyl-quinoline is heated with KNO_2 (Weidel, *M.* 8, 138). Yellow plates, m. sol. alcohol.

m-Nitro-(*B.* 2)-oxy-(*Py.* 1)-phenyl-quinoline. *Methyl derivative*

$${\begin{matrix}MeO.C\ :C.HC.C.(C_6H_4NO_2):CH\\ CH:CH.C.N\text{=========}CH\end{matrix}}$$

[130°]. Formed by heating *m*-nitro-cinnamic aldehyde with *p*-anisidine and HClAq (Miller a. Kinkelin, *B.* 20, 1919). Needles (from benzene), sl. sol. alcohol.

(*Py.* 1,4,2)-Nitro-oxy-phenyl-isoquinoline $C_{15}H_{10}N_2O_3$ *i.e.* $C_6H_4{<}{\begin{matrix}C(NO_2):CPh\\C(OH):N\end{matrix}}{>}$. [c. 245°]. Formed by passing nitrous acid gas through a solution of oxy-phenyl-isoquinoline in HOAc (Gabriel, *B.* 19, 831). Small yellow crystals.

Methyl derivative $C_{15}H_9MeN_2O_3$. [169°].

DI-NITRO-DI-OXY-DI-PHENYL SULPHONE $C_{12}H_8N_2SO_8$ *i.e.* $SO_2\{C_6H_3(NO_2)(OH)\}_2$. Formed by nitrating di-oxy-di-phenyl sulphone (Glutz, *A.* 147, 59). Scales, insol. water, sol. alkalis. Yields $C_{12}H_6Na_2N_2SO_8$ and $C_{12}H_6Ag_2N_2SO_8$, a di-methyl derivative $C_{12}H_6Me_2N_2SO_8$ [215°], a di-ethyl derivative [192°], and a di-isoamyl derivative [151°]. With aniline it forms the compound $C_{12}H_6(NHPh)_2(NO_2)_2SO_2$, crystallising from aniline in red prisms.

Tetra-nitro-di-oxy-di-phenyl sulphone $SO_2\{C_6H_2(NO_2)_2(OH)\}_2$. [253°]. Formed by further nitration of the preceding body (Annaheim, *B.* 11, 1668). Long-yellow needles.—K_2A''.—Na_2A'': octahedra.

TETRA-NITRO-DI-OXY-DIPHENYL DISULPHONIC ACID $\{C_6H(NO_2)_2(OH).SO_3H\}_2$. Formed by nitration (Limpricht, *A.* 261, 336).—Na_2A'' aq. K_2A'': yellow crystals.

***m*-NITRO-*p*-OXY-DI-PHENYL-THIO-UREA** [3:1]$C_6H_4(NO_2).NH.CS.NH.C_6H_4(OH)$ [1:4]. [152°]. Formed from *m*-nitro-phenyl-thiocarbimide and *p*-amido-phenol (Steudemann, *B.* 16, 2335). Needles, sl. sol. ether.

DI-NITRO-OXY-PHENYL-UREA $C_7H_6N_4O_6$ *i.e.* $C_6H_2(NO_2)_2(OH).NH.CO.NH_2$. *Uramido-di-nitro-phenol.* Formed by heating urea with di-nitro-amido-phenol (picramic acid) (Griess, *J. pr.* [2] 5, 1). Plates (from water).—AgA′: pp.

NITRO-DI-OXY-PHTHALIC ACID. *Methyl derivative* $C_6H(OMe)(OH)(NO_2)(CO_2H)_2$ [4:3:6:2:1]. *Normethylnitrohemipic acid.* [220°]. Formed by boiling its imide with KOH (Elbel, *B.* 19, 2310). White needles, v. sol. water.

Imide $C_6H(OMe)(OH)(NO_2){<}{\begin{matrix}C(NH)\\CO\end{matrix}}{>}O$. [252°]. Formed by boiling the oxim $C_6H(OMe)(OH)(NO_2)(CO_2H)CH:NOH$ with HOAc. Yellow needles, sol. hot water and alkalis.

Dimethyl derivative v. *Nitro*-HEMIPIC ACID.

Di-nitro-oxy-phthalic acid $C_6H(NO_2)_2(OH)(CO_2H)_2$. *Juglonic acid.* Formed by oxidation of juglone or its acetyl derivative by boiling with HNO_3.

Salts.—$A''(NH_4)_2$: reddish-yellow tables or thin needles, v. sol. water.—A″HK.—A′ Ba×: yellow tables (Bernthsen a. Semper, *B.* 18, 210).

NITRO-OXY-ISOPROPYL-BENZOIC ACID $CMe_2(OH).C_6H_3(NO_2).CO_2H$ [4:3:1]. [191°]. Formed by oxidising nitro-cuminic acid or nitro-cuminol with $KMnO_4$ (Widman, *B.* 15, 2549; 16,

2567; 21, 2232). Long needles (from water).—NH_4A' 2aq.— CaA'_2.—BaA'_2 6aq.—PbA'_2 5aq.—CuA'_2 $1\frac{1}{2}$aq.—AgA' $\frac{1}{2}$aq: crystals, m. sol. hot Aq.

Acetyl derivative [133°].

Ethyl ether EtA'. [96°].

Nitro-oxy-isopropyl-benzoic acid $CMe_2(OH).C_6H_3(NO_2)CO_2H$ [4:2:1]. [168°]. Formed by oxidising nitro-cymene or the acid $C_6H_3Pr(NO_2).C_2H_2.CO_2H$ with alkaline $KMnO_4$ (Widman, *B.* 19, 270; Söderbaum, *B.* 21, 2128). Tables (from ether), m. sol. hot water.

Isomeride *v.* NITRO-OXY-CUMINIC ACID.

Di-nitro-oxy-propyl-benzoic acid. *Lactone* $C_6H_4\langle{}^{C(NO_2)(CHMe.NO_2)}_{CO\text{———————}O}\rangle$. [90°]. Formed from ethylidene-phthalide and NO_2 (Gabriel, *B.* 19, 838). Colourless needles (from alcohol).

NITRO-β-OXY-*p*-ISOPROPYL-PHENYL-PROPIONIC ACID [4:2:1] $C_6H_3Pr(NO_2).CH(OH).CH_2.CO_2H$. [120°]. Formed by boiling $C_6H_3Pr(NO_2).CHBr.CH_2.CO_2H$ with aqueous Na_2CO_3 (Einhorn a. Hess, *B.* 17, 2024). Silvery plates.

Amide $C_{12}H_{16}N_2O_4$. [150°].

Anhydride $C_6H_3Pr(NO_2).CH\langle{}^{CH_2}_{O}\rangle CO$. [73°]. Formed by the action of cold aqueous Na_2CO_3 on bromo-nitro-cumyl-propionic acid. Crystals, v. sol. alcohol.

NITRO-DI-OXY-PYRIMIDINE $C_4H_3N_3O_4$ *i.e.* $CO\langle{}^{NH.CH}_{NH.CO}\rangle C.NO_2$. *Nitro-uracil.* Formed by heating the K salt of its carboxylic acid at 130° (Behrend, *A.* 229, 35; 240, 8). Yellow needles, which explode on heating. Yields iso-barbituric acid on reduction. Urea forms crystalline $C_5H_7N_5O_5$. Guanidine gives a similar salt $C_5H_8N_6O_4$ aq.—KA'aq: prisms, sl. sol. water.—CaA'_2 6aq. — BaA'_2 5aq. — ZnA'_2 $3\frac{1}{2}$aq. — CuA'_2 7CuO.

Nitro-di-oxy-pyrimidine carboxylic acid $C_5H_3N_3O_6$ *i.e.* $CO\langle{}^{NH.C(CO_2H)}_{NH.CO}\rangle C.NO_2$. Formed by warming di-oxy-methyl-pyrimidine (methyl-uracil) with H_2SO_4 and HNO_3 at 80° (Behrend, *A.* 229, 32; 240, 4; Köhler, *A.* 236, 32). Yellow crystals (containing 2aq).—KHA''aq: plates, sl. sol. water.—BaA'' $\frac{1}{2}$aq.—Ag_2A'' aq.—PbA'' $1\frac{1}{2}$aq.

Ethyl ether EtHA''. [250°]. Prisms.

(α)-NITRO-(*Py.* 3)-OXY-QUINOLINE $C_9H_6N_2O_3$. 'α'-*Nitro-carbostyril.* Formed by heating 'α'-nitro-*o*-amido-cinnamic acid with HClAq at 150° (Friedländer a. Lazarus, *A.* 229, 243). Needles (from alcohol). Does not melt below 220°.

(β)-Nitro-(*Py.* 3)-oxy-quinoline. [260°]. Formed in like manner from 'β'-nitro-amido-cinnamic acid (F. a. L.). Needles (from HOAc).

(γ)-Nitro-(*Py.* 3)-oxy-quinoline. [280°]. Formed by nitrating carbostyril (F. a. L.). Needles (from HOAc).

Methyl derivative [181°]. From the silver salt and MeI (Feer a. Königs, *B.* 18, 2396).

(*B.* 4)-Nitro-(*Py.* 3)-oxy-quinoline $\begin{matrix}CH{:}CH\text{——}C.CH{:}CH\\ CH{:}C(NO_2).C\text{—}N{:}C.OH\end{matrix}$ [168°]. Formed from di-methyl *o*-nitro-coumarinate and alcoholic NH_3, the resulting (3, 2, 1)-nitro-amido-cinnamic amide being heated with HClAq at 140° (Miller a. Kinkelin, *B.* 22, 1711). Prisms, v. sol. hot water.

(*B.* 4, 2)-Nitro-oxy-quinoline $\begin{matrix}C(OH){:}CH.C.CH{:}CH\\ CH{:}C(NO_2).C.\ N{:}CH\end{matrix}$ [136°]. Formed by nitrating (*B.* 2)-oxy-quinoline (Skraup, *M.* 3, 551) and by the action of nitric acid on (*B.* 2)-oxy-quinoline carboxylic acid (Schmidt a. Altschul, *B.* 20, 2697; 21, 2255) and on nitroso-oxy-quinoline (Mathëus, *B.* 21, 1642, 1886). Yellow needles.—$B'HNO_3$ aq: orange prisms, v. sol. hot alcohol.

Nitro-(*B.* 4)-oxy-quinoline. [173°]. Formed by heating its carboxylic acid with glycerin at 200° (Schmitt a. Engelmann, *B.* 20, 2693) and by the action of HNO_3 (S.G. 1·38) on nitroso-(*B.*4)-oxy-quinoline (Von Kostanecki, *B.* 24, 154). Needles, sl. sol. alcohol.

Nitro-(*B.* 3)-oxy-quinoline. [255°]. Formed by nitrating *m*-oxy-quinoline (Skraup, *M.* 3, 564). Yellow plates, decomposed by fusion.

Nitro-oxy-quinoline. Formed by the action of HNO_3 on a syrupy acid obtained by oxidation of cinchonine (Weidel a. Hazura, *M.* 3, 773). Crystalline powder, melting far above 300°.—$B'_2H_2PtCl_6$: monoclinic prisms.

(*B.* 1, 3)-Di-nitro-(*B.* 4)-oxy-quinoline $\begin{matrix}CH{:}C(NO_2)\text{—}C.CH{:}CH\\ C(NO_2){:}C(OH).C.\ N{:}CH\end{matrix}$ [276°]. Formed by the action of HNO_3 on o-oxy-quinoline carboxylic acid, and on *ana*-nitroso-*o*-oxy-quinoline (Schmitt a. Engelmann, *B.* 20, 2692; Kostanecki, *B.* 24, 155; *cf.* Bedall a. Fischer, *B.* 14, 1368). Plates.

NITRO-(*B.* 4)-OXY-QUINOLINE CARBOXYLIC ACID $C_9H_4(NO_2)N(OH)(CO_2H)$. Formed by boiling the nitrate of o-oxy-quinoline carboxylic acid with HOAc (Schmitt a. Engelmann, *B.* 20, 2693). Needles, sl. sol. HOAc.

NITRO-OXY-QUINONE. *Carbonyl derivative* $(C_6H_2O_2(NO_2)O)_2CO$. [260°]. Formed by oxidation of nitro-amido-phenyl carbonate by chromic acid mixture (Löwenberg, *C. C.* 1886, 390). Pale-brown needles.

Nitro-di-oxy-quinone $CO\langle{}^{CH:C(OH)}_{C(OH):C(NO_2)}\rangle CO$. Formed by warming nitro-di-imido-resorcin with dilute (10 p.c.) NaOHAq (Nietzki a. Schmidt, *B.* 22, 1659). Golden needles, m. sol. water.—K_2A'': orange needles.

Di-nitro-di-oxy-quinone $CO\langle{}^{C(NO_2):C(OH)}_{C(OH):C(NO_2)}\rangle CO$. *Nitranilic acid.*

Formation.—1. By the action of nitrous acid on hydroquinone (Nietzki, *B.* 10, 2147).—2. By the action of a mixture of fuming HNO_3 and conc. H_2SO_4 on di-acetyl-hydroquinone below −5°; the yield in this case being 65 p.c. (Nietzki, *B.* 16, 2092; 18, 499).—3. By adding dinitrohydroquinone to a cooled mixture of HNO_3 (3 pts.) and HOAc (6 pts.) (Nietzki, *A.* 215, 142).—4. By boiling *s*-di-nitro-di-amido-quinone with dilute potash (Nietzki, *B.* 20, 2116).—5. By the action of fuming HNO_3 on $CO_2H.C\langle{}^{CO.C(OH)}_{C(OH).CO}\rangle C.CO_2H$ (Hantzsch, *B.* 19, 2398; *cf.* Loewy, *B.* 19, 2385).

Preparation.—By slowly adding a hot saturated alcoholic solution of chloranil (4 pts.) to a concentrated aqueous solution of sodium nitrite (10 pts.) heated to 80°–90°; a yellow crystalline

pp. of the sodium nitranilate soon separates, and a small quantity which remains in solution is precipitated by NaOH; the whole is recrystallised from hot water (Nef, *B.* 20, 2027).

Properties.—Golden tables, v. sol. water and alcohol, insol. ether. When anhydrous it explodes at 170° without previous fusion. $FeCl_3$ gives a green crystalline pp. Chlorine forms oxalic acid and chloropicrin (Levy, *A.* 249, 66). On reduction it yields tetra-oxy-di-amido-benzene which gives *p*-phenylene-diamine on distillation with zinc-dust (Nietzki, *B.* 19, 2727). Hydroxylamine hydrochloride forms an explosive salt $C_6O_4(NO_2)_2(NH_4O)_2$ (Nef, *Am.* 11, 17).

S a l t s.—Na_2A'': dichroic monoclinic crystals; $a:b:c = \cdot946:1:\cdot985$; $\beta = 87° 51'$.—K_2A'': yellow needles (from hot water).—$(NH_4)_2A''$.—BaA'': plates, insol. water.

Di-nitro-di-oxy-quinone. A product of the action of nitrous acid on protocatechuic acid dissolved in ether (Gruber, *B.* 12, 519). Greenish-yellow needles, v. sol. water.—Na_2A'' 2aq: explodes when heated.

NITRO-OXY-STYRENE. *Methyl derivative* [1:2:4] $C_6H_3(OMe)(NO_2).CH:CH_2$. [89°]. Formed, together with the di-nitro- derivative $C_6H_2(OMe)(NO_2)_2.C_2H_3$ [163°], by the action of conc. HNO_3 on [4:1] $C_6H_4(OMe).CH:CH.CO_2H$ (Einhorn a. Grabfield, *A.* 243, 366). Crystals, volatile with steam. Yields a dibromide [79°]. Forms, on oxidation, nitranisic acid [187°].

NITRO-OXY-STYRYL METHYL KETONE *Methyl derivative* $C_{11}H_{11}NO_4$ *i.e.* [4:3:1] $C_6H_3(OMe)(NO_2).CH:CH.CO.CH_3$. [159°]. Formed by nitration of the ketone, and also by condensation of $C_6H_3(OMe)(NO_2)CHO$ with acetone (Einhorn a. Grabfield, *A.* 243, 364). Yellow needles (from water), sol. ether.

NITRO-OXY-SULPHO-BENZOIC ACID $C_7H_5NSO_8$ *i.e.* $C_6H_2(NO_2)(OH)(SO_3H)(CO_2H)$. Formed from nitro-o-oxy-benzoic acid and fuming H_2SO_4 (Mandt, *B.* 10, 1701).—$Ba_3A'''_2$ 12aq: hair-like needles.

NITRO-OXY-TOLUENE *v.* NITRO-CRESOL.

Nitro-di-oxy-toluene *v.* NITRO-ORCIN.

Nitro-tetra-oxy-toluene $C_6Me(NO_2)(OH)_4$. [157°]. Formed by the action of HCl and $SnCl_2$ on nitro-di-oxy-toluquinone (Kehrmann a. Brasch, *J. pr.* [2] 39, 382). Black needles, forming a violet powder. Its solution forms HCy, oxalic acid, and other products on boiling.

Di-nitro-di-oxy-toluene $C_6HMe(NO_2)_2(OH)_2$ [1:3:5:2:4]. *Di-nitro-cresorcin.* [90°]. Formed from cresorcin and HNO_3 (Von Kostanecki, *B.* 20, 3136). Needles, m. sol. cold water.

NITRO-OXY-o-TOLUIC ACID $C_8H_7NO_5$ *i.e.* $C_6H_2Me(OH)(NO_2)CO_2H$ [1:4:*x*:2]. [172°]. Formed by nitration of oxy-o-toluic acid (Kostanecki a. Niementowski, *B.* 18, 254). Needles, sol. hot Aq.

Nitro-oxy-*m*-toluic acid $C_6H_2Me(OH)(NO_2).CO_2H$ [3:4:5:1]? [87°]. Formed by heating (4,3,1)-oxy-toluic acid with conc. HNO_3 (Mahon, *Am.* 4, 186). Yellow needles, sl. sol. water. Its salts explode when heated.—CaA'_2 4aq.—BaA'_2 4aq: orange needles; crimson when anhydrous.

Nitro-oxy-*p*-toluic acid $C_6H_2Me(OH)(NO_2).CO_2H$ [4:3:*x*:1]. [188°]. Formed by the action of nitrous acid on (3,4,1)-amido-toluic acid (Ahrens, *Z.* 1869, 105). Golden needles.—BaA'_2 7aq: scarlet, sl. sol. alcohol.

Nitro-oxy-toluic acid. *Methyl derivative* $C_6H_2Me(OMe)(NO_2)CO_2H$. [175°]. Formed from the methyl ether of thymol and dilute HNO_3 (Paterno a. Canzoneri, *G.* 9, 445). Slender needles, v. sol. alcohol.—BaA'_2 2aq: straw-coloured crystals.

Ethyl derivative [162°]. Formed, in like manner, from the ethyl ether of thymol. Long slender needles.

Nitro-ω-oxy-o-toluic acid $C_6H_3(NO_2)(CH_2OH)CO_2H$ [4:2:1]. [129°]. Formed by dissolving nitro-phthalide in aqueous KOH (Hoenig, *B.* 18, 3451). Minute needles.—AgA'.

Tri-nitro-oxy-*m*-toluic acid $C_6HMe(OH)(NO_2)_3CO_2H$ [1:3:2:4:6:5]. *Nitrococcic acid.* [170°–180°]. Formed by the action of boiling nitric acid (S.G. 1·37) on cochineal (De la Rue, *A.* 64, 23; Liebermann a. Dorp, *A.* 163, 100) and on (5,3,1)-oxy-toluic acid (Kostanecki a. Niementowski, *B.* 18, 250). Colourless plates (containing aq). On boiling with moist Ag_2O it yields silver tri-nitro-cresol and CO_2.—$(NH_4)_2A''$ ½aq.—BaA'_2 aq.—Ag_2A'': needles.

NITRO-OXY-*m*-TOLUIC ALDEHYDE $C_8H_7NO_4$ *i.e.* $C_6H_2Me(NO_2)(OH)CHO$ [5:3:2:1]. [141°]. Formed by warming oxy-toluic aldehyde with HNO_3 (Schotten, *B.* 11, 788). Yellow needles, sl. sol. hot water.

Nitro-oxy-*m*-toluic aldehyde $C_6H_2Me(NO_2)(OH)CHO$ [5:3:4:1]. [152°]. Formed by nitrating (4,3,1)-oxy-toluic aldehyde (S.). Needles, sl. sol. hot water.

NITRO-DI-OXY-TOLUQUINONE $C_6Me(NO_2)(OH)_2O_2$ [2:5:3:6:4:1]. *Tolunitranilic acid.* [180°]. Formed by the action of a dilute alcoholic solution of KNO_2 on tri-chloro-toluquinone (Kehrmann, *B.* 21, 1779; *J. pr.* [2] 39, 377). Golden needles (containing *x*aq). Its aqueous solution decomposes on boiling forming HCy, oxalic acid, and CO_2.—K_2A'' 3aq: yellowish-red prisms.

DI-NITRO-DI-OXY-DITOLYL $C_{14}H_{12}N_2O_6$. [273°] (G.); [270°] (D.). Formed by boiling tetrazo-ditolyl sulphate with HNO_3 (Gerber, *B.* 21, 750); by the action of nascent nitrous acid on di-amido-ditolyl (the yield being quantitative); and by heating di-oxy-ditolyl di-carboxylic acid with HNO_3 (Deninger, *J. pr.* [2] 40, 300; *B.* 21, 1639). Yellow needles (from toluene or pyridine).

NITRO - OXY - TOLYLENE - ETHENYL - AMIDINE $C_9H_9N_3O_3$. [256°]. Formed by the action of alcoholic ammonium sulphide on the acetyl derivative of di-nitro-*p*-toluidine (Bankievitch, *B.* 21, 2404). Lustrous green needles, not affected by HClAq at 200°.

NITRO-PENTANE $C_5H_{11}NO_2$ *i.e.* $Pr.CH_2.CH_2.NO_2$. (150°–160°). Formed from isoamyl iodide and $AgNO_2$ (V. Meyer, *B.* 5, 203; *A.* 171, 43; 175, 135).

Di-nitro-pentane $C_4H_9.CH(NO_2)_2$. Formed from di-amyl ketone and HNO_3 (Chancel, *C. R.* 94, 399). Heavy oil. Forms *n*-valeric acid on reduction.—$KC_5H_9N_2O_4$.—AgA'.

o-**NITRO-PHENOL** $C_6H_5NO_3$ *i.e.* $C_6H_4(NO_2).OH$ [1:2]. Mol. w. 139. [45°]. (214°). S.V.S. 107·64 (Schiff).

Formation.—1. Together with the *p*-isomeride by nitration of phenol (Hofmann, *A.* 103, 347; Fritzsche, *A.* 110, 150; *J. pr.* 73, 293; Gold-

stein, *B.* 11, 1943).—2. By heating o-bromo-nitro-benzene [38°] or o-chloro-nitro-benzene with aqueous potash in sealed tubes (Zincke a. Walker, *B.* 5, 117; Engelhardt a. Latschinoff, *B.* 3, 423).—3. By boiling o-di-nitro-benzene with NaOHAq (Laubenheimer, *B.* 9, 1828).—4. Together with *p*-nitro-phenol by boiling diazobenzene sulphate with nitric acid (Nölting a. Wild, *B.* 18, 1338).—5. Together with *p*-nitro-phenol by adding liquid N_2O_4 to cooled CS_2 containing C_6H_5ONa in suspension (Schall, *B.* 16, 1901).—6. By heating diazo-benzene nitrate with dry toluene, nitrogen being given off (Remsen a. Orndorff, *Am.* 9, 390).—7. By the action of $NaNO_2$ and H_2SO_4 on aniline (Deninger, *J. pr.* [2] 40, 298).

Preparation.—Phenol (1 pt.) is slowly added to a mixture of HNO_3 (1 pt. of S.G. 1·38) and water (6 pts.), cooled to 0°; the product is neutralised with Na_2CO_3 and distilled with water (Neumann, *B.* 18, 3320).

Properties.—Light-yellow prisms or needles, v. sol. alcohol and ether, sl. sol. cold water.

Reactions.—1. Reduced by tin and HCl to o-amido-phenol.—2. Aqueous NH_3 (35 p.c.) at 160°-200° yields *o*-nitro-aniline (Merz a. Ris, *B.* 19, 1749).—3. *Phenyl-hydrazine* dissolved in xylene at 100° produces o-amido-phenol, benzene, NH_3, and nitrogen (Barr, *B.* 20, 1497).

Salts.—The colour of the salts has been examined by Carnelley a. Alexander (*C. J. Proc.* 4, 64).—NH_4A': scarlet plates.—$KA'\frac{1}{2}aq$: orange-red crystals (F.).—$KA'aq$ (Post, *B.* 8, 1552). S. 16 at 6°; 21 at 15°.—NaA': scarlet plates, v. e. sol. water.—BaA'_2. S. 9 at 6°. $SrA'_2 3aq$.—$CaA'_2 4aq$: plates.—$CaA'_2 aq$: orange needles.—AgA': orange-red pp. S. ·14 at 15°.

Acetyl derivative $C_6H_4(NO_2)OAc$. [41°]. (253°). Long colourless needles or prisms, v. sol. alcohol (Böttcher, *B.* 16, 1933).

Benzoyl derivative $C_6H_4(NO_2)(OBz)$. [59°]. Formed from o-nitro-phenol and BzCl (Hübner, *A.* 210, 386; Schiaparelli, *G.* 11, 73; Neumann, *B.* 18, 3320; 19, 2018). Prisms or needles. Yields on nitration the compound $C_6H_4(NO_2).O.CO.C_6H_4(NO_2)$ [1:3] [126°], crystallising in needles.

Methyl ether $C_6H_4(NO_2)(OMe)$. o-*Nitro-anisole.* [9°]. (277°) at 735 mm. Formed, together with the *p*- isomeride, by nitration of anisole. Formed also by methylation of o-nitro-phenol (Brunck, *Z.* 1867, 204; Mühlhauser, *A.* 207, 237) and by boiling *o*-chloro-nitro-benzene with NaOMe in HOMe (De Bruyn, *R. T. C.* 9, 200). Oil. Converted into *o*-nitro-aniline by heating with ammonia (Salkowski, *A.* 174, 278).

Ethyl ether $C_6H_4(NO_2)(OEt)$. o-*Nitro-phenetol.* (267°). Formed by ethylation of *o*-nitro-phenol (Groll, *J. pr.* [2] 12, 207; Seidel, *J. pr.* [2] 42, 448) and by heating $C_6H_4Cl(NO_2)$ with NaOEt (De Bruyn). Oil. When distilled with alcoholic potash it yields $C_6H_4(NH_2)(OEt)$ and no azo- compound; but when reduced in alcoholic solution by sodium-amalgam it forms $N_2(C_6H_4OEt)_2$ and $N_2O(C_6H_4OEt)_2$ (Schmitt a. Möhlau, *J. pr.* [2] 18, 200).

Bromo-ethyl ether $C_6H_4(NO_2)O.C_2H_4Br$. [44°]. Formed from $C_6H_4(NO_2)(ONa)$ and ethylene bromide (Weddige, *J. pr.* [2] 24, 246). Yellow prisms (from alcohol).

Reactions.—1. With an alcoholic solution of NH_3 it yields $C_6H_4(NO_2)O.C_2H_4NH_2$ [73°] and $NH(C_2H_4O.C_6H_4NO_2)_2$ [192°].—2. Heated with potassium salicylic ether $C_6H_4(OK)CO_2Et$ in alcoholic solution it yields two products: (*a*) an ether $C_6H_4(NO_2).O.C_2H_4.O.C_6H_4.CO_2Et$ [c. 100°] saponified by HCl yielding the corresponding acid [145°], which may be reduced to an amido- acid [110°] whose hydrochloride melts at 177°; and (*b*) a compound of the formula $C_6H_4(NO_2).O.C_2H_4.O.CO_2.C_6H_4OH$ [106°] which gives an acetyl derivative [80°] (Wagner, *J. pr.* [2] 27, 212). — 3. Heated with [4:1] $C_6H_4(OK)CO_2Et$ in alcoholic solution it forms o-nitro-phenoxy-ethyl-*p*-oxy-benzoic ether [103°] which is saponified by HCl at 140°, forming an acid $C_6H_4(NO_2)O.C_2H_4.O.C_6H_4.CO_2H$ [c. 206°]. The corresponding amido- acid melts at 185° (Wagner).—4. Potassium benzoate at 140° yields $C_6H_4(NO_2).O.C_2H_4.OBz$ [77°].

Amido-ethyl ether $C_6H_4(NO_2).O.C_2H_4NH_2$. [73°]. Formed as above. Small plates (from water). Yields a benzoyl derivative [95°] and a dibenzoyl derivative $C_6H_4(NO_2).O.C_2H_4.NBz_2$ [122°]. The benzoyl derivative reduced by tin and hydrochloric acid yields $C_2H_4{<}\begin{matrix}NH.CPh\\O.C_6H_4\end{matrix}{>}N$. [151°] (Weddige, *J. pr.* [2] 24, 250).

Ethylene ether $C_2H_4(OC_6H_4.NO_2)_2$. [163°]. Formed from $C_6H_4(NO_2)ONa$ and $C_2H_4Br_2$.

Isobutyl ether (275°–280°). S.G. $\frac{20}{}$ 1·136 (Riess, *B.* 3, 780).

Benzyl ether $C_6H_5.CH_2.O.C_6H_4(NO_2)$. [29°]. From the K salt and C_7H_7Cl (Kumpf, *A.* 224, 121).

p-Nitro-benzyl ether $C_6H_4(NO_2).CH_2.O.C_6H_4.NO_2$. [129°]. Needles (K.).

Phenacyl ether $C_6H_4(NO_2).O.CH_2.CO.C_6H_5$. [118°]. (194°). Formed from the K salt and ω-bromo-aceto-phenone (Lellmann a. Donner, *B.* 23, 172). Needles, m. sol. alcohol. $ZnCl_2$ and HCl at 100° convert it into $C_6H_4{<}\begin{matrix}O.CH_2\\N:CPh\end{matrix}$ [103°] crystallising in needles, and forming the salts $B'H_2PtCl_6$ and $B'HAuCl_4$.

m-Nitro-phenol $C_6H_4(NO_2)OH$[1:3]. [96°]. (194° at 70 mm.). Obtained from *m*-nitro-aniline by the diazo- reaction (Fittig a. Bantlin, *B.* 7, 179; 11, 2099; Henriques, *A.* 215, 323; Wagner, *J. pr.* [2] 32, 70). Yellow crystals, sol. hot water; not volatile with steam.—$KA'2aq$: orange needles. S. 12 at 6° (Post a. Mehrtens, *B.* 8, 1552).—$BaA'_2 2aq$. S. 1·7 at 6°.—$PbA'(OH)$. S. ·013 at 15°.—AgA': brownish-red pp.

Benzoyl derivative $C_6H_4(NO_2).OBz$. [95°]. Pale-yellow crystals (Neumann, *B.* 19, 2979). Nitric acid (S.G. 1·48) converts it into the crystalline *m*-nitro-benzoyl derivative $C_6H_4(NO_2).O.CO.C_6H_4(NO_2)$ [129°].

Methyl ether MeA'. [38°]. (254°). Needles, volatile with steam (Bantlin).

Ethyl ether EtA'. [34°]. (264°) (Bantlin, Wagner, *J. pr.* [2] 32, 71).

Bromo-ethyl ether C_2H_4BrA'. [39°]. Formed, with the following, from the K salt and ethylene bromide (Weddige, *J. pr.* [2] 24, 255).

Ethylene ether $C_2H_4A'_2$. [139°].

p-Nitro-phenol $C_6H_4(NO_2).OH$. [114°]. S.V.S. 108·28 (Schiff).

Formation.—1. Together with the o-isomer-

ide, by the nitration of phenol, especially at low temperatures (Fritzsche, *J. pr.* 75, 257; Goldstein, *J. R.* 10, 353).—2. By heating *p*-chloro-nitro-benzene [85°] or bromo-nitro-benzene [125°] with aqueous potash at 130° (Engelhardt a. Latschinoff, *B.* 3, 423; Richter, *B.* 4, 460).—3. From acetanilide by nitrating, and heating the [4:1]$C_6H_4(NO_2)$(NHAc) with conc. NaOHAq (Wagner, *B.* 7, 76).—4. From *p*-nitro-aniline by the diazo- reaction (Fittig, *B.* 7, 280).—5. By dry distillation of nitro-*o*-oxy-benzoic acid (Schmidt a. Cook, *K.* 3, 41).—6. By oxidation of nitroso-phenol (Baeyer, *B.* 7, 965).—7. Together with the *o*-isomeride, by adding liquid N_2O_4 to cooled CS_2 containing C_6H_5ONa in suspension (Schall, *B.* 16, 1901).—8. By the action of $NaNO_2$ (in excess) and H_2SO_4 on aniline, *o*-nitro-phenol being also formed (Deninger, *J. pr.* [2] 40, 298).

Preparation.—The mixture of *o*- and *p*-nitro-phenols is distilled with steam. The residue is dissolved in hot water and mixed with excess of Na_2CO_3 when $C_6H_4(NO_2)ONa$ crystallises out on cooling (Salkowski, *A.* 174, 280).

Properties.—Slender colourless needles (from water. Dimorphous (Lehmann, *Z. K.* 1, 45). V. sol. alcohol. Not volatile with steam. Sol. hot HClAq (Kollrepp, *A.* 234, 1).

Reactions.—1. Distillation with PCl_5 yields *p*-chloro-nitro-benzene [85°].—2. Aqueous *ammonia* at 160° to 200° forms *p*-nitro-aniline (Merz a. Ris, *B.* 19, 1749).—3. *Phenyl-hydrazine* at 100° produces *p*-amido-phenol, benzene, NH_3, and nitrogen (Barr, *B.* 20, 1499).

Salts.—The colour of the salts has been examined by Carnelley (*C. J. Proc.* 4, 64).—NaA′4aq: yellow tables.—NaA′2aq. *Heat of neutralisation* 12,840 (Alexejeff a. Werner, *Bl.* [3] 2, 718).—$NaHA'_2$2aq: orange-red prisms (from water).—KA′2aq. S. 4·5 at 6° (Post a. Mehrtens, *B.* 8, 1552).—$KHA'_2$2aq.—$BaA'_2$8aq: monoclinic prisms. S. 1 at 6°; 1·3 at 15°.—$BaH_2A'_4$4aq. — $SrA'_2$7aq: yellow needles. — $CaA'_2$4aq.—$CaH_2A'_4$8aq.—$MgA'_2$8aq.—$Pb_5O_2A'_6$. — $Pb_2HA'_5$. — AgA′aq: scarlet pp., changing to orange prisms.—AgA′2aq. S. ·3 at 15°.—$AgHA'_2$aq: yellowish green laminæ.—$Ag_5HA'_6$: purple needles.

Benzoyl derivative $C_6H_4(NO_2)$.OBz. [142·5°]. Colourless efflorescent needles (from alcohol) (Schiaparelli, *G.* 11, 73; Neumann, *B.* 19, 2020). On treatment with HNO_3 (S.G. 1·48) it forms [4:1]$C_6H_4(NO_2)$.O.CO.$C_6H_4NO_2$[1:3] [135·5°].

Methyl ether MeA′. [51°]. (259°). Formed by methylation of *p*-nitro-phenol (Brunck, *Z.* [2] 3, 202; Willgerodt a. Ferko, *J. pr.* [2] 33, 152; Skraup, *M.* 6, 761). Formed also by heating *p*-chloro-nitro-benzene with KOH dissolved in MeOH (Willgerodt, *B.* 14, 2632; 15, 1004). Prisms.

Ethyl ether EtA′. [58°]. (283°) (Andrew, *J. pr.* [2] 21, 331). Formed from the Ag salt and EtI (Fritzsche) and also from C_6H_5OEt and fuming HNO_3 (Hallock, *Am.* 1, 271). Obtained also by boiling *p*-chloro-nitro-benzene with KOH and dilute (60 p.c.) alcohol (Willgerodt, *B.* 15, 1002). Prepared by heating $C_6H_4(NO_2)$(OK) with $KEtSO_4$ in alcoholic solution for 3 hours (Willgerodt a. Ferko, *J. pr.* [2] 33, 153). Prisms. Sodium-amalgam rapidly reduces it, in alcoholic solution, to $N_2(C_6H_4.OEt)_2$ (Schmitt a. Möhlau, *J. pr.* [2] 18, 199).

Ethylene ether $C_2H_4A'_2$. [143°]. Formed, at the same time as the bromo-ethyl ether, by heating the Na compound with ethylene bromide at 140° (Weddige, *J. pr.* [2] 21, 127; 24, 254).

Bromo-ethyl-ether $CH_2Br.CH_2A'$. [63°]. Yellowish plates, insol. water, v. sol. alcohol.

Reactions.—1. Heated with potassium *p*-oxy-benzoic ether [4:1] C_6H_4(OK).CO_2Et it forms $C_6H_4(NO_2)$.O.C_2H_4.O.C_6H_4.CO_2Et [131°], which when saponified by HClAq at 130° yields the corresponding acid [218°] (Wagner, *J. pr.* [2] 27, 224).—2. Alcoholic [2:1]C_6H_4(OK).CO_2Et forms $C_6H_4(NO_2)$.O.C_2H_4.O.CO_2.C_6H_4OH [131°] and the ether $C_6H_4(NO_2)$.O.C_2H_4.O.C_6H_4.CO_2Et [c. 81°] whence HCl liberates the acid [132°].

Amido-ethyl ether $C_2H_4(NH_2)A'$. [109°]. Formed by heating the bromo-ethyl ether with alcoholic ammonia. Yellow scales (from water).

Isobutyl ether (285°–290°). S.G. $\frac{20}{}$ 1·105.

Benzyl ether $C_6H_5CH_2A'$. [106°]. Prisms. Yields on nitration a compound melting at 168° (Kumpf, *A.* 224, 123).

p-Nitro-benzyl-ether [183°]. Needles.

Fourth and fifth nitro-phenols have been described by Fittica (*J. pr.* [2] 24, 5; *B.* 13, 711) but their existence has not been confirmed by other chemists (Natanson, *B.* 13, 415).

(α)-Di-nitro-phenol $C_6H_3(NO_2)_2(OH)$ [4:2:1]. [114°]. S. 4·8 at 100°; ·5 at 18°; ·014 at 0° (Gruner, *J. pr.* 102, 222).

Formation.—1. By nitration of phenol, *o*-nitro-phenol, and *p*-nitro-phenol (Laurent, *A. Ch.* [3] 3, 212; Körner, *Z.* [2] 2, 662, 731).—2. From anisole by nitration and saponification (Cahours, *A. Ch.* [3] 25, 22).—3. From di-nitro-amido-phenol (picramic acid) by elimination of NH_2 (Griess, *A.* 113, 210).—4. From chloro-di-nitro-benzene [50°] and bromo-di-nitro-benzene [72°] by heating with potash (Clemm, *J. pr.* [2] 1, 145; Engelhardt a. Latschinoff, *B.* 3, 97).—5. By boiling *i*-tri-nitro-benzene with aqueous Na_2CO_3 or by heating it with water at 160° (De Bruyn, *R. T. C.* 9, 191).—6. By boiling *i*-di-nitro-aniline with KOHAq for a long time (Willgerodt, *B.* 9, 979).—7. From di-nitro-di-ethyl-aniline and dilute potash (Van Romburgh, *R. T. C.* 2, 35).

Properties.—Yellowish rectangular plates (from water), v. sl. sol. cold alcohol.

Reactions.—1. Yields only picric acid on further nitration (Hübner a. Schneider).—2. Aqueous KCy at 70° forms potassium meta-purpurate $C_7H_4KN_3O_4$ which separates as brownish-red crystals with green lustre (Pfaundler a. Oppenheim, *Z.* 1865, 470; Sommaruga, *A.* 157, 335).

Salts.—KA′aq. S. 1·4 at 6° (Post a. Mehrtens, *B.* 8, 1554); 1·6 at 7° (Hübner a. Schneider, *A.* 167, 92).—KA′aq (Romburgh).—NaA′aq.—$BaA'_2$7aq: golden needles.—$BaA'_2$6aq: yellow needles.—$BaA'_2$5aq: orange prisms. S. ·3 at 7°.—$BaA_2$4aq: monoclinic crystals (P. a. M.).—$MgA'_2$9aq.—$MgA'_2$12aq.—Pb(OH)A′2aq. S. ·08 at 15°.—$MnA'_2$5aq.—$NiA'_2$8aq.—AgA′aq. S. ·4 at 15°.

Benzoyl derivative $C_6H_3(NO_2)_2OBz$. Plates (from alcohol) (Laurent a. Gerhardt, *A.* 75, 77).

m-Nitro-benzoyl derivative [161°]. Formed by nitration of [2:1] $C_6H_4(NO_2).OBz$ or of the *p*-isomeride (Neumann, *B.* 18, 3322; 19, 2021). Needles.

Methyl ether MeA′. [88°]. Formed by boiling anisole or anisic acid with fuming HNO_3 (Cahours, *A.* 69, 236) or by heating (4, 2, 1)-chloro-di-nitro-benzene or *i*-tri-nitro-benzene with KOH dissolved in MeOH (Willgerodt, *B.* 12, 762; De Bruyn, *R. T. C.* 9, 190). Needles.

Ethyl ether EtA′. [86°]. Formed by the action of HNO_3 on C_6H_5OEt (Cahours, *A.* 74, 315) and on $N_2(C_6H_4.OEt\ [1:4])_2$ (Andreæ, *J. pr.* [2] 21, 335); and also in the same way as the methyl ether (W.). Needles.

Allyl ether C_3H_5A'. [47°].

Di-oxy-propyl ether $C_3H_5(OH)_2A'$. [c. 83°]. Formed from [1:2:4] $C_6H_3Cl(NO_2)_2$, glycerin, and KOH (W.).

Phenyl ether C_6H_5A'. [71°] (W.).

Benzyl ether $C_6H_5CH_2A'$. [149°].

p-Nitro-benzyl ether [201°] (Kumpf).

(β)-Di-nitro-phenol $C_6H_3(NO_2)_2(OH)$ [4:3:1]. [64°]. Formed, together with the (α)-isomeride, by nitrating o-nitro-phenol (Hübner a. Schneider, *A.* 167, 89; Salkowski, *A.* 174, 270; Körner, *G.* 4, 325). Pale-yellow needles (from water), sl. sol. water, v. e. sol. hot alcohol. Somewhat volatile with steam.—NaA′3aq: red needles.—KA′. S. 1·3 at 6°.—BaA'_2aq: golden needles. S. ·18 at 7°.—$MgA'_2$6aq.—$Pb_2OA'_2$. S. ·037 at 15°.—AgA′. S ·3 at 6° (Post a. Mehrtens, *B.* 8, 1552).—AgA′aq: red needles.

m-Nitro-benzoyl derivative [149°]. Got from [3:1] $C_6H_4(NO_2)OBz$ and HNO_3 (Neumann, *B.* 19, 2980). Yellow needles, sl. sol. ether.

Methyl ether MeA′. [117°]. Converted by NH_3Aq at 130° into di-nitro-aniline [138°].

Ethyl ether EtA′. [58°]. Needles.

Benzyl ether $PhCH_2A'$. [76°]. Prisms. Yields [4:1] $C_6H_4(NO_2).CH_2.O.C_6H_3(NO_2)_2$ [1:2:6] [137°] on nitration (Kumpf, *A.* 224, 130).

(γ)-Di-nitro-phenol $C_6H_3(NO_2)_2(OH)$ [5:3:1]. [104°] (B.); [122°] (De B.). Formed, together with the (δ)- and (ε)- isomerides, by nitration of *m*-nitro-phenol (Bantlin, *B.* 11, 2103; *A.* 215, 324). Obtained also by heating its methyl ether with conc. HClAq at 180° (De Bruyn, *R. T. C.* 9, 208). Needles, volatile with steam.—KA′2aq.—$BaA'_2$3aq.—$BaA'_2$2aq: red feathery crystals.

Methyl ether MeA′. [96°] (B.); [105°] (De B.) (above 360°). Formed by heating *s*-tri-nitro-benzene with NaOMe in HOMe for 24 hours (De Bruyn). Needles.

(δ)-Di-nitro-phenol $C_6H_3(NO_2)_2(OH)$ [4:3:1]. [134°]. Prepared, together with the (ε)- and (γ)-isomerides, by nitration of *m*-nitro-phenol (Bantlin, *B.* 11, 2104). Colourless needles, not volatile with steam.—$BaA'_2$3aq: brown prisms.

Methyl ether MeA′. [70°]. Needles.

(ε)-Di-nitro-phenol $C_6H_4N_2O_5$ *i.e.* $C_6H_3(NO_2)_2(OH)$ [3:2:1]. [144°]. Prepared, together with the (γ) and (δ) isomerides, by nitration of *m*-nitro-phenol (Bantlin, *B.* 11, 2104). Yellow needles (from water).—KA′2aq: yellow needles.—BaA'_2: brown needles.

Methyl ether MeA′. [118°]. Tables.

Tri-nitro-phenol $C_6H_2(NO_2)_3OH$ [6:4:2:1]. *Picric acid.* Mol. w. 229. [122°]. S. ·626 at 5°; 1·225 at 20°; 3·89 at 77° (Marchand, *J. pr.* 64, 91). R_∞ 78·82 in a 1·74 p.c. benzene solution (Kanonnikoff, *J. pr.* [2] 31, 348).

Formation.—1. By the action of hot nitric acid on phenol, tri-bromo-phenol, o- and *p*- nitro-phenols, (α)- and (β)- di-nitro-phenols, saligenin, salicylic aldehyde, salicin, salicylic acid, phlorizin, indigo, coumarin, aloes, gum benzoïn, balsam of Peru, and from the resin of *Xanthorrhœa hastilis* (Hausmann, *Journ. de Phys. et de Chimie*, 1788; Welter, *A. Ch.* 29, 301; Liebig, *P.* 13, 191; 14, 466; *A.* 9, 80; 39, 350; Dumas, *A. Ch.* [2] 53, 178; [3] 2, 228; Laurent, *A. Ch.* [3] 3, 221; *A.* 43, 219; Perra, *D. P. J.* 165, 386; Piria, *A.* 56, 63; Stenhouse, *A.* 57, 88; 66, 243; Carey Lea, *Am. S.* [2] 26, 279; E. Kopp, *A. Ch.* [3] 13, 233; Delalande, *A.* 45, 337; Marchand, *A.* 48, 336; 52, 345; Schunck, *A.* 39, 6; 65, 234).—2. By boiling (1,2,4,6)-chloro-tri-nitro-benzene (picryl chloride) with aqueous Na_2CO_3 (Engelhardt a. Latschinoff, *B.* 3, 98; Clemm, *J. pr.* [2] 1, 145).—3. By oxidation of *s*-tri-nitro-benzene with K_3FeCy_6 in slightly alkaline solution (Hepp, *B.* 13, 2346).—4. By heating iodo-benzene with silver nitrite at 150° (Geuther, *A.* 245, 100).

Preparation.—Phenol (1 mol.) is dissolved in conc. H_2SO_4 and the resulting phenol sulphonic acid treated with HNO_3 (4½ mols. of S.G. 1·35) (Schmitt a. Glutz, *B.* 2, 52).

Properties. — Light-yellow laminæ (from water) or trimetric prisms (from ether). May be sublimed if slowly heated, but if a few milligrammes be dropped into a red-hot tube violent detonation occurs; with a larger quantity a less violent decomposition occurs (Berthelot, *A. Ch.* [6] 16, 21). Sl. sol. water, a ·01 p.c. solution being distinctly yellow. V. sol. alcohol and ether. Tastes bitter. Dyes silk and wool yellow. It is poisonous. Forms crystalline compounds with aromatic hydrocarbons (Fritzsche, *J. pr.* 73, 212; *A.* 109, 247).

Reactions.—1. *Bleaching-powder* yields, on boiling, chloropicrin CCl_3NO_2 and tetra-chloro-quinone. A mixture of $KClO_3$ and HCl acts in like manner.—2. Distillation with aqueous NaOBr forms bromopicrin (Stenhouse, *P. M.* [4] 8, 363). 3. *Ferrous sulphate* and *lime* reduce it to di-nitro-amido-phenol (picramic acid) (Girard, *C. R.* 36, 421).—4. *Tin* and HClAq reduce it to tri-amido-phenol (picramine) (Roussin, *Bl.* 1861, 60; Beilstein, *A.* 130, 244). *Iodide of phosphorus* acts in like manner on its aqueous solution (Lautemann, *A.* 125, 1). — 5. Hot conc. KCyAq forms a blood-red solution of potassium isopurpurate which crystallises in brownish-red scales with green lustre having either the formula $KC_8H_4N_5O_6$ (Hlasiwetz, *A.* 110, 289) or $KC_8H_2N_5O_5$ (Baeyer, *J.* 1859, 458). Ammonium chloride converts this salt into an ammonium salt $NH_4C_8H_4N_5O_6$ greatly resembling murexide.—6. PCl_5 yields $C_6H_2Cl(NO_2)_3$ (Pisani, *C. R.* 39, 852).

Salts. — Explode when struck or when strongly heated. — NH_4A': trimetric prisms (Laurent, *Rev. Scient.* 9, 26).—LiA′. S.G. $\frac{12}{}$ 1·716: slender yellow prisms (Beamer a. Clarke, *Am.* 1, 153).—$_x$NaA′. S. about 8 at 15°. S. (alcohol) 1·25 in the cold (Hager, *Pharm. Centr.* 22, 225).- KA′. Trimetric prisms; *a*:*b*:*c* = 1:2·70:1·88 (Laurent, *Rev. Scient.* 10, 26). S. ·4 at 15°; 7 at 100°. S. (alcohol) ·04 (Hager). Explodes when struck, giving off CO_2, CO, and

nitrogen, with smaller quantities of hydrogen and CH_4, and leaving a residue of KCy, carbon, and K_2CO_3 (Sartan a. Vieille, *C. R.* 93, 61).—BaA'_2 5aq: monoclinic crystals.—BaA'_2 6aq. S. (of BaA'_2) 1·2 at 17° (Tscheltzoff, *A. Ch.* [6] 8, 233).—BaA'_2 4aq. S. ·6 at 6° (Post a. Mehrtens).—CaA'_2 5aq. S. (of CaA'_2) 50 at 20°.—SrA'_2 5aq: yellow crystals (Marchand). S. (of CaA'_2) 1·4 at 20°.—MgA'_2 8aq. S. (of MgA'_2) 10 at 22°.—$MgA'_2$3NaA' 9aq (Müller, *Z.* 1865, 189). —CdA'_2 7aq.—$CdA'_2 3NH_3$ (Carey Lea, *Am. S.* [2] 31, 78).—$CdA'_2$6NaA' 12aq.—CuA'_2 5aq: green needles.—CuA'_2 8aq.—CuA'_2 10aq.—$CuA'_2 4NH_3$.—CoA'_2 5aq: brown needles.—$CoA'_2 4NH_3$.—$CoA'_2$6NaA' 12aq.—NiA'_2 8aq.—$NiA'_2$6NaA' 12aq.—FeA'_2 5aq: yellow crystals.—$FeA'_2$6NaA' 12aq.—$FeA'_2(OH)$ 8aq. — MnA'_2 5aq (Müller). —MnA'_2 8aq (Marchand).—PbA'_2 aq (E. Kopp, *A. Ch.* [3] 13, 233). S. ·9 at 15°.—PbA'_2 2aq.—PbA'(OH). — $Pb_3A'_2O_2$ 3aq. — $Pb_5A'_2O_4$. — Pb(OAc)A' 4aq. — $Hg_2A'_2$. — $AlA'_2(OH)$ 8aq. — ZnA'_2 8aq. S. (of ZnA'_2) 12·5 in the cold.—$ZnA'_2 3NH_3$.—$ZnA'_2$6NaA' 12aq.—AgA' aq. S. ·9 at 15°.—$AgA'_2 2NH_3$. Compounds of picric acid with organic bases and with aromatic hydrocarbons, are described under those bases and hydrocarbons.

Acetyl derivative $C_6H_2(NO_2)_3OAc$. [76°]. Yellow crystals (Tommasi a. David, *C. R.* 77, 207).

Benzoyl derivative $C_6H_2(NO_2)_3OBz$.

Methyl ether MeA'. *Trinitroanisole.* [60°]. (C.); [64°] (Post a. Mehrtens, *B.* 8, 1552). Formed by nitrating PhOMe (Cahours, *A.* 69, 238) and by methylation of picric acid. Monoclinic tables (Friedländer, *J.* 1879, 514).

Ethyl ether EtA'. [78°]. Long needles (Stenhouse a. Müller, *A.* 141, 80; Willgerodt, *B.* 12, 1277).

Iodoethyl ether C_2H_4IA'. [70°]. From the Ag salt and $C_2H_4I_2$ (Andrews, *B.* 13, 244).

Phenyl ether PhA'. Formed from KOPh and $C_6H_2Cl(NO_2)_3$. Needles (W.).

o-*Nitro-phenyl ether* $C_6H_4(NO_2)A'$. [173°].

p-Nitro-phenyl ether $C_6H_4(NO_2)A'$. [153°]. Plates (from alcohol) (Willgerodt, *B.* 17, 1766).

Benzyl ether $C_6H_5CH_2A'$. [147°]. Yellow prisms (Kumpf, *A.* 224, 131).

p-Nitro-benzyl ether $C_6H_4(NO_2).CH_2A'$. [108°]. Formed from silver picrate and *p*-nitro-benzyl iodide (K.).

(β)-Tri-nitro-phenol $C_6H_2(NO_2)_3OH$[6:4:3:1]. [96°]. Formed, together with the (γ)-isomeride and tri-nitro-resorcin (styphnic acid) by the action of conc. HNO_3 on (γ)-di-nitro-phenol (Henriques, *A.* 215, 325; *cf.* Bantlin, *B.* 8, 21). Needles, v. e. sol. alcohol and ether, m. sol. hot water. Forms with naphthalene a compound [72°].—KA': violet needles, insol. alcohol.—BaA'_2 4aq: red prisms.

(γ)-Tri-nitro-phenol $C_6H_2(NO_2)_3(OH)$[6:3:2:1]. [118°]. Formed by nitrating (ε)-dinitrophenol, and also, together with the (β)-isomeride, by nitrating (γ)- or (δ)-dinitrophenol (Henriques). White needles. Readily converted into styphnic acid by boiling with fuming HNO_3. Forms with naphthalene a compound crystallising in yellow needles [100°].—KHA': red needles, insol. alcohol.—BaA'_2: golden-yellow scales.

References.—CHLORO-, BROMO, and IODO-NITRO-PHENOL.

o-NITRO-PHENOL SULPHONIC ACID $C_6H_3(OH)(NO_2)(SO_3H)$[1:2:4]. [122°]. Formed by sulphonating o-nitro-phenol (Kekulé, *Z.* 1867, 641; Armstrong, *Z.* 1871, 321; Armstrong a. Brown, *B.* 7, 923). Formed also by nitration of phenol *p*-sulphonic acid (Schmitt a. Glutz, *B.* 2, 51; Körner, *G.* 2, 444; Kolbe a. Gauhe, *A.* 147, 71) and by boiling (1, 2, 4)-bromo-nitro-benzene sulphonic acid (Goslich, *A.* 180, 105). Needles (containing 3aq). Melts at 52° when hydrated, 122° when anhydrous.—NH_4A'.—NaA' 3aq.—$Na_2C_6H_3NSO_6$ 3aq.—KA'.—K_2A'' aq.—K_2A'' 2aq.—BaA'_2 aq.—BaA'' 2aq: red crystals, sl. sol. water.

***p*-Nitro-phenol sulphonic acid** $C_6H_5NSO_6$ *i.e.* $C_6H_3(OH)(NO_2)(SO_3H)$[1:4:2]. Formed from *p*-nitro-phenol and fuming H_2SO_4 (Körner a. Post, *B.* 5, 852, 1055; 6, 395; 7, 163; *A.* 205, 38). Formed also by nitrating phenol o-sulphonic acid (Stückenberg, *A.* 205, 45). Crystals (containing 3aq), beginning to decompose when heated at 110°. Give a brown pp. with $FeCl_3$.—KA': monoclinic crystals, $a:b:c = 1·704:1:1·524$; $\beta = 117° 59'$.—K_2A'' aq.—NaA' 2aq.—Na_2A'' 2aq.—CaA'_2 3aq.—CaA'' $2\frac{1}{2}$aq.—BaA'_2aq.—BaA'' aq.—PbA'_2 $1\frac{1}{2}$aq.—CuA''.

Nitro-phenol disulphonic acid $C_6H_5NS_2O_9$ *i.e.* $C_6H_2(OH)(NO_2)(SO_3H)_2$. Formed from di-nitro-benzene disulphonic acid by reduction to nitro-amido-benzene disulphonic acid and displacement of NH_2 by OH (Limpricht, *B.* 8, 289). Minute needles.—BaA'' 2aq: crystalline.

Di-nitro-phenol sulphonic acid $C_6H_4N_2SO_8$ *i.e.* $C_6H_2(OH)(NO_2)_2(SO_3H)$. Formed by the action of nitrous acid on *s*-di-phenyl-hydrazine disulphonic acid (Balentine, *A.* 202, 358). Prisms (from alcohol), v. sol. water. Decomposes at 160°.—KA' $\frac{1}{2}$aq.—K_2A'' 2aq.—BaA'' $3\frac{1}{2}$aq (Bertram, *P. Beibl.* 6, 779).

Tri-nitro-phenol sulphonic acid $C_6H(NO_2)_3(OH)(SO_3H)$[6:4:2:1:3]. Formed from phenol *m*-sulphonic acid and HNO_3 (Berndsen, *A.* 177, 92).—KA' aq: prisms, exploding when heated.—BaA'_2 3aq: crystals, m. sol. water.

o-NITRO-DIPHENYL $C_{12}H_9NO_2$ *i.e.* $C_6H_5.C_6H_4NO_2$[1:2]. [37°]. (c. 320°). Formed, together with the *p*- isomeride, by nitration of diphenyl (Lüddens, *B.* 8, 870; Hübner, *A.* 209, 341; Schultz, *A.* 207, 352). Thick plates (from dilute alcohol).

***p*-Nitro-diphenyl.** [113°]. (340° i.V.). Formed as above (Schultz, *A.* 174, 210; Hübner; Zimmermann, *B.* 13, 1960). Long needles (from alcohol). Yields *p*-nitro-benzoic acid on oxidation.

oo-Di-nitro-diphenyl $C_{12}H_8N_2O_4$ *i.e.* [2:1]$C_6H_4(NO_2).C_6H_4NO_2$[1:2]. [124°]. Formed from di-nitro-di-*p*-amido-diphenyl by elimination of amidogen (Täuber, *B.* 24, 197). Straw-yellow needles, sl. sol. cold alcohol.

o*p*-Di-nitro-diphenyl $C_{12}H_8N_2O_4$ *i.e.* [2:1]$C_6H_4(NO_2).C_6H_4(NO_2)$[1:4]. [93·5°]. Formed, together with the *pp*-isomeride, by heating diphenyl with HNO_3 and H_2SO_4 (Fittig, *A.* 124, 275; Schultz, Schmidt, a. Strasser, *A.* 207, 349). Golden monoclinic needles; $a:b:c = 1·08:1:·91$; $\beta = 87° 30'$. More sol. alcohol than the *pp*- isomeride.

mm-**Di-nitro-diphenyl** [3:1]$C_6H_4(NO_2).C_6H_4(NO_2)$[1:3]. [198°]. Formed from di-nitro-di-*p*-amido-diphenyl by elimination of the NH_2 groups (Brunner a. Witt, *B.* 20, 1028). Small yellow needles. Yields di-*m*-amido-diphenyl on reduction.

pp-**Di-nitro-diphenyl** [4:1]$C_6H_4(NO_2).C_6H_4(NO_2)$[1:4]. [233°] (Schultz, *A.* 174, 221). Formed as above. Needles. Yields benzidine on reduction.

Tetra-nitro-diphenyl $C_{12}H_6(NO_2)_4$. [140°]. Formed from diphenyl, H_2SO_4, and HNO_3 (Losanitsch, *B.* 4, 404). Amorphous mass, sl. sol. alcohol.

o-NITRO-PHENYL-ACETIC ACID $C_8H_7NO_4$ *i.e.* $C_6H_4(NO_2).CH_2.CO_2H$. [138°] (B.); [141°] (S.). Formed, in small quantity, in the preparation of the *p*- isomeride by nitration of phenyl-acetic acid (Radziszewski, *B.* 3, 648; Bedson, *C. J.* 37, 93). Obtained also by saponifying its nitrile (Gabriel a. Borgmann, *B.* 16, 2066). Needles (from water) or monoclinic plates (from alcohol). Yields o-nitro-benzoic acid on oxidation with $KMnO_4$. Gives oxindole on reduction. —BaA'_2 2aq.

Nitrile $C_6H_4(NO_2).CH_2.CN$. *o-Nitro-benzyl cyanide.* [83°] (B.); [84°] (S.). Formed in small quantity, together with the *m*- and *p*-isomerides, by nitration of benzyl cyanide (H. Salkowski, *B.* 17, 507). Formed also, together with a larger quantity of the compound $C_6H_4(NO_2).CHCy.CH_2.C_6H_4NO_2$ [111°] and small quantities of $C_{15}H_9N_3O_3$ [c. 238°] and $C_{22}H_{14}N_4O_5$ [191°], by boiling o-nitro-benzyl chloride with alcoholic KCy (Bamberger, *B.* 19, 2635). Trimetric prisms.

m-**Nitro-phenyl-acetic acid** [3:1]$C_6H_4(NO_2).CH_2.CO_2H$. [117°] (G. a. B.); [120°] (S.). Formed from the nitrile which is obtained from *m*-nitro-benzyl chloride and KCy. Needles.—AgA′: silky needles.

Nitrile [61°]. Monoclinic crystals.

p-**Nitro-phenyl-acetic acid** [4:1]$C_6H_4(NO_2).CH_2.CO_2H$. [152°]. Formed as above (Radziszewski, *B.* 2, 209; Maxwell, *B.* 12, 1765; Gabriel, *B.* 14, 2342; 15, 834; Bedson, *C. J.* 37, 92). Silky needles. With o-nitro-phenyl-acetic acid it forms a molecular compound [114°]. Yields *p*-oxy-benzoic acid on oxidation. Sodium-amalgam yields $N_2(C_6H_4.CH_2.CO_2H)_2$ [above 300°] (Wittenberg, *Bl.* [2] 43, 111).—NaA′ 2aq. — BaA'_2. — BaA'_2 7aq. — ZnA'_2 aq. — AgA′: needles.

Methyl ether MeA′. [55°]. Needles.

Ethyl ether EtA′. [65°]. Plates.

Amide [192°]. Long prisms.

Nitrile [116°]. Plates. Alcoholic KOH forms a crimson solution in which diazobenzene chloride ppts. $C_{14}H_{10}N_4O_2$ [202°] (Czumpelik, *B.* 3, 474; Perkin, *C. J.* 43, 111).

Di-nitro-phenyl-acetic acid $C_8H_6N_2O_6$ *i.e.* [4:2:1]$C_6H_3(NO_2)_2CH_2.CO_2H$. [160°]. Formed from phenyl-acetic acid, H_2SO_4, and fuming HNO_3 (R.; Gabriel a. Meyer, *B.* 14, 823). Formed also by boiling di-nitro-phenyl-aceto-acetic ether with dilute H_2SO_4 (Heckmann, *A.* 220, 128). Pale-yellow needles, sol. hot water. Decomposed by heat into di-nitro-toluene [71°] and CO_2.

Methyl ether MeA′. Forms with diazobenzene chloride $C_6H_3(NO_2)_2.C(N.NHPh).CO_2Me$ [183°] (V. Meyer, *B.* 22, 319). Diazotoluene forms the homologous tolyl-hydrazide of methyl di-nitro-phenyl-glyoxylate [168°] crystallising in red needles (Hausknecht, *B.* 22, 325). The corresponding derivatives of diazoxylene and diazonaphthalene melt at 159° and 94° respectively.

Ethyl ether EtA′. [55°]. Needles. When heated with alcoholic potash it yields $C_{24}H_{18}N_6O_{15}$ [151°], which forms the salt $K_2C_{24}H_{16}N_6O_{15}$, crystallising in golden plates.

Tetra-nitro-di-phenyl-acetic ether $\{C_6H_3(NO_2)_2\}_2CH.CO_2Et$. [154°]. Formed from sodium di-nitro-phenyl-acetoacetic ether and bromo-di-nitro-benzene (Von Richter, *B.* 21, 2470). Crystalline.—$C_{16}H_{11}NaN_4O_{10}$ [80°]: very hygroscopic plates.

p-**NITRO-PHENYL-ACETIC ALDEHYDE** $C_6H_4(NO_2).CH_2.CHO$. [86°]. Formed by boiling the barium salt of $C_6H_4(NO_2).CHCl.CH(OH).CO_2H$ with water (Lipp, *B.* 19, 2645; *cf.* Forrer, *B.* 17, 984). Needles, sl. sol. cold water.

DI-NITRO-PHENYL-ACETOACETIC ETHER [4:2:1] $C_6H_3(NO_2)_2.CHAc.CO_2Et$. [94°]. Formed from $C_6H_3Br(NO_2)_2$, acetoacetic ether, and NaOEt (Heckmann, *A.* 220, 128). Plates.

Tri-nitro-phenyl-acetoacetic ether $C_6H_2(NO_2)_3.CHAc.CO_2Et$. [98°]. Formed, together with $\{C_6H_2(NO_2)_3\}_2CAc.CO_2Et$ [205°], from picryl chloride $C_6H_2Cl(NO_2)_3$ and sodium acetoacetic ether (Dittrich, *B.* 23, 2720). Crystals, v. sol. hot alcohol.

p-**NITRO-PHENYL-ACETURIC ACID** $C_6H_4(NO_2).CH_2.CO.NH.CH_2.CO_2H$. [173°]. Got by nitrating phenylaceturic acid (Hotter, *J. pr.* [2] 38, 110). Needles, decomposed by boiling HClAq into glycocoll and *p*-nitro-phenyl-acetic acid.—$ZnA'_2 2\frac{1}{2}$aq.—AgA′: needles, v. sl. sol. cold water.

o-NITRO-PHENYL-ACETYLENE $C_8H_5NO_2$ *i.e.* $C_6H_4(NO_2).C{:}CH$. [82°]. Formed by boiling o-nitro-phenyl-propiolic acid with water (Baeyer, *B.* 13, 2259). Needles, sol. hot water. Gives pps. with ammoniacal $AgNO_3$ and Cu_2Cl_2.

p-**Nitro-phenyl-acetylene** [149°] (M.); [152°] (D.). Formed by boiling *p*-nitro-phenyl-propiolic acid with water (Drewson, *A.* 212, 158). Formed also from $C_6H_4(NO_2).CHBr.CHBr.CO_2Et$ and alcoholic potash (C. L. Müller, *A.* 212, 133). Needles (from hot water). Gives a red pp. with ammoniacal Cu_2Cl_2 and a greenish-yellow pp. with ammoniacal $AgNO_3$.

Di-*p*-nitro-di-phenyl-acetylene $C_{14}H_8N_2O_4$ *i.e.* $C_6H_4(NO_2).C{:}C.C_6H_4NO_2$. [288°]. Formed from $C_6H_4(NO_2).CHBr.CHBr.C_6H_4NO_2$ by heating with soda-lime at 180° (Elbs a. Bauer, *J. pr.* [2] 34, 346). Yellow needles (by sublimation).

o-Nitro-di-phenyl-di-acetylene $C_{16}H_9NO_2$ *i.e.* $C_6H_4(NO_2).C{:}C.C{:}CPh$. [155°]. Formed by the action of K_3FeCy_6 on a mixture of the cuprous salts of phenyl-acetylene and o-nitro-phenyl-acetylene (Baeyer a. Landsberg, *B.* 15, 57). Yellow plates, sol. alcohol.

Di-o-nitro-di-phenyl-diacetylene $C_6H_4(NO_2).C{:}C.C{:}C.C_6H_4(NO_2)$. [212°]. Formed by the action of an alkaline solution of K_3FeCy_6 on the cuprous salt of o-nitro-phenyl-acetylene (Baeyer, *B.* 15, 51). Golden needles, sol. chloroform. Fuming H_2SO_4 converts it into the isomeric diisatogen.

NITRO-PHENYL-ACRYLIC ACID *v.* NITRO-CINNAMIC ACID.

NITRO - DI - PHENYL - ACRYLIC ACID. *Nitrile.* The o-, *m*-, and *p*-, varieties, melting at 128°, 134°, and 118° respectively, are formed by the action of the corresponding nitro-benzoic aldehydes on phenyl-acetic nitrile (benzyl cyanide) in presence of alcoholic NaOEt (Frost, *A.* 250, 160).

o-**NITRO - PHENYL - ALLENYL - MALONIC ACID** $C_6H_4(NO_2).CH:CH.CH:C(CO_2H)_2$. [213°]. Formed by heating o-nitro-cinnamic aldehyde with malonic acid and HOAc at 100° (Einhorn, *A.* 253, 374). Needles.—CuA″.—Ag_2A'': yellowish plates.

p-Nitro-phenyl-allenyl-malonic acid [208°]. Formed from *p*-nitro-cinnamic aldehyde, malonic acid, and HOAc (Einhorn a. Gehrenbeck, *B.* 22, 45). Yellow needles (from HOAc). Br forms $C_6H_4(NO_2).CHBr.CHBr.CBr:C(CO_2H)_2$ [206°] crystallising in plates. — $(NH_4)_2A''$. — CuA″.—Ag_2A'' : flocculent pp.

Ethyl ether Et_2A''. [105°]. Needles.

o-**NITRO-PHENYL-AMIDO-ACETIC ACID** $C_6H_4(NO_2).NH.CH_2.CO_2H$. [193°]. Formed from bromo-acetic acid and o-nitro-aniline at 125° (Plöchl, *B.* 19, 6). Dark-red prisms, sl. sol. ether. Yields oxy-quinoxaline dihydride on reduction.—NH_4A': flat orange prisms.

p - **NITRO - PHENYL - ω - AMIDO - ACETOPHENONE** $C_6H_5.CO.CH_2.NH.C_6H_4.NO_2$. [167°]. Formed by heating its nitrosamine with HCl Möhlau, *B.* 15, 2474). Golden needles (from HOAc). Yields acetophenone and *p*-phenylene-diamine on reduction.

Nitrosamine $C_{14}H_{11}N_3O_4$ *i.e.* $C_6H_5.CO.CH_2.N(NO).C_6H_4.NO_2$. Formed from phenyl-amido-acetophenone, HOAc, and nitrous acid gas (M.). Plates, decomposing at 135°–145°.

Di - nitro - phenyl - ω - amido - acetophenone $C_6H_5.CO.CH_2.NH.C_6H_3(NO_2)_2$. [172°]. Formed by nitration of phenyl - amido - acetophenone (Möhlau, *B.* 15, 2479). Golden prisms (from HOAc). Yields *i*-tri-amido-benzene on reduction.

s - **TRI - NITRO - TRI - PHENYL-TRI-AMIDO-BENZENE** $C_6(NHPh)_3(NO_2)_3$. [238°]. Formed from $C_6Br_3(NO_2)_3$ and aniline (Jackson a. Wing, *Am.* 10, 283). Orange powder, insol. water.

m - **NITRO - PHENYL** - *p* - **AMIDO - BENZOIC ACID** $C_6H_3(NO_2)(NHPh).CO_2H[3:4:1]$. [254°]. Formed by heating (4,3,1)-bromo-nitro-benzoic acid with aniline (Schöpff, *B.* 22, 3281). Garnet-red needles. Yields an amido- acid [153°].—NaA′. — NaA′aq. — BaA'_2 3aq. — AgA′: orange plates.

Ethyl ether EtA′. [123°]. Hexagonal.

Anilide $C_6H_3(NO_2)(NHPh).CONHPh$. [216°]. Formed by heating aniline with bromo nitro-benzoyl chloride (Grohmann, *B.* 23, 3448). Blood-red leaflets from HOAc.

Nitrile $C_6H_3(NH_2)(NHPh).CN$. [126°]. Formed from bromo-nitro-benzonitrile and aniline (Schöpff, *B.* 23, 3444).

o-Nitro-phenyl-*m*-amido-benzoic acid $C_6H_3(NO_2)(NHPh).CO_2H[2:3:1]$. [248°]. Formed from (3,2,1)-bromo-nitro-benzoic acid and aniline (Schöpff, *B.* 23, 3440). Yellow needles.—NaA′ 2aq.—BaA'_2 5aq.

Ethyl ether EtA′. [112°]. Needles.

m-Nitro-phenyl-o-amido-benzoic acid. *Nitrile.* $C_6H_3(NO_2)(NHPh)CN[5:2:1]$. [170°]. Formed from (2,5,1)-bromo-nitro-benzonitrile and aniline (S.). Lemon-yellow needles.

Di-nitro-phenyl-o-amido-benzoic acid $C_{13}H_9N_3O_6$ *i.e.* $[4:2:1]C_6H_3(NO_2)_2.NH.C_6H_4.CO_2H$. [264°]. Formed by warming o-amido-benzoic acid with $C_6H_3Cl(NO_2)_2$ (Jourdan, *B.* 18, 1448). Orange needles, almost insol. water.—BaA'_2: dark-red crystalline powder.

NITRO-PHENYL - AMIDO - NAPHTHOQUINONE *v.* (α)-NAPTHOQUINONE, *Reactions* 16 and 17.

DI-NITRO-PHENYL-DI-AMIDO-DIPHENYL $C_{18}H_{14}N_4O_4$ *i.e.* $C_6H_4(NH_2).C_6H_4.NH.C_6H_3(NO_2)_2$. [245°]. Formed by boiling benzidine with alcohol and (1,2,4)-chloro-di-nitro-benzene (Willgerodt, *B.* 9, 981). Long needles (from HOAc).

Di-o-nitro-di-phenyl-diamido-diphenyl $C_6H_4(NO_2).NH.C_6H_4.C_6H_4.NH.C_6H_4(NO_2)$. [240°]. Formed by boiling benzidine with o-chloro-nitro-benzene and alcohol (Schöpff, *B.* 22, 904). Needles (from HOAc).

Tetra - nitro - di - phenyl - di - amido - diphenyl $C_6H_3(NO_2)_2.NH.C_6H_4.C_6H_4.NH.C_6H_3(NO_2)_2$. [above 330°]. Formed from $[1:2:4]C_6H_3Cl(NO_2)_2$, alcohol, and benzidine at 120° (W.). Yellow powder, sl. sol. alcohol.

DI-NITRO-PHENYL-AMIDO-TOLYL-AMINE $[4:2:1]C_6H_3(NO_2)_2.NH.C_6H_3Me.NH_2$. [147°]. Formed from tolylene-o-diamine and *i*-chloro-di-nitro-benzene (Ernst, *B.* 23, 3428). Brownish-yellow needles. Yields with HNO_2 the azimide

$$C_6H_3(NO_2)_2N{<}^{C_7H_6}_{N}{>}N. \quad [186°].$$

o-**NITRO-DI-PHENYL-AMINE** $C_{12}H_{10}N_2O_2$ *i.e.* $[2:1]C_6H_4(NO_2).NHC_6H_5$. [75°]. Formed from aniline and o-chloro-nitro-benzene or o-bromo-nitro-benzene at 100° (Schöpff, *B.* 22, 903; 23, 1839). Trimetric crystals (from alcohol); $a:b:c = \cdot 468:1:\cdot 671$. Yields on reduction the amido- compound [80°].

p-Nitro-diphenylamine $[4:1]C_6H_4(NO_2).NH.C_6H_5$. [133°]. Formed from benzoyl-diphenylamine by nitration and elimination of Bz (Hofmann, *A.* 132, 167; Lellmann, *B.* 15, 825). Formed also from its nitrosamine by treatment with aniline (Witt, *C. J.* 33, 205). Pale-yellow scales (from dilute alcohol). Colours alcoholic potash scarlet. Dyes silk yellow.

Benzoyl derivative [129°]. Prisms.

Nitrosamine $C_6H_4(NO_2).N(NO).C_6H_5$. [134°]. Formed by warming diphenylamine with HNO_3, isoamyl nitrite, and alcohol (W.). Crystals, sol. chloroform.

Di-o-nitro-diphenylamine $NH(C_6H_4NO_2)_2$. [220°] (L.); [212°] (W.). Obtained from its benzoyl derivative, and also, together with the *p*- isomeride, by the action of alcohol (50 c.c.), aniline (25 g.) and aniline hydrochloride (30 g.) at 100° on the mixed di-nitro-di-phenyl-nitrosamines prepared from diphenylamine (17 g.), amyl nitrite (48 g.), alcohol (50 c.c.), nitric acid (40 c.c. of S.G. 1·424), and HOAc (50 c.c.) (Witt, *C. J.* 33, 208). Red felted needles.

Benzoyl derivative $NBz(C_6H_4NO_2)_2$. Formed, together with that of the *p*- isomeride from benzoyl diphenylamine and fuming HNO_3 (Lellmann, *B.* 15, 827).

Di-*p*-nitro-diphenylamine $C_{12}H_9N_3O_4$ *i.e.* $NH(C_6H_4.NO_2[1:4])_2$. [216°] (L.); [214°] (W.). Got as above. Yellow needles with blue reflex.

Benzoyl derivative. [224°]. Monoclinic crystals, sl. sol. alcohol.

Di-nitro-diphenylamine $C_{12}H_9N_3O_4$ *i.e.* $C_6H_5.NH.C_6H_3(NO_2)_2$[1:2:4]. [157°]. Formed from $C_6H_3Br(NO_2)_2$ or $C_6H_3Cl(NO_2)_2$ and aniline or di-phenyl-thio-urea (Clemm, *B.* 3, 128; Willgerodt, *B.* 9, 977; 11, 601; *cf.* Hepp, *Bl.* [2] 30, 4).

Tri-nitro-diphenylamine $C_{12}H_8N_4O_6$ *i.e.* $C_6H_5.NH.C_6H_2(NO_2)_3$[1:2:4:6]. [175°]. Formed from $C_6H_2Cl(NO_2)_3$ (picryl chloride) and aniline (Clemm, *B.* 3, 126). Scarlet prisms.

Tri-nitro-diphenylamine [3:1]$C_6H_4(NO_2).NH.C_6H_3(NO_2)_2$[1:2:4]. [194°]. Formed from $C_6H_3Br(NO_2)_2$ or $C_6H_3Cl(NO_2)_2$ and *m*-nitro-aniline (Austen, *B.* 7, 1250; Willgerodt, *B.* 9, 1178). Short yellow needles (from HOAc).

Tri-nitro-diphenylamine [4:1]$C_6H_4(NO_2).NH.C_6H_3(NO_2)_2$. [181°]. Formed from *p*-nitro-aniline and bromo-di-nitro-benzene (A.). Yellow powder, v. e. sol. HOAc.

Tri-nitro-diphenylamine. [135°]. Formed by boiling the acetyl derivative of diphenylamine with dilute nitric acid (S.G. 1·029) (Norton a. Allen, *B.* 18, 1997). Yellow needles, v. sol. alcohol.

Tetra-nitro-diphenylamine $C_{12}H_7N_5O_8$ *i.e.* [3:1]$C_6H_4(NO_2).NH.C_6H_2(NO_2)_3$[1:2:4:6]. [205°]. Formed from *m*-nitro-aniline and picryl chloride (Austen, *B.* 7, 1248). Orange crystals (from HOAc).

Tetra-nitro-diphenylamine [4:1]$C_6H_4(NO_2).NH.C_6H_2(NO_2)_3$[1:2:4:6]. [216°]. Formed in like manner from *p*-nitro-aniline (A.).

Tetra-nitro-diphenylamine $NH\{C_6H_3(NO_2)_2\}_2$. [180°]. Got by heating $C_6H_3(NO_2)_2.NH.CO_2Et$ with alcoholic potash (Hager, *B.* 17, 2629). Reddish-brown plates (from alcohol).

Tetra-nitro-diphenylamine [192°]. Formed by nitration of diphenylamine, diphenyl-nitrosamine, and diphenyl methylamine $NMePh_2$ (Gnehm a. Wyss, *B.* 10, 1318). Yellow crystals (from alcohol). Forms a scarlet solution in NaOHAq.

Hexa-nitro-diphenylamine $\{C_6N_2(NO_2)_3\}_2NH$. *Dipicrylamine.* [238°] (A.); [234°] (M.). Formed by nitrating diphenylamine, diphenyl methylamine, or tetra-nitro-diphenylamine [216°] (Austen, *B.* 7, 1250; Gnehm, *B.* 7, 1399; 9, 1245, 1557; Mertens, *B.* 11, 845). Yellow prisms (from acetic acid). Its ammonium salt $NH_4C_{12}H_4N_7O_{12}$ is used as a yellow dye ('aurantia').—$Ba(C_{12}H_4N_7O_{12})_2$: red rhombohedra.

Hexa-nitro-diphenylamine [261°]. Formed by nitrating tetra-nitro-diphenylamine [205°] (A.). Small yellow crystals (from HOAc). Explodes when heated.

Nitro-tri-phenyl-amine $(C_6H_5)_2N.C_6H_4(NO_2)$. [140°]. Formed from triphenylamine, HOAc, and HNO_3 (Herz, *B.* 23, 2537). Golden plates.

Di-nitro-tri-phenyl-amine $C_6H_5N(C_6H_4NO_2)_2$. [207°]. Formed from triphenylamine (2 g.), HOAc (35 g.) and HNO_3 (2 g.) at 60° (Herz, *B.* 23, 2538). Yellow needles, v. sol. benzene.

Tri-nitro-tri-phenylamine $N(C_6H_4NO_2)_3$. [280°]. Formed from triphenylamine (2 g.), HOAc (35 g.), and HNO_3 (4 g.) at 100° (Heydrich, *B.* 18, 2156; Herz, *B.* 23, 2539). Bronze-yellow needles, v. sl. sol. HOAc.

***m*-NITRO-PHENYL-ANGELIC ALDEHYDE** $C_6H_4(NO_2).CH:CEt.CHO$. [46°]. Formed from *m*-nitro-benzoic aldehyde, butyric acid, and dilute NaOHAq (Von Miller a. Rohde, *B.* 22, 1838). Plates; reduced by tin and HCl to amido-ethyl-indonaphthene [89°].

Phenyl-hydrazide [135°]. Red needles.

DI-NITRO-DI-*p*-PHENYL-BENZENE $C_{18}H_{12}(NO_2)_2$. [277°]. Formed by nitration of diphenylbenzene (Schmidt a. Schultz, *B.* 11, 1755; *A.* 203, 125). Yellow monoclinic needles (from nitro-benzene).

Tri-nitro-di-*p*-phenyl-benzene $C_{18}H_{11}(NO_2)_3$. [195°]. Formed from diphenylbenzene and fuming HNO_3 (S. a. S.). Needles. Yields on reduction a base [170°].

Tri-nitro-diphenylbenzene [200°]. Formed by nitration of isodiphenylbenzene (S. a. S.). Needles. Yields on reduction a base [288°].

Tetra-nitro-tri-phenyl-benzene $C_{24}H_{14}(NO_2)_4$. [above 370°]. Formed, together with an isomeride [108°], by nitrating triphenylbenzene (Mellin, *B.* 23, 2535). Both bodies crystallise in needles.

NITRO-PHENYL-BENZYLIDENE-AMINE $C_{13}H_{10}N_2O_2$ *i.e.* $C_6H_5.CH:N.C_6H_4NO_2$. [66°] (Lazorenko, *J.* 1870, 760); [73°] (Lachovitch, *M.* 9, 695). Formed from benzoic aldehyde (or hydrobenzamide) and *m*-nitro-aniline. Needles.

***p*-Nitro-phenyl-benzylidene-amine** $C_7H_6:N.C_6H_4(NO_2)$ [1:4]. [115°]. Formed from hydrobenzamide by warming with *p*-nitro-aniline. Yellow needles (Lachovitch).

Isomerides *v.* NITRO-BENZYLIDENE-ANILINE.

NITRO-PHENYL BENZYL OXIDE $C_6H_4(NO_2).O.CH_2Ph$. Formed from potassium nitro-phenol, alcohol, and benzyl chloride (Kumpf, *A.* 224, 121). The o- compound melts at 29°, and the *p*- compound at 106°. Both are crystalline.

Di-nitro-phenyl benzyl oxide $C_{13}H_{10}N_2O_5$ *i.e.* $C_6H_3(NO_2)_2.O.CH_2Ph$. Formed from silver dinitrophenol and benzyl iodide (K.). The (4,2,1)-compound melts at 149°, and the (6,2,1)-compound at 76° (OH=1). Both crystallise from HOAc.

Tri-nitro-phenyl benzyl oxide $C_{13}H_9N_3O_7$ *i.e.* [6:4:2:1] $C_6H_2(NO_2)_3.O.CH_2Ph$. [147°]. Formed from silver picrate and benzyl iodide (K.). Yellowish prisms (from benzene).

TRI-NITRO-DI-PHENYL-BENZYL-PHOSPHINE OXIDE $PO(C_6H_4NO_2)_2(C_7H_6NO_2)$. [206°]. Formed from the oxide, fuming HNO_3, and conc. H_2SO_4 (Dörken, *B.* 21, 1505). Crystals, m. sol. HOAc.

DI-NITRO-PHENYL-BENZYL SULPHIDE $C_7H_7.S.C_6H_3(NO_2)_2$ [1:2:4]. [128°]. Formed from (1,2,4)-chloro-di-nitro-benzene, alcoholic K_2S, and benzyl chloride (Willgerodt, *B.* 18, 331). Yellowish plates.

NITRO-PHENYL-BROMO-PROPIONIC ACID *v.* BROMO-NITRO-PHENYL-PROPIONIC ACID.

o-NITRO-PHENYL-BUTINYL METHYL KETONE $C_6H_4(NO_2).C_4H_4.CO.CH_3$. [73·5°]. Formed, together with $(C_6H_4(NO_2).C_4H_4)_2CO$ [208·5°], from o-nitro-cinnamic aldehyde, acetone, alcohol, and dilute (2 p.c.) NaOHAq (Diehl a. Einhorn, *B.* 18, 2327). Broad needles (from alcohol).

o-NITRO-PHENYL-BUTINYL PHENYL-BUTINYL KETONE $C_{20}H_{17}NO_3$ *i.e.* $C_6H_4(NO_2).C_4H_4.CO.C_4H_4.C_6H_5$. [136·5°]. Formed from *o*-nitro-cinnamic aldehyde, phenyl-butinyl methyl ketone, alcohol, and dilute NaOHAq

(Diehl a. Einhorn, *B.* 18, 2329). Golden crystals (from acetone).

p-**NITRO-PHENYL-ISOBUTYRIC ACID** $C_6H_4(NO_2).CH_2.CHMe.CO_2H$. [121°]. Formed from phenyl-isobutyric acid and conc. HNO_3 (Edeleanu, *C. J.* 53, 559). Small prisms, sol. alcohol.

NITRO-PHENYL-CARBAMIC ETHER $C_6H_4(NO_2).NHCO_2Et$. The o- compound [58°] and the *p*- compound [129°] are got from the corresponding nitro-aniline and $ClCO_2Et$ (Rudolph, *B.* 12, 1295; Hager, *B.* 17, 2625). The *p*- compound is also got by nitration of phenyl-carbamic ether (Behrend, *A.* 233, 9). Both are crystalline.

Di-nitro-phenyl-carbamic ether $C_9H_9N_3O_6$ *i.e.* [4:2:1] $C_6H_3(NO_2)_2NH.CO_2Et$. [111°]. Formed by nitration of either o- or *p*- nitro-phenyl-carbamic ether (Hager, *B.* 17, 2629). Needles (from alcohol). An isomeride [210°] is got by the action of HNO_3 on $C_6H_5NH.CS.OEt$ (Losanitsch, *B.* 10, 691).

Di-nitro-di-phenyl-carbamic ether $(C_6H_4.NO_2)_2N.CO_2Et$. The oily *o*- compound is formed together with the *p*- compound [134°] by nitration of di-phenyl-carbamic ether (Hager, *B.* 18, 2574). The *p*- compound is the less sol. alcohol.

m-**NITRO-TRI-PHENYL-CARBINOL** $C_6H_4(NO_2).CPh_2.OH$. [75°]. Formed from $C_6H_4(NO_2).CHPh_2$ by bromination in sunlight, followed by successive treatment with KOAc and KOH (Tschacher, *B.* 21, 190). Colourless crystals, sol. ligroïn.

p-Nitro-tri-phenyl-carbinol. [136°]. Formed by oxidising *p*-nitro-tri-phenyl-methane with CrO_3 in HOAc (Baeyer a. Löhr, *B.* 23, 1623). Crystals (from dilute HOAc).

Tri-*p*-nitro-tri-phenyl-carbinol $C_{19}H_{13}N_3O_7$ *i.e.* $(C_6H_4.NO_2)_3COH$. [172°]. Formed by oxidising tri-nitro-tri-phenyl-methane (E. a. O. Fischer, *B.* 11, 1079). Colourless crystals (from HOAc).

TETRA-NITRO-DI-PHENYL CARBONATE $(C_6H_3(NO_2)_2)_2CO$. [127°]. Formed from di-phenyl carbonate, HNO_3, and H_2SO_4 (Kempf, *J. pr.* [2] 1, 407; Löwenberg, *C. C.* 1886, 390). Nodules, v. sl. sol. ether.

NITRO-DIPHENYL CARBOXYLIC ACID $C_{13}H_9(NO_2)O_2$. [222°]. Formed by nitration of diphenyl *o*-carboxylic acid (Schmidt, *A.* 193, 115). Monoclinic crystals (from alcohol).—BaA'_2.—CaA'_2: nodules, v. sol. water.

Nitro-diphenyl carboxylic acid $C_{14}H_9NO_6$ *i.e.* [2:1] $C_6H_4(CO_2H).C_6H_3(NO_2).CO_2H$ [1:4:2]. [217°]. Formed by oxidation of nitro-phenanthraquinone [257°] (Strasburger, *B.* 16, 2347). Light-yellow needles (from water).

Di-nitro-diphenyl carboxylic acid [4:1] $C_6H_4(NO_2).C_6H_3(NO_2).CO_2H$ [1:2:4]. [252°]. Formed by nitrating diphenyl *p*-carboxylic acid (Strasser a. Schultz, *A.* 210, 192). Needles, m. sol. alcohol.

Methyl ether MeA'. [156°]. Needles.

(α)-Di-nitro-diphenyl dicarboxylic acid $C_{12}H_6(NO_2)_2(CO_2H)_2$. [249°] (H.); [253°] (Schultz, *A.* 196, 26). Formed by oxidation of di-nitro-phenanthraquinone (Struve, *B.* 10, 75), and, together with the following acid, by nitration of diphenyl di-o-carboxylic acid (Hummel, *A.* 193, 129). Pale-yellow needles (containing aq).—BaA'_2 6aq: long prisms.

Methyl ether Me_2A''. [178°]. Prisms.

(β)-Di-nitro-diphenyl dicarboxylic acid. [297°]. Formed as above (Schultz, *A.* 203, 105). Needles (from hot water).—BaA'_2 4aq: triclinic prisms.

Methyl ether Me_2A''. [132°]. Tables.

NITRO-PHENYL CHLORO-METHYL KETONE *v.* CHLORO-NITRO-ACETOPHENONE.

o-**NITRO-PHENYL-CINNAMIC ACID** $C_{15}H_{11}NO_4$. [196°]. Formed from *o*-nitro-benzoic aldehyde, sodium phenyl acetate, and Ac_2O at 160° (Oglialoro a. Rosini, *G.* 20, 396). Needles. —BaA″ 5aq.—BaA″ 8aq.

NITRO-PHENYLENE-o-DIAMINE $C_6H_3(NO_2)(NH_2)_2$ [4:2:1]. [198°]. Formed by reducing (4,2,1)-di-nitro-aniline with alcoholic ammonium sulphide (Gottlieb, *A.* 85, 27; Heim, *B.* 21, 2305). Dark-red plates (from toluene). Ac_2O at 190° forms $C_6H_3(NO_2){:}N_2H{:}CMe$ [216°]. —B′HCl aq.—$B'_2H_2PtCl_6$.—$B'HNO_3$.—$B'_2H_2SO_4$. —$B'_2H_2C_2O_4$.—$B'_2H_2PtCy_4$ 5aq.

Di-acetyl derivative [227°]. Needles.

Nitro-phenylene-*m*-diamine $C_6H_7N_3O_2$ *i.e.* $C_6H_3(NO_2)(NH_2)_2$. [161°]. Obtained from its diacetyl derivative, which is got by nitrating $C_6H_4(NHAc)_2$ (Barbaglia, *B.* 7, 1259). Yellowish-red prisms, sol. water.

Di-acetyl derivative $C_6H_3(NO_2)(NHAc)_2$. [246°]. Slender needles (from alcohol).

Di-benzoyl derivative $C_6H_3(NO_2)(NHBz)_2$. [222°]. Got by nitrating dibenzoyl phenylene-*m*-diamine (Ruhemann, *B.* 14, 2652). Needles (from HOAc).

Nitro-phenylene-*p*-diamine $C_6H_3(NO_2)(NH_2)_2$ [2:4:1]. [137°]. Formed from its diacetyl or dibenzoyl derivatives, got by nitrating the corresponding derivatives of phenylene-*p*-diamine (Ladenburg, *B.* 17, 149; Hinsberg, *A.* 254, 255). Dark needles with green lustre.

Di-acetyl derivative $C_6H_3(NO_2)(NHAc)_2$. [186°]. On warming with NaOHAq it yields the mono-acetyl derivative crystallising in red needles [195°].

Di-nitro-phenylene-diamine $C_6H_6N_4O_4$ *i.e.* $C_6H_2(NO_2)_2(NH_2)_2$. [211°]. Formed by reducing picramide $C_6H_2(NO_2)_3NH_2$ [6:4:2:1] with ammonium sulphide (Norton a. Elliott, *B.* 11, 327). Red needles, almost insol. cold water.

Di-acetyl derivative $C_6H_2(NO_2)_2(NHAc)_2$. [246°]. Yellow needles.

Di-nitro-phenylene-*m*-diamine $C_6H_2(NO_2)_2(NH_2)_2$ [4:2:3:1]. [c. 250°]. Formed by heating di-nitro-resorcin with aqueous ammonia (Barr, *B.* 21, 1545). Brownish needles (from HOAc), sl. sol. alcohol.

Di-nitro-phenylene-*m*-diamine $C_6H_2(NO_2)_2(NH_2)_2$. [c. 300°]. Obtained by saponification of its di-acetyl derivative which is formed by nitration of di-acetyl-*m*-phenylene-diamine (Nietzki a. Hagenbach, *B.* 20, 333). Orange-yellow crystals.

Di-acetyl derivative. [228°]. Needles.

Di-nitro-phenylene-*p*-diamine. *Di-acetyl derivative.* [258°]. Formed by nitrating di-acetyl-phenylene-*p*-diamine (Nietzki a. Hagenbach, *B.* 20, 331). Yellow solid, sl. sol. alcohol.

Tri-nitro-phenylene-*m*-diamine $C_6H_5N_5O_6$ *i.e.* $C_6H(NO_2)_3(NH_2)_2$ [6:4:2:3:1]. [above 250°]. Formed by boiling the di-ethyl ether of tri-nitro-resorcin with alcoholic ammonia (Nölting a. Collin, *B.* 17, 260; Barr, *B.* 21, 1546).

Yellow granules. Reduced by $SnCl_2$ and HCl to unstable penta-amido-benzene.

NITRO-DIPHENYLENE-KETONE $C_{13}H_7NO_3$ *i.e.* $\left[3:\begin{smallmatrix}6\\1\end{smallmatrix}\right]C_6H_3(NO_2)<\begin{smallmatrix}C_6H_4\\CO\end{smallmatrix}>$. [220°]. Formed, as well as di-nitro-diphenylene ketone [290°], by nitration of o-diphenylene ketone (Schultz, *A.* 203, 103). The isomeric nitro- derivative of iso-diphenylene-ketone [83°] melts at 220°–230° (Carnelley a. Dunn, *B.* 21, 2005).

Nitro-diphenylene-ketone carboxylic acid $C_{14}H_7(NO_2)O_3$. [246°]. Got by warming di-phenylene-ketone carboxylic acid with HNO_3 (Fittig a. Liepmann, *A.* 200, 6). Golden needles (from alcohol).—$BaA'_2$4aq: yellow needles, sl. sol. water.

(α) - DI - NITRO - DIPHENYLENE - KETONE OXIDE $C_6H_3(NO_2)<\begin{smallmatrix}O\\CO\end{smallmatrix}>C_6H_3(NO_2)$. [190°]. Formed, together with a (β)-isomeride [260°], by warming diphenylene-ketone oxide with HNO_3 (Wichelhaus a. Salzmann, *B.* 10, 1401; R. Richter, *J. pr.* [2] 28, 292; A. G. Perkin, *C. J.* 43, 189; Graebe, *A.* 254, 286). An isomeric body [224°] is formed, together with a di-nitro- derivative [235°], by nitration of iso-di-phenylene-ketone oxide [91°] (R.).

NITRO - PHENYLENE - DI - METHYL-o-DI-AMINE $C_6H_3(NO_2)(NMe_2)(NH_2)$ [4:1:2]. [63°]. Formed by reducing di-nitro-dimethylaniline by ammonium sulphide (Heim, *B.* 21, 2308). Orange needles (from water).

Nitro-phenylene-tri-methyl-diamine $C_6H_3(NO_2)(NMe_2)(NHMe)$.

Acetyl derivative. [c. 210°].

Nitrosamine $C_6H_3(NO_2)(NMe_2)(NMeNO)$. [87°]. Formed from $C_6H_4(NMe_2)_2$ and HNO_2 in excess (Wurster a. Schobig, *B.* 12, 1811). Needles.

Tri-nitro-phenylene-di-methyl-diamine $C_8H_9N_5O_6$ *i.e.* $C_6H(NO_2)_3(NHMe)_2$. [235°]. Formed by heating its nitramine with phenol or aqueous methylamine (Romburgh, *R. T. C.* 7, 6; 8, 279). Golden crystals (from HOAc).

Di-nitramine $C_6H(NO_2)_3(NMe.NO_2)_2$. Formed by boiling $C_6H_4(NMe_2)_2$ with fuming HNO_3 (Romburgh, *R. T. C.* 6, 252). Pale-yellow crystals, decomposing at about 205°. A nitramine $C_6H(NO_2)_3(NHMe)(NMeNO_2)$ is got by the action of methylamine on $C_6H(NO_2)_4NMeNO_2$. It separates from HOAc in golden crystals [192°].

NITRO - PHENYLENE - (α) - NAPHTHYL - o-DIAMINE $C_6H_3(NO_2)(NH_2)(NHC_{10}H_7)$. [147°]. Formed from (4, 2, 1)-di-nitro-phenyl-(α)-naph-thylamine and ammonium sulphide (Heim, *B.* 21, 2302). Needles (from HOAc), v. e. sol. alcohol. The isomeric compound from di-nitro-phenyl-(β)-naphthylamine melts at 195°, and yields an acetyl derivative [200°], which is converted by Ac_2O into nitro-phenylene-(β)-naph-thyl-acetamidine [162°].

DI-NITRO-PHENYLENE-NAPHTHYLENE OXIDE $C_{16}H_8(NO_2)_2O$. [235°]. Formed by ni-trating (α)-phenylene-(α)-naphthylene oxide (Arx, *A.* 209, 141). V. sol. ether and HOAc.

NITRO - PHENYLENE - NAPHTHYL - ACET - AMIDINE $C_6H_3(NO_2)<\begin{smallmatrix}N(C_{10}H_7)\\N:CMe\end{smallmatrix}>$. [162°]. Formed from nitro-amido-phenyl-(β)-naphthyl-amine and Ac_2O (Heim, *B.* 21, 589). Needles.

DI-NITRO-DIPHENYLENE OXIDE $C_{12}H_6(NO_2)_2O$. [200°]. Formed from diphenyl-ene oxide and fuming HNO_3 (Hoffmeister, *A.* 159, 211). Crystals (from alcohol).

NITRO-PHENYLENE-UREA $C_7H_5N_3O_3$ *i.e.* $C_6H_3(NO_2)<\begin{smallmatrix}NH\\NH\end{smallmatrix}>CO$. Formed by heating nitro-amido-phenyl-carbamic ether (Hager, *B.* 17, 2630). Colourless needles, not melted at 300°.

NITRO-u-DI-PHENYL-ETHANE $C_6H_4(NO_2).CHPh.CH_3$. [80°]. Formed, together with $(C_6H_4.NO_2)_2CH.CH_3$ [149°], by nitration of *u*-di-phenyl-ethane (Anschütz a. Romig, *B.* 18, 664). Long yellow needles.

Di-p-nitro-s-di-phenyl-ethane [4:1] $C_6H_4(NO_2).CH_2.CH_2.C_6H_4(NO_2)$ [1:4]. [179°]. Formed, together with an isomeride [75°], from dibenzyl and fuming HNO_3 (Stelling a. Fittig, *A.* 137, 260; Leppert, *B.* 9, 15). Formed also from *p*-nitro-benzyl chloride, $SnCl_2$, and NaOHAq (W. Roser, *A.* 238, 364). Needles, sl. sol. alcohol.

DI-NITRO-DI-PHENYL-ETHANE DICARB-OXYLIC ACID $C_{16}H_{12}(NO_2)_2O_4$. Formed by ni-trating *s*-di-phenyl-ethane di-o-carboxylic acid (Dobreff, *A.* 239, 70). Minute crystals, melting above 300°.—CaA″.

Ethyl ether EtHA″. [60°].

Di-nitro-di-phenyl-ethane dicarboxylic acid [226°]. Formed by nitration of *s*-di-phenyl-ethane αβ-dicarboxylic acid (Reimer, *B.* 14, 1802). Amorphous (containing aq). An isomeric acid [242°] is got by nitrating *s*-di-phenyl-ethane αα-dicarboxylic acid. Both acids yield *p*-nitro-benzoic acid on oxidation.

o-NITRO-PHENYL-ETHYL CARBONATE $C_6H_4(NO_2).OCO.OEt$. (275°–285°). Formed by the action of chloro-formic ether upon the potassium salt of o-nitro-phenol (Bender, *B.* 19, 2268). Heavy yellow oil.

NITRO-PHENYL-ETHYLENE *v.* NITRO-STYRENE.

Nitro-s-di-phenyl-ethylene $C_6H_4(NO_2).CPh:CH_2$. [86°]. Formed from $C_6H_4(NO_2).CPh(OH).CH_3$ and AcCl (Anschütz a. Romig, *B.* 18, 664). Yellow crystals (from ether).

Di-o-nitro-di-phenyl-ethylene $(C_6H_4(NO_2))_2C_2H_2$. Formed in two modifications '*cis*' [126°] and '*trans*' [196°], by the action of alcoholic potash upon o-nitro-benzyl chloride (Bischoff, *B.* 21, 2072; 23, 2072). Both crystallise in needles.

Di-p-nitro-di-phenyl-ethylene. Formed in two modifications, [c. 213°] and [c. 282°], by the action of alcoholic potash on *p*-nitro-benzyl chloride (Walden, *B.* 23, 1959; *cf.* Strakosch, *B.* 6, 328). Both are crystalline.

DI - m - NITRO - DI - PHENYL - ETHYLENE - DIAMINE $(C_6H_4(NO_2).NH)_2C_2H_4$. [206°]. Obtained by heating *m*-nitro-aniline with ethylene bromide at 130° (Gattermann a. Hager, *B.* 17, 778). Reddish-yellow crystals, insol. alcohol.

NITRO-s-DI-PHENYL-ETHYLENE CARB-OXYLIC ACID. *Nitrile* $C_6H_4(NO_2).CCy:CHPh$. [176°]. Got from *p*-nitro-phenyl-acetonitrile, benzoic aldehyde, and alcoholic NaOEt at 50° (Remse, *B.* 23, 3134). Yellow needles. By using o- or *m*- nitro-benzoic aldehyde, the corresponding di-nitro- compounds [4:1] $C_6H_4(NO_2).CCy:CH.C_6H_4(NO_2)$ [2:1] [185°] and [4:1] $C_6H_4(NO_2).CCy:CH.C_6H_4(NO_2)$ [3:1] [195°] may be made. Both crystallise in needles.

m-NITRO-PHENYL - ETHYLENE - QUINOL-INE $C_9NH_6.CH:CH.C_6H_4NO_2$. [136°]. Ob-

tained by heating methyl-quinoline (lepidine) with *m*-nitro-benzoic aldehyde and $KHSO_4$ at 160° (Heymann a. Königs, *B.* 21, 1424). Needles.

NITRO-PHENYL ETHYL KETONE $C_6H_4(NO_2).CO.C_2H_5$. [100°]. Formed, together with a syrupy isomeride, by nitration of phenyl-ethyl ketone (Barry, *B.* 6, 1007). Prisms.

NITRO - PHENYL - FURFURYL - ACRYLIC ACID. *Nitrile* $C_6H_4(NO_2).CCy:CH.C_4H_3O$. [173°]. Formed from furfuraldehyde, *p*-nitro-phenyl-acetonitrile, and alcoholic NaOEt (Freund a. Immerwahr, *B.* 23, 2852). Needles.

o-NITRO-PHENYL-GLYCIDIC ACID $C_9H_7NO_5$ aq *i.e.* $C_6H_4(NO_2).C_2H_2O.CO_2H$. *Nitro-phenyl oxyacrylic acid.* [108°]. Formed from $C_6H_4(NO_2).CH(OH).CHCl.CO_2H$ and alcoholic potash (Baeyer, *B.* 13, 2262; Morgan, *B.* 17, 219; Lipp, *B.* 19, 2649). Prisms (containing aq). Melts at 94° when hydrated; 108° when anhydrous. Yields indigo and CO_2 on heating. —NH_4A' aq.—AgA': white crystalline pp.

p-**Nitro-phenyl-glycidic acid.** [188°]. Formed in the same way as the o- isomeride (Lipp), and also by the action of HOCl on sodium *p*-nitro-cinnamate (Erlenmeyer, *B.* 14, 1868). Plates (from hot water). Yields $C_6H_4(NO_2).CH(OH).CH(OH).CO_2H$ on boiling with dilute H_2SO_4.

NITRO-PHENYL-GLYCOCOLL *v.* NITRO-PHENYL-AMIDO-ACETIC ACID.

NITRO-PHENYL-GLYCOLLIC ACID *v.* GLYCOLLIC ACID.

o-NITRO-PHENYL-GLYOXYLIC ACID $C_6H_4(NO_2).CO.CO_2H$. [49°]. Formed from its amide, which is got by the action of cold conc. HClAq on $C_6H_4(NO_2).CH_2Cy$ (Claisen a. Shadwell, *B.* 12, 352; Fehrlin, *B.* 23, 1577). Needles.

Amide [189°] (C. a. S.); [199°] (F.)

Nitrile [54°]. Prisms (from ligroïn).

Phenyl hydrazide [166°]. Changed by dissolving in alcoholic KOH and adding HCl into an isomeride [190°]. HNO_3 converts the first phenyl-hydrazide into a body melting at 77°–80°, and the second into one melting at 95°–100°. Both yield isatin phenyl-hydrazide on reduction. The ethyl ether of the phenyl-hydrazide $C_{16}H_{15}N_4O_3$ crystallises in yellow prisms [128°] (Krause, *B*, 23, 3617).

Phenyl-methyl-hydrazide. [142°].

Oxim of the ethyl ether $C_6H_4(NO_2).C(NOH).CO_2Et$. [163°]. Needles (from boiling water) (Gabriel, *B.* 16, 519).

m-**Nitro-phenyl-glyoxylic acid** [78°]. Formed by boiling its amide with alkalis (Claisen a. Thompson, *B.* 12, 1944; 14, 1187. Prisms.—KA': flat prisms.—BaA'_2 aq.—AgA': nodules.

Amide $C_6H_4(NO_2).CO.CONH_2$. [152°]. Formed from *m*-nitro-phenyl-acetonitrile, and also by nitration of phenyl-glyoxylic amide.

Nitrile (231° at 145 mm.). Oil.

Phenyl hydrazide [176°] (F.). Crystals. Successive treatment with KOH and HClAq yields a green compound [285°].

Di-nitro-phenyl-glyoxylic acid.

Phenyl-hydrazide of the methyl ether. $C_6H_3(NO_2)_2.C(N_2HPh).CO_2Me$. [183°]. Formed from methyl-di-nitro-phenyl-acetate and diazobenzene chloride (V. Meyer, *B.* 22, 319). Alcoholic potash forms a blue solution, changing to yellow, and forming $C_6H_3(NO_2)\langle{}^{C(CO_2H)}_{NPh.N}\rangle\!\!>$ [272°], which yields a methyl ether [192°].

m-**NITRO-DIPHENYL-GUANIDINE** $NH:C(NHPh).NHC_6H_4NO_2$. [132°]. Formed from *m*-nitro-di-phenyl-thio-urea, PbO, and alcoholic NH_3 (Brückner, *B.* 7, 1236). Cyanogen, followed by dilute HClAq, changes it to the oxalyl derivative [168°], whence hot conc. HCl forms nitro-di-phenyl-parabanic acid (Hirsch, *C. C.* 1888, 624).

m-**Nitro-tri-phenyl-guanidine.** [159°]. Formed from *m*-nitro-di-phenyl-thio-urea, PbO, and aniline (B.; Losanitsch, *B.* 16, 50). Yellow plates.—$B'_2H_2PtCl_6$.

m-**Di-nitro-di-phenyl-guanidine** $NH:C(NH.C_6H_4NO_2)_2$. [190°]. Formed from *m*-nitro-aniline and cyanogen chloride (Hofmann, *A.* 67, 156), or from di-nitro-di-phenyl-thio-urea, PbO, and alcoholic NH_3 (B.). Scales. B'HCl.—$B'_2H_2PtCl_6$.

Tri-*m*-nitro-tri-phenyl-guanidine $C_6H_4(NO_2).N:C(NH.C_6H_4.NO_2)_2$. [189°]. Formed from di-nitro-di-phenyl-thio-urea, iodine, and alcohol (L.). Yellow plates, sol. hot alcohol.

DI-NITRO-DI-PHENYL-HEPTANE $C_7H_{14}(C_6H_4NO_2)_2$. Oil (Auger, *Bl.* [2] 47, 42).

o-**NITRO-PHENYL-HYDRAZINE** $C_6H_4(NO_2)NH.NH_2$. [90°]. Formed from o-nitro-diazobenzene chloride, HCl, and $SnCl_2$ at 0° (Bischler, *B.* 22, 240, 2801). Brick-red needles from benzene), sl. sol. cold alcohol. With benzoic aldehyde it yields $C_6H_5.CH:N.NH.C_6H_4NO_2$ [187°].—$B'HSnCl_3$: prisms.—B'HCl: needles.—$B'_2H_2SO_4$: flesh-coloured needles.

Formyl derivative $C_6H_4(NO_2).NH.NHCHO$. [177°]. Formed from o-nitro-phenyl-hydrazine hydrochloride, formic acid, and some Na_2CO_3. Needles, v. e. sol. hot Aq.

Acetyl derivative [141°]. Needles.

Di-acetyl derivative [58°]. Prisms.

Benzoyl derivative [166°]. Needles.

Oxalyl derivative $C_2O_2(NH.NH.C_6H_4NO_2)_2$. Formed from the hydrazide and oxalic ether. Yellow needles, sol. hot nitrobenzene.

m-**Nitro-phenyl-hydrazine** $C_6H_4(NO_2)NH.NH_2$. [93°]. Prepared in the same way as the *o*- compound (Bischler a. Brodsky, *B.* 22, 2809). Canary-yellow needles. Reacts with ketonic compounds, yielding their *m*-nitro-phenyl-hydrazides, with the following melting-points: from aldehyde [98°]; from acetone [112°]; from benzoic aldehyde [118°]; from acetophenone [160°]; from benzil [158°]; and from aceto-acetic ether [117°].

Salts.—B'HCl.—$B'_2H_2SO_4$: yellow crystalline groups, v. sol. hot water.

Acetyl derivative [145°]. Plates.

Di-acetyl derivative [150°]. Tables.

(α)-*Acetyl*-(β)-*benzoyl derivative* $C_6H_4(NO_2)NBz.NHAc$. [137°]. Formed from the acetyl derivative and Bz_2O at 160°. Yellowish aggregates of crystals.

(α)-*Benzoyl*-(β)-*acetyl derivative* $C_6H_4(NO_2)NAc.NHBz$. [147°]. Formed from the benzoyl derivative, Ac_2O, and NaOAc. Needles (by sublimation).

Benzoyl derivative. [151°]. Needles.

Di-benzoyl derivative. [153°]. Plates.

Di-nitro-di-phenyl-hydrazine $C_6H_5.NH.NH.C_6H_3(NO_2)_2$ [1:2:4]. [120°]. Formed from $C_6H_3Cl(NO_2)_2$ and phenyl-hydrazine (Willgerodt, *J. pr.* [2] 37, 350; 40, 252; 42, 132). Red plates. Converted by shaking with HgO into $C_6H_5.N_2.C_6H_3(NO_2)_2$ [117°]. On boiling with alcohol it yields $C_6H_5.N_2.C_6H_3(NO)_2$ [178°]; boiling HOAc forms $C_6H_5.N_2.C_6H_3(NO)(NO_2)$ [175°].

Di-*m*-nitro-*s*-di-phenyl-hydrazine $(C_6H_4(NO_2))_2N_2H_2$. [220°]. Formed from di-nitro-azobenzene and cold alcoholic ammonium sulphide (Lermontoff, *B.* 5, 236). Yellow needles.

Tri-nitro-di-phenyl-hydrazine $C_6H_5NH.NHC_6H_2(NO_2)_3$ [1:2:4:6]. [185°]. Formed from $C_6H_2Cl(NO_2)_3$ and phenyl-hydrazine hydrochloride (Willgerodt, *J. pr.* [2] 37, 346; 40, 264; Fischer, *A.* 190, 132; 253, 1). Red crystals, melting at 175°-180° when slowly heated, but 183°-185° when quickly heated. By boiling with MeOH it is converted into the compound $C_6H_5.N_3:C_6H_2(NO_2)_2$ [218°]. On heating with HOAc it yields $C_6H_5N_2C_6H_2(NO_2)_2(NO)$ [248°] (Freund, *B.* 22, 1663), which yields a mono-sulphonic acid crystallising from water in yellow needles, not melted at 360°.

o - NITRO - PHENYL - HYDRAZINE SULPHONIC ACID $C_6H_3(NO_2)(SO_3H).NH.NH_2$. Formed from o-nitro-diazobenzene sulphonic acid and a well-cooled, strongly acid, solution of $SnCl_2$ (Nietzki a. Lerch, *B.* 21, 3220).—HA'HCl.

***m*-Nitro-phenyl-hydrazine sulphonic acid** [3:6:1] $C_6H_3(NO_2)(SO_3H).NH.NH_2$. Formed from nitro-diazobenzene sulphonic acid and cold $SnCl_2$ (Limpricht, *B.* 18, 2194). Yellow needles (containing aq).—KA' 1½aq.—BaA'$_2$ 1½aq.—PbA'$_2$ 4aq.

NITRO - PHENYL - HYDROXYLAMINE *v.* HYDROXYLAMINE DERIVATIVES.

DI-NITRO-DI-PHENYL-HYPOPHOSPHOROUS ACID $(C_6H_4NO_2)_2PO.OH$. [268°]. Formed from Ph_2PO_2H, nitric acid, and H_2SO_4 (Dörken, *B.* 21, 1513). Yellow pp., v. sol. water.—NH_4A'. [260°].—KA' 2aq.—BaA'$_2$ 6aq.—PbA'$_2$.—AgA'.

NITRO-PHENYL-ψ-INDAZINE CARBOXYLIC ACID $C_6H_3(NO_2)<\begin{matrix}N(C_6H_5)\\C(CO_2H)\end{matrix}>N$. [272°]. Formed by the action of alcoholic potash on the red needles [183°] formed from di-nitro-phenyl-acetic ether and diazobenzene (V. Meyer, *B.* 22, 319; *A.* 264, 149). Sulphur-yellow needles, v. sl. sol. alcohol. Reduced by $SnCl_2$ to a dihydride [235°].

Methyl ether MeA'. [192°]. Needles. Converted by HNO_3 into $C_{15}H_{10}N_4O_6$ [281°]; and by H_2SO_4 into a sulphonic acid (Strassmann, *B.* 23, 714).

Ethyl ether EtA'. [158°]. Needles.

NITRO-DI-PHENYL-KETONE *v.* NITRO-BENZOPHENONE.

DI - NITRO - PHENYL - MALONIC ETHER $C_6H_3(NO_2)_2.CH(CO_2Et)_2$. [51°]. Formed from sodium malonic ether and $C_6H_3Br(NO_2)_2$ (Von Richter, *B.* 21, 2472). Pale-yellow prisms.

***m*-NITROPHENYL MERCAPTAN** $C_6H_4(NO_2).SH$. Formed by the action of alcoholic potash on the ether formed from potassium xanthate and *m*-diazobenzene (Leuckart, *J. pr.* [2] 41, 197). Yellow liquid with nasty smell.

***p*-Nitro-phenyl mercaptan** $C_6H_4(NO_2)SH$. [77°]. Formed from $C_6H_4Cl(NO_2)$ and alcoholic KSH (Willgerodt, *B.* 18, 331). Crystals.

Di-nitro-phenyl mercaptan $C_6H_3(NO_2)_2SH$ [4:2:1]. [131°]. Formed from $C_6H_3Cl(NO_2)_2$ and KHS (Willgerodt, *J.* 1884, 974). Needles.

Ethers (Willgerodt, *B.* 18, 330). MeA'. [126°].—EtA'. [113°].—PrA'. [94°].—$PrCH_2A'$. [72°].—$C_6H_5CH_2A'$. [128°].—BzA'. [113°].

Di-nitro-phenyl-mercaptan [195°]. Formed by heating $C_6H_3(NO_2)_2SCN$ with conc. H_2SO_4 (Austen a. Smith, *Am.* 8, 90). Yellow powder.

Tri-nitro-phenyl mercaptan $C_6H_2(NO_2)_3SH$ [6:4:2:1]. [114°]. Formed from $C_6H_2Cl(NO_2)_3$ and alcoholic KSH (W.). Small yellowish needles. Explodes at 115°.—KA': brown needles.

o-NITRO-PHENYL-METHACRYLIC ACID $C_6H_4(NO_2).CH:CMe.CO_2H$. [165°]. Formed by hydrolysis of its ether, which is prepared from methyl phenyl-methacrylate and HNO_3. Formed also from phenyl-isobutyric acid and HNO_3 (Edeleanu, *B.* 20, 621; *C. J.* 53, 559). Crystalline powder, yielding o-nitro-benzoic acid on oxidation.

***m*-Nitro-phenyl-methacrylic acid** [197°]. Formed from *m*-nitro-benzoic aldehyde by heating with sodium propionate and propionic anhydride (Von Miller, *B.* 23, 1900). White powder, v. sol. hot alcohol.

***p*-Nitro-phenyl-methacrylic acid** [208°]. Formed in the same way as the *o*- isomeride (E.). Crystals.—AgA': white needles.

Methyl ether MeA'. [115°]. Plates.

***m*-NITRO-PHENYL-METHACRYLIC ALDEHYDE** $C_6H_4(NO_2).CH:CMe.CHO$. [83°]. Formed from *m*-nitro-benzoic aldehyde, propionic aldehyde, and dilute (10 p.c.) aqueous NaOH (Miller a. Kinkelin, *B.* 19, 530). Thin prisms (from alcohol). Aniline yields oily $C_9H_8(NO_2).CH:NPh$ and crystalline $C_9H_8(NO_2).CH(NHPh)_2$ [170°]. Tin and HCl yield a base $C_{10}H_{11}N$ [98°], whence Ac_2O forms $C_{10}H_{10}AcN$ [148°], and benzoic aldehyde produces $C_{10}H_9N(CHPh)$ [73°].

Phenyl-hydrazide $C_{16}H_{15}N_3O_2$. [135°].

NITRO-DI-PHENYL-METHANE $C_{13}H_{11}NO_2$ *i.e.* $C_6H_5.CH_2.C_6H_4NO_2$.

o- compound. Formed from o-nitro-benzyl chloride, benzene, and $AlCl_3$ (Geigy a. Kœnigs, *B.* 18, 2402). Oil.

***m*- compound.** [141°]. Formed from *m*-nitro-benzyl alcohol and conc. H_2SO_4 (Becker, *B.* 15, 2091). Oil; sol. alcohol.

***p*- compound.** [31°]. Formed by either of the above methods (Basler, *B.* 16, 2716; Manns, *C. C.* 1888, 1363). Prisms, v. sol. alcohol.

***m*-Nitro-tri-phenyl-methane** $CHPh_2.C_6H_4NO_2$. [90°]. Formed from *m*-nitro-benzoic aldehyde, benzene, and H_2SO_4 (Tschacher, *B.* 19, 2463; 21, 188). Crystals (from ligroïn).

***p*-Nitro-tri-phenyl-methane.** [93°]. Formed in like manner (Baeyer a. Löhr, *B.* 23, 1622).

Di-nitro-di-phenyl-methane $C_{13}H_{10}(NO_2)_2$. By nitrating diphenyl-methane Doer (*B.* 5, 795) obtained two compounds of this formula, melting at 183° and 172°; while Staedel (*A.* 194, 363) obtained the (α)- compound [183°] and a (β)-isomeride [118°]. By nitrating *m*-nitro-di-phenyl-methane Becker (*B.* 15, 2092) obtained a fourth isomeride [94°], while Basler (*B.* 16, 2719) got a fifth isomeride [175°] by the nitration of *p*-nitro-di-phenyl-methane.

Tri-nitro-tri-phenyl-methane $CH(C_6H_4.NO_2)_3$. [207°]. Formed by nitrating tri-phenyl-methane

(E. a. O. Fischer, *A.* 194, 254; *cf.* Hemilian, *B.* 7, 1203). Scales (from benzene).

Tetra - nitro - di - phenyl - methane. [172°]. Formed from CH_2Ph_2 and fuming HNO_3 at 0° Staedel, *A.* 218, 339). Long pointed needles.

DI-NITRO-DI-PHENYL-METHYL-AMINE $C_6H_4(NO_2)NMe.C_6H_5$. [167°]. Formed from $C_6H_3Cl(NO_2)_2$ and $C_6H_5NMe_2$ or C_6H_5NHMe (Leymann, *B.* 15, 1235). Reddish needles.

NITRO-DI-PHENYL-METHYL-CARBINOL $C_6H_4(NO_2).CPh(OH).CH_3$. [107°]. Formed from *u*-di-phenyl-ethane and HNO_3 (Anschütz a. Romig, *B.* 18, 664). White prisms, yielding an acetyl derivative [86°].

o-**NITRO-PHENYL-TRIMETHYLENE GLYCOL** $C_6H_4(NO_2).CH(OH).CH_2.CH_2(OH)$. [109°]. Formed from *o*-nitro-benzoic aldehyde, acetic aldehyde, and an alkali (Baeyer a. Drewson, *B.* 15, 2861). Colourless needles.

NITRO-PHENYL TRIMETHYLENYL KETONE CARBOXYLIC ACID

$C_6H_3(NO_2).CO.C(CO_2H){<}^{CH_2}_{CH_2}$. [176°]. Obtained from its ether, which is produced by the action of ethylene bromide on sodium *p*-nitro-benzoyl-acetic ether (Perkin a. Bellinot, *B.* 18, 958). Colourless needles.—AgA′: amorphous.

Ethyl ether EtA′. [84°]. Prisms.

NITRO-PHENYL-METHYL KETONE *v.* NITRO-ACETOPHENONE.

p-**NITRO-PHENYL-METHYL-OXAZOLE** $\begin{matrix}CH:C(C_6H_4NO_2)\\N{=\!=}C(CH_3)-\end{matrix}{>}O$. [157°]. Formed by the action of conc. HNO_3 on the base obtained from acetamide and bromo-acetophenone (Lewy, *B.* 21, 925). Yellow needles, v. sol. hot alcohol. Yields an amido- derivative [115°].

p-**NITRO-PHENYL-(β)-METHYL-PIPERIDINE** $C_6H_4(NO_2).NC_5H_9Me$. [61°]. Formed by heating (β)-methyl-piperidine with $C_6H_4Cl(NO_2)$ at 150° (Lellmann a. Büttner, *B.* 23, 1389). Golden plates (from alcohol).—$B'HAuCl_4$ 2aq.

Di-nitro-phenyl-(β)-methyl-piperidine [67°]. Formed in like manner, using the compound $C_6H_3Cl(NO_2)_2$ [1:2:4]. Yellow needles.

o-**NITRO-DI-PHENYL-METHYL-PYRAZOLE** $C_{16}H_{13}N_3O_2$ *i.e.* $C_6H_4(NO_2).C{<}^{N\ .\ NPh}_{CH:CMe}$ [95°] or [105°]. (285° at 70 mm.). Formed by heating its carboxylic acid [218°] (Knorr a. Jödicke, *B.* 18, 2261). Iridescent plates [95°], slender needles, or thick prisms [105°].—$B'_2H_2PtCl_6$. [198°].

p-Nitro-di-phenyl-methyl-pyrazole $C_{16}H_{13}N_3O_2$. Formed by heating its carboxylic acid [202°]. Oil.—$B'_2H_2PtCl_6$: slender needles.

Tri-nitro-di-phenyl-methyl-pyrazole $C_6H_4(NO_2).C{<}^{N.N(C_6H_4NO_2)}_{C(NO_2)=CMe}{>}$. [178°]. Formed by nitrating di-phenyl-methyl-pyrazole (Knorr a. Laubmann, *B.* 22, 174). V. sl. sol. alcohol.

NITRO-DI-PHENYL-METHYL-PYRAZOLE CARBOXYLIC ACID

$C_6H_4(NO_2).C{<}^{N.N(C_6H_5)}_{C(CO_2H):CMe}{>}$. The ethers of the *o*- acid [218°] and of the *p*- acid [202°] are respectively formed by heating *o*- and *p*- nitro-benzoyl-acetoacetic ether with phenyl-hydrazine in HOAc (Knorr a. Jödicke, *B.* 18, 2257). The *o*- ether melts at 146° and the *p*- ether at 128°. Both crystallise well.

m-**NITRO-PHENYL-DI-METHYL-PYRIDINE DICARBOXYLIC ETHER** $C_{19}H_{20}N_2O_4$ *i.e.* $C_6H_4(NO_2).C_5NMe_2(CO_2Et)_2$. [65°]. Formed from its dihydride and fuming HNO_3 (Lepetit, *G.* 17, 461). Colourless crystals (from alcohol).—$B'_2H_2PtCl_6$. [202°]. Orange-yellow needles.—$B'HNO_3$. [130°]. Colourless needles.

NITRO-PHENYL-DI-METHYL-PYRIDINE DIHYDRIDE DICARBOXYLIC ETHER $C_6H_4(NO_2).C_5NH_2Me_2(CO_2Et)_2$. Formed from nitro-benzoic aldehyde, acetoacetic ether, alcohol, and NH_3 (Lepetit, *G.* 17, 460; *B.* 20, 1341).

o- isomeride. [120°]. Yellow tables.

m- isomeride. [161°]. Tables.

p- isomeride. [118°–122°].

m-**NITRO-PHENYL-METHYL-QUINOLINE** $C_6H_4{<}^{CH:CMe}_{N\ :\ C.C_6H_4NO_2}$. [145°]. Formed by heating aniline with *m*-nitro-α-methyl-cinnamic aldehyde and conc. HClAq (Miller a. Kinkelin, *B.* 19, 531). Small plates, v. sol. hot alcohol.—$B'HCl$.—$B'_2H_2PtCl_6$: long needles.

DI-NITRO-PHENYL-(α)-NAPHTHYLAMINE $C_{16}H_{11}N_3O_4$ *i.e.* [4:2:1]$C_6H_3(NO_2)_2.NHC_{10}H_7$. [190·5°]. Formed from (α)-naphthylamine and $C_6H_3Br(NO_2)_2$ [72°] (Heim, *B.* 21, 2302). Orange-red needles (from alcohol). Conc. H_2SO_4 forms a dark-blue solution.

Isomeride. [77°]. Prepared by nitration of phenyl-(α)-naphthylamine (Streiff, *B.* 13, 1853).

Di-nitro-phenyl-(β)-naphthylamine [169°] (H.); [179°] (E.). Prepared by the action of $C_6H_3Br(NO_2)_2$ or $C_6H_3Cl(NO_2)_2$ on (β)-naphthylamine (Heim, *B.* 21, 589; Ernst, *B.* 23, 3429). Prisms. By nitration of phenyl-(β)-naphthylamine Streiff obtained $C_{16}H_{12}(NO_2)N$ [85°] and $C_{16}H_{11}(NO_2)_2N$ [192°–195°], both crystalline.

Tetra-nitro-phenyl-naphthylamine $C_{10}H_3(NO_2)_4NHC_6H_5$. The (α)- compound [162·5°] and the (β)- isomeride [253°] are formed from aniline and the corresponding bromo-tetra-nitro-naphthalenes (Merz a. Weith, *B.* 15, 2712). Both crystallise from benzene in orange-needles (containing benzene).

DI-NITRO-PHENYL-(α)-NAPHTHYL-HYDRAZINE $C_{16}H_{12}N_4O_4$. [181°]. Formed from (α)-chloro-di-nitro-benzene and (α)-naphthyl-hydrazine (Willgerodt, *J. pr.* [2] 43, 184). Red prisms. (β)-Naphthylamine yields an isomeride [188°].

Tri-nitro-phenyl-(α)-naphthyl-hydrazine $C_{16}H_{11}N_5O_6$. [176°]. Got from an alcoholic solution of picryl chloride and (α)-naphthyl-hydrazine (W.). Occurs in a red stable modification and an unstable yellow one. (β)-Naphthylamine forms an isomeride [175°] also occurring in two forms.

DI-NITRO-PHENYL-(β)-NAPHTHYL OXIDE $C_{10}H_7.O.C_6H_3(NO_2)_2$[1:2:4]. [95°]. Formed from $C_6H_3Cl(NO_2)_2$ and (β)-naphthol (Ernst, *B.* 23, 3430). Yellow needles (from alcohol).

NITRO-PHENYL NITRO-BENZYL OXIDE $C_6H_4(NO_2).O.CH_2.C_6H_4(NO_2)$. The compound formed from *p*-nitro-benzyl chloride, *o*-nitro-phenol, and alcoholic potash melts at 129°; the *pp*- isomeride at 183° (Kumpf, *B.* 17, 1077; *A.* 224, 107).

Di-nitro-phenyl nitro-benzyl oxide. [4:2:1]$C_6H_3(NO_2)_2.O.CH_2.C_6H_4NO_2$[1:4] [201°] and [6:2:1]$C_6H_3(NO_2)_2.O.CH_2.C_6H_4NO_2$[1:4] [137°] have been prepared (Staedel, *B.* 14, 899; Kumpf).

They yield di-nitro-aniline and *p*-nitro-benzyl alcohol [91°] on heating with alcoholic ammonia.

Tri-nitro-phenyl nitro-benzyl oxide [6:4:2:1]$C_6H_2(NO_2)_3.O.CH_2.C_6H_4NO_2$[1:4]. [108°]. Long thin needles (K.).

DI-NITRO-DI-PHENYL OXIDE $C_{12}H_8(NO_2)_2$. [135°]. Formed by nitrating di-phenyl oxide (Hoffmeister, *A.* 159, 191). Needles.

Di-nitro-di-phenyl oxide $C_6H_3(NO_2)_2.OC_6H_5$. [71°]. Formed from $C_6H_3Cl(NO_2)_2$ and PhOK (Willgerodt). Needles.

Tri-nitro-di-phenyl oxide [4:2:1]$C_6H_3(NO_2)_2.O.C_6H_4NO_2$[1:$x$]. Formed from $C_6H_3Cl(NO_2)_2$ and $C_6H_4(NO_2)(OK)$. The o- compound ($x=2$) melts at 119°, the *p*- isomeride ($x=4$) at 114° (Willgerodt a. Hüetlin, *B.* 17, 1764). Both are v. sol. benzene.

Tetra-nitro-di-phenyl oxide [6:4:2:1]$C_6H_2(NO_2)_3.O.C_6H_4(NO_2)$[1:$x$]. Formed from $C_6H_2Cl(NO_2)_3$ and $C_6H_4(NO_2)(OK)$. The o-compound ($x=2$) melts at 173° and the *p*-isomeride at 153° (W. a. H.). Both are crystalline.

Tetra-nitro-di-phenyl oxide $\{C_6H_3(NO_2)_2\}_2O$. [195°]. Formed by the action of $C_6H_3Cl(NO_2)_2$ on $C_6H_3(OK)(NO_2)_2$ (Willgerodt, *B.* 13, 887). Thick crystals, almost insol. alcohol.

NITRO-PHENYL-OXY-ACETIC ACID *v.* Nitro-mandelic acid.

***p*-NITRO-PHENYL OXY-BUTYL KETONE ANHYDRIDE CARBOXYLIC ACID** $C_{12}H_{11}(NO_2)O_3$ *i.e.* $O\!<\!\begin{matrix}C(C_6H_4NO_2)\\CH_2.CH_2.CH_2\end{matrix}\!\!>\!C.CO_2H$. Formed from trimethylene bromide and sodium *p*-nitro-benzoyl-acetic ether (Perkin, jun., *B.* 18, 954; *C. J.* 51, 735). Melts at 172° when crystallised from benzene; 183° when crystallised from water.—AgA′: light-yellow needles.

Ethyl ether EtA′. [63°]. Lustrous yellow monoclinic crystals; $a{:}b{:}c = 2{\cdot}353{:}1{:}1{\cdot}853$; $\beta = 80°\ 42'$.

***m*-NITRO-PHENYL-PARACONIC ACID** $C_{11}H_9NO_6$ *i.e.* $C_6H_4(NO_2).CH\!<\!\begin{matrix}CH(CO_2H)\\O.CO\end{matrix}\!>\!CH_2$. [171°]. Formed by heating *m*-nitro-benzoic aldehyde with Ac_2O and NaOAc at 125° (Salomonson, *B.* 18, 2154; *R. T. C.* 6, 1). Crystals. Yields with baryta the salt $C_{11}H_9NO_7Ba$. The corresponding *p*- isomeride melts at 163° (S.; *cf.* Erdmann, *B.* 18, 2742).

***p*-NITRO-PHENYL-PENTINOIC ACID** $C_6H_4(NO_2).CH{:}CH.CH{:}CH.CO_2H$. [271°]. Formed from *p*-nitro-cinnamic aldehyde, Ac_2O, and NaOAc (Einhorn a. Gehrenbeck, *B.* 22, 45; *A.* 253, 357). Formed also by oxidising the ketone $C_6H_4(NO_2).CH{:}CH.CH{:}CH.COMe$ with NaOCl. Yellowish needles (from alcohol). Forms a tetrabromide [254°].—AgA′: flocculent pp.

Ethyl ether EtA′. [118°]. Plates.

o-Nitro-di-phenyl-pentinoic acid. *Nitrile* $C_6H_5.CH{:}CH.CH{:}C(C_6H_4NO_2).CN$. [206°]. Formed from *p*-nitro-benzyl cyanide, cinnamic aldehyde, and NaOEt (Remse, *B.* 23, 3135). Needles.

***p*-NITRO-PHENYL-PHENYL-(β)-AMIDO-PROPIONIC ACID** $C_6H_4(NO_2).CH(NHPh).CH_2.CO_2H$. [122°]. Formed from aniline and $C_6H_4(NO_2).CHBr.CH_2.CO_2H$ (Basler, *B.* 17, 1500). Yellow crystals.

Ethyl ether EtA′. [78°]. Crystals.

DI-NITRO-PHENYL-PHENYLENE-DI-AMINE $C_6H_3(NO_2)_2.NH.C_6H_4.NH_2$. [172°]. Formed from $C_6H_3Cl(NO_2)_2$[1:2:4] and phenylene-*m*-diamine (Leymann, *B.* 15, 1237).

NITRO-PHENYL PHOSPHATES. The following compounds have been prepared by Rapp (*A.* 224, 158), the NO_2 being in the *p*- position: $C_6H_4(NO_2)O.PO(OH)_2$ [112°]; $(C_6H_4(NO_2)O)_2PO.OH$ [133°]; $(C_6H_4(NO_2).O)_2PO.OEt$ [135°]; and $(C_6H_4(NO_2)O)_3PO$ [155°]. Tri-o-nitro-tri-phenyl phosphate melts at 126° (Engelhardt a. Latschinoff, *Z.* 1870, 230).

TRI-NITRO-TRI-PHENYL-PHOSPHINE OXIDE $OP(C_6H_4NO_2)_3$. [243°]. Got by nitrating tri-phenyl-phosphine hydrate (Michaelis a. Soden, *B.* 17, 921; *A.* 229, 324). It is accompanied by an isomeride [68°].

***m*-NITRO-PHENYL-PHTHALIMIDE** $C_6H_4\!<\!\begin{matrix}CO\text{———}O\\C(NC_6H_4NO_2)\end{matrix}\!>$. [243°]. Prepared by heating phthalic anhydride with *m*-nitro-aniline (Gabriel, *B.* 11, 2261). Needles, v. sl. sol. EtOH.

NITRO-PHENYL-PIPERIDINE. The following compounds are formed by the action of piperidine upon the corresponding halogen derivatives of nitro- and di-nitro- benzene respectively (Lellmann, *B.* 20, 680; 21, 2281): [1:4] $C_6H_4(NO_2).NC_5H_{10}$ [81°]: red prisms, yielding the salts B′HCl and $B'_2H_2PtCl_6$. [1:2] $C_6H_4(NO_2).NC_5H_{10}$ [105·5°]: yellow plates, yielding the salts B′HCl and $B'_2H_2PtCl_6$. [4:2:1] $C_6H_3(NO_2)_2.NC_5H_{10}$ [92°]: orange needles.

o-NITRO-PHENYL-PROPIOLIC ACID $C_9H_5NO_4$ *i.e.* $C_6H_4(NO_2).C{:}C.CO_2H$. Formed from $C_6H_4(NO_2).CHBr.CHBr.CO_2H$ (or its ether) and aqueous NaOH (Baeyer, *B.* 13, 2258; Müller, *A.* 212, 127). Needles (from hot water), decomposing at 156°. On boiling with water it gives o-nitro-phenyl-acetylene. Boiling alkalis yield isatin. Reduction with glucose and alkalis produces indigo. $FeSO_4$ also reduces it, in alkaline solution, to indigo-white. Its Na salt boiled with aqueous KCN and glucose yields indigo, even in presence of much HCN (Michael, *J. pr.* [2] 35, 254).

Ethyl ether EtA′. [61°]. Tables. Converted by conc. H_2SO_4 into isatogenic ether (*q.v.*).

p-Nitro-phenyl-propiolic acid [181°] (M.); [198°] (D.). From $C_6H_4(NO_2).CHBr.CHBr.CO_2Et$ and alcoholic potash (C. Müller, *A.* 212, 127; Drewson, *A.* 212, 154; Perkin, *C. J.* 49, 442). Yields *p*-nitro-phenyl-acetylene and CO_2 on distilling with steam.—AgA′: amorphous powder.

Ethyl ether EtA′. [126°]. Needles.

o-NITRO-β-PHENYL-PROPIONIC ACID $C_6H_4(NO_2).CH_2.CH_2.CO_2H$. [112°]. Formed from (2, 4, 1)-nitro-amido-phenyl-propionic acid by elimination of NH_2 (Gabriel a. Zimmermann, *B.* 12, 600; 13, 1680). Yellow crystals.—AgA′.

m-Nitro-phenyl-propionic acid. [118°]. Formed in like manner from the (3, 4, 1)-nitro-amido-phenyl-propionic acid (Gabriel, *B.* 15, 845). Yellow needles, sl. sol. water.

p-Nitro-β-phenyl-propionic acid. [164°]. Formed, together with the o- acid, by nitration of (β)-phenyl-propionic acid (Glaser a. Buchanan, *Z.* 1869, 193; Beilstein a. Kuhlberg, *A.* 163, 132).—CaA'_2 2aq.—BaA'_2 2aq: small needles.

Ethyl ether EtA′.

o-Nitro-α-phenyl-propionic acid $C_6H_4(NO_2).CHMe.CO_2H$. [110°]. Formed, together with the *p*- isomeride [88°], by nitration

of α-phenyl-propionic acid (Trinius, *A.* 227, 262). The *o-* acid forms the salt CaA'_2 2aq; the *p-* acid gives CaA'_2 2aq and BaA'_2 2aq.

Di-nitro-phenyl-propionic acid $C_6H_3(NO_2)_2.CH_2.CH_2.CO_2H$. [127°]. Formed by nitration of β-phenyl-propionic acid (G. a. Z.).

Ethyl ether EtA'. [32°]. Needles.

α-NITRO-PHENYL-PROPYLENE $C_6H_5.CH:C(NO_2).CH_3$. [64°]. Formed from benzoic aldehyde, nitro-ethane, and $ZnCl_2$ at 140° (Priebs, *A.* 225, 354); yellow needles.

Di-nitro-phenyl-propylene $C_6H_4(NO_2).CH:C(NO_2).CH_3$. The o- compound [77°] is formed, together with the *p-* isomeride [115°], by nitrating α-nitro-phenyl-propylene (T.).

Di-nitro-phenyl-propylene $C_6H_3(NO_2)_2CH:CHMe$. [118°]. Formed from $C_6H_5.CH:CMe.CO_2H$ and HNO_3 (Edeleanu, *B.* 20, 622). Yellowish needles.

***m*-NITRO-PHENYL-PYRIDYL-ETHYLENE** $C_6H_4(NO_2).CH:CH.C_5H_4N$. [120°]. Formed from *m*-nitro-benzoic aldehyde and methyl-pyridine (Schuftan, *B.* 23, 2716). Plates.—$B'_2H_2PtCl_6$. [240°].—*Mercury double salt* $B'HClHgCl_2$. [211°].—Picrate: yellow plates.

TETRA-NITRO-TETRA-PHENYL-PYRROLE $NH(C.C_6H_4NO_2)_4$. Formed from tetra-phenyl-pyrrole and HNO_3 (Fehrlin, *B.* 22, 554). Yellow needles (from HOAc), decomposing at 123°.

(α)-NITRO-(*Py.* 1)-PHENYL-QUINOLINE $C_{15}H_{10}N_2O_2$. [187°]. Formed together with a smaller quantity of a (β)-isomeride [118°] and a little of a (γ)-isomeride [135°] by nitration of (*Py.* 1)-phenyl-quinoline $C_6H_4<\begin{matrix}CPh:CH\\N{=}CH\end{matrix}$ (Königs a. Nef, *B.* 20, 624). They are all crystalline.

***m*-Nitro-(*Py.* 3)-phenyl-quinoline** $C_6H_4<\begin{matrix}CH:CH\\N:C.C_6H_4.NO_2\end{matrix}$. [124°]. Obtained by heating *m*-nitro-cinnamic aldehyde with aniline and HClAq at 140° (Miller a. Kinkelin, *B.* 18, 1900). White needles.—B'HCl.—$B'_2H_2PtCl_6$.

Tetrahydride $C_6H_4<\begin{matrix}CH_2.CH_2\\NH.CH.C_6H_4NO_2\end{matrix}$ [101°]. Tables. Yields a nitrosamine [71°].—B'HCl: silky needles.

Nitro-(*B.* 2)-phenyl-quinoline $C_{15}H_{10}N_2O_2$. [173°]. Formed, as well as a di-nitro- derivative [208°], by the nitration of (*B.* 2)-phenyl-quinoline $\begin{matrix}CPh:CH\\CH\ :CH\end{matrix}>C_5H_3N$ (La Coste a. Sorger, *A.* 230, 28). —$B'_2H_2PtCl_6$: yellow needles.

DI-NITRO-DI-PHENYL-SUCCINIC ACID $C_{16}H_{14}O_4(NO_2)_2$. The (α)- compound [226°] and its (β)- isomeride are formed by nitrating (α)- and (β)-di-phenyl-succinic acid respectively (Reimer, *B.* 14, 1804). Both give *p*-nitro-benzoic acid on oxidation.

DI-NITRO-DI-PHENYL-SULPHAZIDES $C_{12}H_{10}(NO_2)_2N_2SO_2$ *i.e.* $C_6H_4(NO_2)NH.NH.SO_2C_6H_4NO_2$? Compounds formed by the action of SO_2, nitrous acid, and alcohol on the nitro-anilines (Limpricht, *B.* 20, 1241). The *o-*, *m-*, and *p-* compounds melt at 150°, 162°, and 160° respectively. They yield nitrogen, nitro-benzene, and nitro-benzene sulphinic acid on boiling with baryta.

DI-*p*-NITRO-DI-PHENYL DISULPHIDE $(C_6H_4.NO_2)_2S_2$. [181°] (W.); [170°] (L.). Formed by oxidation of *p*-nitro-phenyl mercaptan (Willgerodt, *B.* 18, 333), or by boiling with alcoholic potash the product of the combination of potassium xanthate with *p*-nitro-diazobenzene (Leuckart, *J. pr.* [2] 41, 199). Prisms (from HOAc).

Tetra-nitro-di-phenyl-sulphide $S(C_6H_3(NO_2)_2)_2$. [193°]. Obtained from [1:2:4] $C_6H_3Cl(NO_2)_2$ and alcoholic KSH (Beilstein a. Kurbatoff, *B.* 11, 2056; Willgerodt, *B.* 12, 768). Yellow needles. An isomeric body [245°] is formed by the action of H_2SO_4 and fuming HNO_3 on $C_6H_3(NO_2)_2SCN$ (Austen a. Smith, *Am.* 8, 91).

Tetra-nitro-di-phenyl disulphide $S_2(C_6H_3(NO_2)_2)_2$. Obtained by oxidising [4:2:1] $C_6H_3(NO_2)_2SH$ (Willgerodt, *Bn.* 2, 527). Yellow needles, exploding at about 280°.

Penta-nitro-di-phenyl-sulphide $C_6H_3(NO_2)_2.S.C_6H_2(NO_2)_3$. [217°]. Formed from $C_6H_3Cl(NO_2)_2$, K_2S, and $C_6H_2Cl(NO_2)_3$ (W.). Thick crystals (from HOAc).

Hexa-nitro-di-phenyl sulphide $S(C_6H_2(NO_2)_3)_2$. [226°]. Formed from picryl chloride and K_2S (W.). Golden plates (from HOAc).

DI-NITRO-PHENYL SULPHOCYANIDE $C_6H_3(NO_2)_2SCN$. [139°]. Formed by heating [1:2:4]$C_6H_3Br(NO_2)_2$ with potassium sulphocyanide in MeOH (Austen a. Smith, *Am.* 8, 89). Buff-yellow crystals (from chloroform).

NITRO-DI-PHENYL SULPHONE $C_6H_5.SO_2.C_6H_4NO_2$. [92°]. Formed by heating di-phenyl sulphone with fuming HNO_3 (Gericke, *A.* 100, 208). Minute crystals.

Di-nitro-di-phenyl sulphone $(C_6H_4(NO_2))_2SO_2$. [164°] (G.); [197°] (S. a. N.). Formed by nitrating di-phenyl sulphone (G.) and by the action of SO_3 on nitro-benzene (Schmid a. Nölting, *B.* 9, 79). Small tables.

Tetra-nitro-di-phenyl sulphone $(C_6H_3(NO_2)_2)_2SO_2$. [241°]. Prepared by oxidising the corresponding sulphide [193°] (Beilstein a. Kurbatoff, *A.* 197, 78). Yellowish prisms.

***p*-NITRO-DIPHENYL *p*-SULPHONIC ACID** $C_6H_4(NO_2).C_6H_4SO_3H$. Prepared by sulphonation of *p*-nitro-diphenyl or by nitration of diphenyl *p*-sulphonic chloride (Gabriel a. Damberger, *B.* 13, 1408).—NaA'.—CuA'_2 4aq.—BaA'_2 4aq: small needles.

Chloride $C_{12}H_8(NO_2).SO_2Cl$. [178°].

Amide $C_{12}H_8(NO_2).SO_2NH_2$. [228°].

Ethyl ether EtA'. [169°].

Nitro-diphenyl disulphonic acid. The chloride $C_{12}H_7(NO_2)(SO_2Cl)_2$ [130°] is formed, together with $C_{12}H_6(NO_2)_2(SO_2Cl)_2$ [166°], by nitration of diphenyl disulphonic chloride (G. a. D.).

DI-NITRO-DI-PHENYL SULPHOXIDE $(C_6H_4(NO_2))_2SO$. [116°]. Formed from di-phenyl sulphoxide, $NaNO_3$, and H_2SO_4 (Colby a. McLoughlin, *Am.* 9, 70; *B.* 20, 198). Minute yellow crystals, v. sol. alcohol.

NITRO-PHENYL-THIO-CARBAMIC ACID $C_6H_4(NO_2).CS.OH$.

Methyl ether MeA'. The *m-* compound [120°] is formed by boiling *m*-nitro-phenyl-thio-carbimide with MeOH (Steudemann, *B.* 16, 551). Colourless needles.

Ethyl ether EtA'. The *m-* compound [115°] and its *p-* isomeride [176°] are formed by boiling the corresponding nitro-anilines with CS_2, alcohol, and potash (Losanitsch, *B.* 15, 470; 16, 49). Both are crystalline.

***m*-NITRO-DI-PHENYL-THIO-SEMICARBAZIDE** $C_6H_4(NO_2).NH.NH.CS.NHPh$. [147°]. Formed from phenyl-thio-carbimide and *m-*

nitro-phenyl-hydrazine (Bischler a. Brodsky, *B.* 22, 2815). Dark-yellow globular aggregates.

m - **NITRO - PHENYL - THIO - CARBIMIDE** $C_6H_4(NO_2).N.CS$. [61°]. (c. 277°). Formed by heating *m*-nitro-phenyl-thio-urea with Ac_2O (Steudemann, *B.* 16, 549, 2331). White needles.

DI-NITRO-PHENYL-THIOPHENE $C_6H_4(NO_2).C_4SH_2(NO_2)$. [178°]. Formed from phenyl-thiophene and fuming HNO_3 (Renard, *C. R.* 109, 699). Amorphous yellow powder.

m-**NITRO-PHENYL-THIO-UREA** $C_7H_7N_3SO_2$ *i.e.* $C_6H_4(NO_2).NH.CS.NH_2$. [158°]. Formed from *m*-nitro-phenyl-thiocarbimide (Steudemann, *B.* 16, 550). Lemon-yellow crystals.

m-**Nitro-di-phenyl-thio-urea** $C_6H_4(NO_2).NH.CS.NHPh$. [155°]. Formed from *m*-nitro-aniline and phenyl thiocarbimide (Brückner, *B.* 7, 1235; Losanitsch, *B.* 14, 2365; Gebhardt, *B.* 17, 3045). Small needles, sl. sol. cold alcohol.

Di-*m*-nitro-phenyl-thio-urea $CS(NH.C_6H_4NO_2)_2$. [160°]. Formed from *m*-nitro-aniline and *m*-nitro-phenyl thiocarbimide (Brückner, *B.* 6, 1103; S.). Yellow crystals.

o-NITRO-PHENYL-*p*-TOLUIDINE $C_6H_4(NO_2).NH.C_7H_7$. [68°]. Formed from *p*-toluidine and o-bromo-nitro-benzene (Schöpff, *B.* 23, 1842). Orange plates.

Di-nitro-phenyl-toluidine [4:2:1] $C_6H_3(NO_2)_2.NHC_6H_4Me$ [1:*x*]. Formed from toluidine and $C_6H_3Cl(NO_2)_2$ (Willgerodt, *B.* 9, 980; Leymann, *B.* 15, 1236). The o- compound ($x = 2$) melts at 102°, the *p*- compound ($x = 4$) at 137°. The isomeric $PhNH.C_6H_2(NO_2)_2Me$ formed from tri-nitro-toluene and aniline, melts at 142° (Hepp, *A.* 215, 369).

DI-NITRO-PHENYL-TOLYLENE-DIAMINE $C_6H_3(NO_2)_2NH.C_6H_3Me.NH_2$. [184°]. Formed from tolylene *m*-diamine and [1:2:4] $C_6H_3Cl(NO_2)_2$ (Leymann, *B.* 15, 1237). Red tables.

Formyl derivative [157°].

Acetyl derivative [164°].

NITRO-PHENYL-TOLYL-KETONE $C_{14}H_{11}(NO_2)O$. [127°]. Formed by the action of HNO_3 on phenyl tolyl ketone and on phenyl-*p*-tolyl-methane (Plascuda a. Zincke, *B.* 7, 983; Milne, *B.* 5, 685). Flat plates (from alcohol).

Di-nitro-phenyl-*m*-tolyl-ketone $C_{14}H_{10}(NO_2)_2O$. [145°]. Formed from di-nitro-phenyl-*m*-tolyl-methane [141°], HOAc, and CrO_3 (Senff, *A.* 220, 236). Pointed needles (from alcohol) or short prisms (from HOAc).

Di-nitro-phenyl-*p*-tolyl-ketone $C_6H_4(NO_2).CO.C_7H_6(NO_2)$. [127°]. Formed, as well as the tri-nitro- derivative [165°], by nitration of phenyl-*p*-tolyl ketone (Z. a. P.). Needles.

m-**NITRO-PHENYL-DI-TOLYL-METHANE** $(C_7H_7)_2CH.C_6H_4NO_2$. [85°]. Formed from *m*-nitro-benzoic aldehyde, toluene, and H_2SO_4 (Tschacher, *B.* 19, 2464; 21, 188). Crystals.

Di-nitro-phenyl-tolyl-methane $C_{14}H_{12}(NO_2)_2$. The three compounds of this composition got by nitrating phenyl- o-, *m*-, and *p*- tolyl-methane melt at 100°, 141°, and 137° respectively (Zincke, *B.* 7, 986; Senff, *A.* 220, 235). Tetra-nitro-phenyl-*p*-tolyl-methane melts at 161°.

NITRO-PHENYL-*p*-TOLYL-THIO-UREA $C_{14}H_{13}N_3SO_2$ *i.e.* $C_6H_5.NH.CS.NH.C_7H_6NO_2$. [143°]. Formed from (2,4,1)-nitro-toluidine and phenyl-thiocarbimide (Steudemann, *B.* 16, 2336). Crystals. Melts, after one fusion, at 167°.

m-**Nitro-phenyl-*p*-tolyl-thio-urea** $C_6H_4(NO_2).NH.CS.NH.C_7H_7$. [173°]. Formed from *m*-nitro-phenyl thiocarbimide and *p*-toluidine (S.). Needles, sl. sol. ether.

Di-nitro-phenyl-*p*-tolyl-thio-urea $C_6H_4(NO_2).NH.CS.NH.C_7H_6NO_2$. [188°]. Formed from *m*-nitro-phenyl thiocarbimide and (2,4,1)-nitro-toluidine (S.). Crystals, sl. sol. alcohol.

m-**NITRO-PHENYL-UREA** $C_7H_7N_3O_3$ *i.e* $C_6H_4(NO_2).NH.CO.NH_2$. Formed from *m*-nitro-aniline and cyanogen chloride (Hofmann, *A.* 67, 156; 70, 137). Yellow needles (from water).

m-**Nitro-di-phenyl-urea** $C_6H_5NH.CO.NHC_6H_4NO_2$. [197°] (G.); [187°] (B.). Formed from *m*-nitro-di-phenyl-thio-urea and PbO (Brückner, *B.* 7, 1236). Formed also by boiling with benzene the compound $PhNH.CO.N(C_6H_4.NO_2).N:NPh$ [104°] obtained by the action of phenyl cyanate on $(C_6H_4NO_2).NH.N:NPh$ (Goldschmidt, *B.* 21, 2573). Yellow needles.

p-**Nitro-di-phenyl-urea** [202°]. Formed by the action of phenyl cyanate on a solution of *p*-nitro-diazoamidobenzene in benzene (G.). Yellow crystals (from alcohol).

m-**Nitro-tri-phenyl-urea** $NPh_2.CO.NHC_6H_4NO_2$. [155°]. Formed from *m*-nitro-aniline and $NPh_2.COCl$ (Lellmann a. Bonhöffer, *B.* 20, 2121). Yellow needles. The isomeride prepared from *p*-nitro-aniline melts at 176°, and crystallises in bluish-green tables.

Di-*m*-nitro-di-phenyl-urea $CO(NH.C_6H_4NO_2)_2$. [233°]. Formed from the thio-urea and PbO (B.). Yellow needles (Losanitsch, *B.* 16, 50).

Tetra-nitro-di-phenyl-urea $CO(NH.C_6H_4(NO_2)_2)_2$. Formed by nitration of di-phenyl-urea (Losanitsch, *B.* 10, 690; 11, 1539). Yellow needles, melting above 200° (L.) or at 189° (Hentschel, *J. pr.* [2] 34, 426). The green K salt $C_{13}H_6K_2N_6O_9$ explodes on heating.

p-**NITRO-PHENYL-VALERIC ACID** $C_6H_4(NO_2).CH_2.CHEt.CO_2H$. Formed by heating *p*-nitro-benzyl-ethyl-malonic ether with aqueous KOH (Lellmann a. Schleich, *B.* 20, 438). Sparingly soluble powder, carbonising above 300°.

p-**NITRO-PHENYL-VINYL-MALONIC ACID** $C_6H_4(NO_2).CH:CH.CH(CO_2H)_2$. [208°]. Formed from *p*-nitro-cinnamic aldehyde, malonic acid, and HOAc (Einhorn a. Gehrenbeck, *B.* 22, 45).

NITRO-PHLOROGLUCIN $C_6H_2(NO_2)(OH)_3$. Formed from phloroglucin and dilute HNO_3. (Hlasiwetz a. Pfaundler, *A.* 119, 199). Reddish-yellow scales, sl. sol. water.

Tri-nitro-phloroglucin $C_6(NO_2)_3(OH)_3$. [158°]. Formed from tri-nitroso-phloroglucin, HNO_3, and H_2SO_4 (Benedikt, *B.* 11, 1376). Hexagonal crystals (containing aq). Its salts are explosive and dye yellow. With KCy it gives the isopurpuric acid reaction.—KH_2A''' aq.—K_2HA'''.—K_3A'''.

NITRO-PHTHALIC ACID $C_6H_3(NO_2)(CO_2H)_2$ [3:2:1]. Mol. w. 211. [220°]. S. (HOAc) 7·5 at 26° (Aguiar, *B.* 5, 899).

Formation.—1. By boiling naphthalene with HNO_3 (Marignac, *A.* 38, 7; Laurent, *A.* 41, 110).—2. By nitration of phthalic acid (Hugo Müller, *Z.* 1863, 257; Faust, *A.* 160, 57; Miller, *A.* 208, 224).—3. By oxidation of nitro-naphthalene or of (α)-di-nitro-naphthalene (Beilstein a. Kurbatoff, *B.* 12, 688; *C. C.* 1881, 359; *A.* 202, 217; Guareschi, *B.* 10, 294).

Properties. — Yellow crystals, v. sol. hot

water. Splits up below its melting-point into water and anhydride when slowly heated.

Salts.—K_2A''aq.—KHA''aq.—$(NH_4)_2A''$.—$(NH_4)HA''$ 2aq. — $BaA''x$aq. — ZnA'' $1\frac{1}{2}$aq. — $PbA''1\frac{1}{2}$aq.—Ag_2A'': white powder.

Mono-ethyl ether $EtHA''$. [111°].

Di-ethyl ether Et_2A''. [45°].

Anhydride $C_8H_3NO_5$. [164°] (Graeff, *B.* 15, 1127).

Nitro-phthalic acid $C_6H_3(NO_2)(CO_2H)_2$ [4:2:1]. [161°].

Formation.—1. Together with the preceding isomeride, by nitration of phthalic acid (O. Miller, *A.* 208, 224).—2. By the oxidation of di-nitro-(β)-naphthol (Graebe a. Drews, *B.* 17, 1171).

Properties.—Small pale-yellow needles (containing aq). Resolved at 165° into water and its anhydride.

Salts. — K_2A''.—BaA''2aq.—$Ba_{12}H_2A''_{13}$.—$Zn_{12}H_2A''_{13}$2aq.—Ag_2A'': long colourless needles.

Mono-ethyl ether $EtHA''$. [128°].

Di-ethyl ether Et_2A''. [33°].

Anhydride $C_8H_3NO_5$. [114°].

Di-nitro-phthalic acid $C_6H_2(NO_2)_2(CO_2H)_2$ [5:3:2:1]. [226°]. Formed by the oxidation of 'β'-di-nitro-naphthalene or tetra-nitro-(α)-naphthol with dilute HNO_3 (Beilstein a. Kurbatoff, *B.* 13, 354; *A.* 202, 225; Merz a. Weith, *B.* 15, 2728). Prisms.—CaA''.—BaA''.

Mono-ethyl ether $EtHA''$. [187°].

Di-nitro-phthalic acid $C_6H_2(NO_2)_2(CO_2H)_2$ [6:3:2:1]. [200°]. Formed by heating 'β'-bromo-tetra-nitro-naphthalene with dilute HNO_3 (Merz a. Weith, *B.* 15, 2728). Needles.—BaA''.

Di-nitro-phthalic acid $C_6H_2(NO_2)_2(CO_2H)_2$. Formed from nitro-anisic acid, HNO_3, and H_2SO_4 (Engelhardt a. Latschinoff, *Z.* [2] 7, 262). Tables (from water).—BaA'': nearly insol. water.

Nitro-isophthalic acid $C_6H_3(NO_2)(CO_2H)_2$ [5:3:1]. [249°]. S. ·146 at 15°; ·171 at 16°; 81·1 at 99°. Prepared, together with an isomeride [260°] by heating isophthalic acid (100 g.) with fuming HNO_3 (1 kilo) for 24 hours (Beyer, *J. pr.* [2] 22, 352; 25, 473; *cf.* Storrs a. Fittig, *A.* 153, 285). Plates (containing $1\frac{1}{2}$ aq).

Salts.—$K_2A''1\frac{1}{2}$aq. S. (80 p.c. alcohol) ·744 at 15°.—Na_2A''aq. S. (80 p.c. alcohol) ·32 at 15°. Explodes above 160°.—$(NH_4)HA''$.—MgA''5aq. S. 2·15 at 15°.—$CaA''3\frac{1}{2}$aq. S. ·72 at 15°. Turned violet by light.—$SrA''4\frac{1}{2}$aq. S. ·47 at 15°.—$BaA''2\frac{1}{2}$aq. S. ·85 at 15°.—ZnA''aq. S. ·55.—CdA''2aq. S. ·75 at 15°.—$Pb_5OA''_4$.—$Cu_3OA''_2$.—MnA''5aq. S. 2·44 at 15°.—$Fe_{14}O_9A''_{12}$.—CoA'' $4\frac{1}{2}$aq. S. 2·16 at 15°.—NiA'' $4\frac{1}{2}$aq. S. 2·74 at 15°.—Ag_2A''. Explodes above 100°.

Methyl ether Me_2A''. [122°].

Ethyl ether Et_2A''. [84°].

Nitro-isophthalic acid $C_6H_3(NO_2)(CO_2H)_2$ [4:3:1]. [246°] (C.); [259°]. Formed by oxidation of nitro-xylene (Claus, *J. pr.* [2] 38, 318; *cf.* Wroblewsky, *Bl.* [2] 34, 332; Noyes, *Am.* 10, 472). White needles (containing 3aq), m. sol. cold water.—BaA'' 4aq (C.).—BaA'' $1\frac{1}{2}$aq (N.).—$CaA''\frac{1}{2}$aq. — MgA''6aq. — PbA''3aq (W.).—$Ag_2A''7\frac{1}{2}$aq: pearly plates.

Di-nitro-isophthalic acid $C_6H_2(NO_2)_2(CO_2H)_2$. [215°]. Formed from isophthalic acid and fuming HNO_3 at 180° (Claus). Needles (containing 5aq). — Na_2A'' 2aq. — K_2A'' 2aq. — BaA'' 7aq.—CaA'' 4aq.—MgA'' 4aq: needles, v. sol. water.

NITRO-PHTHALIDE $\left[4:\frac{1}{2}\right] C_6H_3(NO_2){<}{\genfrac{}{}{0pt}{}{CO}{CH_2}}{>}O$. [141°]. Formed by nitration of phthalide (Hoenig, *B.* 18, 3447). Long needles. Aqueous KOH yields $C_6H_3(NO_2)(CH_2OH)(CO_2K)$. CrO_3 in HOAc oxidises it to nitrophthalic acid [161°]. The acid of which it is the anhydride melts at 129°. An isomeric nitro-phthalide [136°] is formed by oxidising (α)-nitro-naphthalene.

NITRO-DIPHTHALYL $C_{16}H_7NO_6$ *i.e.* $C_6H_4{:}C_4O_4{:}C_6H_3NO_2$. [270°]. Formed by heating nitro-phthalide with phthalic anhydride and NaOAc (Graebe a. Guye, *A.* 233, 244). Yellow needles (from HOAc).

NITRO-PIPERIDINE $C_5H_{10}N(NO_2)$. (245°). Formed by treating piperyl-urea with HNO_3 (S.G. 1·5) at −10°, pouring upon sodium carbonate and extracting with ether (Franchimont a. Klobbie, *R. T. C.* 8, 302). Colourless liquid, solidifying below −10°. Volatile with steam.

NITROPODOCARPIC ACID *v.* PODOCARPIC ACID.

NITRO-PROPANE $C_3H_7NO_2$ *i.e.* $PrNO_2$. (127°) (M. a. R.); (131°) (P.). S.G. $\frac{15}{15}$ 1·0108; $\frac{25}{25}$ 1·0023. M.M. 3·819 (Perkin, *C. J.* 55, 689). Formed, together with propyl nitrite, by the action of silver nitrite on propyl iodide (V. Meyer a. Rilliet, *B.* 5, 1029; *A.* 171, 36; Pribram a. Handl, *M.* 2, 653; Cahours, *C. R.* 77, 749). Oil.—$NaC_3H_6NO_2$: white powder.

Iso-nitro-propane $PrNO_2$. (c. 117°). Formed, together with an isomeride (44°), by the action of silver nitrite on isopropyl iodide (V. Meyer a. Locher, *B.* 7, 670; *A.* 171, 39; Kiesel, *J. R.* 16, 135; *Bl.* [2] 40, 72; *Bn.* 1, 225). Oil, decomposed by HClAq at 100°.

Di-nitro-propane $CH_3.CH_2.CH(NO_2)_2$. (189° cor.). S.G. $\frac{22\cdot5}{}$ 1·258. Formed from bromo-nitro-propane and KNO_2 (Ter Meer, *A.* 181, 19), and by the oxidation of di-propyl ketone (Chancel, *C. R.* 96, 1466; Kurtz, *A.* 161, 208). Oil.—KA'.—AgA': explosive laminæ.

Iso-di-nitro-propane $(CH_3)_2C(NO_2)_2$. [53°]. (187° uncor.). Formed by oxidation of propyl-pseudonitrole $(CH_3)_2C(NO)(NO_2)$ (Meyer a. Locher, *B.* 7, 1613). Formed also by the action of nitric acid on isobutyric and isovaleric acids (Bredt, *B.* 15, 2322). White crystals, volatile with steam.

NITRO-PROPENYL-BENZOIC ACID $C_6H_3(NO_2)(C_3H_5)CO_2H$ [3:4:1]. [155°]. Formed by boiling nitro-oxypropyl-benzoic acid with aqueous HCl (S.G. 1·10) for a long time (Widman, *B.* 15, 2551; 16, 2569). Short needles.—NH_4A'.—CaA'_2 2aq. S. ·555 at 16°.—BaA'_2 $3\frac{1}{2}$aq. S. ·425 at 18°.—CuA'_2 aq.—AgA': slender needles.

β-NITRO-PROPIONIC ACID $C_3H_5NO_4$ *i.e.* $CH_2(NO_2).CH_2.CO_2H$. [67°]. Formed from β-iodo-propionic acid and $AgNO_2$ (Lewkovitch, *J. pr.* [2] 20, 165). Scales (from chloroform).

Ethyl ether EtA'. (c. 163°). V.D. 4·85 (calc. 5·09).

DI-NITRO-PROPYL-ANILINE $C_9H_{11}N_3O_4$ *i.e.* $C_6H_3(NO_2)_2NHC_3H_7$ [4:2:1]. [95°]. Formed from propylamine and $C_6H_3Br(NO_2)_2$, or by oxidising the following body (Van Romburgh, *R. T. C.* 4, 191; 8, 252). Yellow needles.

Di-nitro-di-propyl-aniline $C_6H_3(NO_2)_2N(C_3H_7)_2$ [4:2:1]. [40°] (Romburgh, *R. T. C.* 8, 252).

Tri-nitro-propyl-aniline $C_6H_2(NO_2)_3NH.C_3H_7$. [59°]. Formed from $NH_2C_3H_7$ and $C_6H_2Cl(NO_2)_3$. Yields, with HNO_3, the nitramine $C_6H_2(NO_2)_3N(NO_2)C_3H_7$ [97°].

NITRO-ISOPROPYL BENZENE *v.* NITRO-CUMENE.

Di-nitro-*p*-di-propyl-benzene $C_6H_2Pr_2(NO_2)_2$. [65°]. Formed from di-propyl-benzene and fuming HNO_3 (Körner, *B.* 11, 1865; *A.* 216, 226). Plates, volatile with steam.

Tri-nitro-*m*-di-isopropyl benzene $C_6HPr_2(NO_2)_3$. [111°]. Yellow needles (Uhlhorn, *B.* 23, 3142).

NITRO-PROPYL-BENZOIC ACID *v.* NITRO-*n*-CUMINIC ACID.

NITRO-ISOPROPYL-CINNAMIC ACID [4:2:1] $C_6H_3Pr(NO_2).CH:CH.CO_2H$. '*Nitro-cumenyl-acrylic*' *acid.* [157°]. Formed by nitration of propyl-cinnamic acid (Einhorn a. Hess, *B.* 17, 2016; Widman, *B.* 19, 258). Needles, v. sol. alcohol. Yields o-nitro-cuminic aldehyde on oxidation by $KMnO_4$.

Nitro-isopropyl-cinnamic acid [4:3:1] $C_6H_3Pr(NO_2)C_2H_2.CO_2H$. [141°]. Formed by heating *m*-nitro-cuminic aldehyde (4 pts.) with Ac_2O (5 pts.) and NaOAc (3 pts.) at 175° for 4 hours (Widman, *B.* 19, 413). Tables. Forms a dibromide [184°].—KA′ (dried at 100°).—NaA′ 3aq.—BaA'_2 5½aq.—CaA'_2 3aq.

Ethyl ether EtA′. [59°]. Tables.

Nitro-*n*-propyl-cinnamic acid [4:2:1] $C_6H_3Pr(NO_2)C_2H_2CO_2H$. [123°]. Formed, in small quantity, in the nitration of isopropyl-cinnamic acid (Widman, *B.* 19, 273). On oxidation by alkaline $KMnO_4$ it yields nitro-*n*-cuminic acid and nitro-cuminic acid. Bromine forms a di-bromide [171°].

DI-NITRO-PROPYL-THIOPHENE $C_4HPr(NO_2)_2S$. Formed by nitration (Ruffi, *B.* 20, 1742). Oil.

NITRO-PROTOCATECHUIC ACID $C_7H_5NO_6$.

Methyl derivative $C_6H_2(NO_2)(OMe)(OH)CO_2H$ [*x*:3:4:1]. Formed by boiling its acetyl derivative [182°] which is produced by the nitration of acetyl-vanillic acid $C_6H_3(OMe)(OAc)CO_2H$ (Tiemann a. Matsmoto, *B.* 9, 945; 11, 132). Needles (from alcohol).

The isomeric $C_6H_2(NO_2)(OMe)(OH).CO_2H$ [5:3:4:1] [202°] is formed by oxidation of acetyl-nitro-eugenol (Weselsky a. Benedikt, *M.* 3, 392), and crystallises in yellow needles.

Methyl derivative $C_6H_2(NO_2)(OMe)(OH)CO_2H$ [6:4:3:1]. [173°]. Formed from its acetyl derivative [169°], which is got by nitrating acetyl-isovanillic acid (T. a. M.). Needles.

Di-methyl derivative $C_9H_9NO_6$ *i.e.* $C_6H_2(NO_2)(OMe)_2CO_2H$. Formed by nitration of veratric acid $C_6H_3(OMe)_2CO_2H$ (T. a. M.; Merck, *A.* 108, 59). Yellow needles (containing ½aq). Yields the ethers MeA′ [144°] and EtA′ [100°].

Iso-nitro-protocatechuic acid. *Di-methyl ether* $C_6H_2(NO_2)(OMe)_2CO_2H$. [202°]. Formed by methylation of nitro-vanillic acid (T. a. M.). Needles. Yields MeA′ [128°] crystallising in needles.

Nitro-protocatechuic acid. *Methyl-propyl ether* $C_{11}H_{13}NO_6$ *i.e.* $C_6H_2(NO_2)(OMe)(OPr)CO_2H$. Formed by nitration (Cahours, *Bl.* [2] 29, 270).

Nitro-protocatechuic acid. *Methylene ether* $CH_2O_2:C_6H_2(NO_2)CO_2H$. [172°]. Formed from piperonylic acid $CH_2<\substack{O\\O}>C_6H_3.CO_2H$ by nitration (Jobst a. Hesse, *B.* 11, 1031; *A.* 199, 70). Needles.—KA′ ½aq.—PbA'_2 aq.—CuA_2' 4aq.—AgA′: needles or plates.

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NITROPYROCATECHIN $C_6H_5NO_4$ *i.e.* $C_6H_3(NO_2)(OH)_2$[4:2:1]. [170°]. Formed by the action of nitrous acid on pyrocatechin (Benedikt, *B.* 11, 362; *J. pr.* [2] 18, 455). Formed also by boiling the carbonyl derivative of (5,2,1)-nitro-amido-phenol with potash (Von Chelmicki, *J. pr.* [2] 42, 442). Small yellow needles (from ether). Its aqueous solution is turned purple by alkalis. Dyes stuff mordanted with alumina orange (Kostanecki, *B.* 22, 1347).—BaA″ 3aq: dark-red plates, with metallic lustre.

An isomeric nitropyrocatechin [86°] is formed, together with the preceding, by nitration of pyrocatechin (Weselsky a. Benedikt, *M.* 3, 386). A *di-methyl derivative* of nitro-pyrocatechin $C_6H_3(NO_2)(OMe)_2$ [96°] is formed by nitrating veratrole (Merck, *A.* 108, 60; Tiemann a. Matsmoto, *B.* 9, 939; 11, 131).

The *methylene derivative* $C_6H_3(NO_2)<\substack{O\\O}>CH_2$ [148°] is a product of the action of nitric acid on piperonylic acid (Hesse, *A.* 199, 73, 341). It crystallises in needles.

Di-nitro-pyrocatechin $C_6H_2(NO_2)_2(OH)_2$. *Methyl derivative* $C_6H_2(NO_2)_2(OMe)(OH)$. *Di-nitro-guaiacol.* [123°]. Made by the action of nitrous acid gas upon an ethereal solution of guaiacol at 0° (Herzig, *M.* 3, 825). Plates. The *di-methyl derivative* $C_6H_2(NO_2)_2(OMe)_2$, formed by nitration of veratrol, melts above 100° (M.). The *methylene derivative* $C_6H_2(NO_2)_2O_2CH_2$ [101°] is formed in the nitration of piperonylic acid (H.).

Tri-nitro-pyrocatechin. *Di-methyl-derivative* $C_6H(NO_2)_3(OMe)_2$. [145°]. Got by nitrating $C_6H_3(NO_2)(OMe)_2$ (T. a. M.). Prisms.

DI-NITRO-PYROCOLL $C_{10}H_4(NO_2)_2N_2O_2$. Got by nitrating pyrocoll (Ciamician a. Danesi, *G.* 12, 39). Yellow crystals, decomposing before fusion.

NITRO-PYROGALLOL $C_6H_2(NO_2)(OH)_3$. [205°]. Got by passing nitrous fumes into an ethereal solution of pyrogallol (Barth, *M.* 1, 882). Triclinic olive-brown prisms (containing aq); $a:b:c = 2{\cdot}842:1:{\cdot}493$. $C_6H_2(NO_2)(OEt)_2(OH)$ [123°] and $C_6H_2(NO_2)(OEt)(OH)_2$ [139°] are formed in the same way (Weselsky a. Benedikt, *M.* 2, 214). The compounds $C_6H(NO_2)_2(OEt)_3$ [73°] and $C_6(NO_2)_3(OEt)_3$ [93°] are formed by nitration.

NITROPYROMECONIC ACID $C_5H_3(NO_2)O_3$. Formed by nitrating pyromeconic acid (Ost, *J. pr.* [2] 19, 192). Crystals (from alcohol).—NaA′.—AgA′.

DI-NITRO-PYROMELLITIC ACID $C_6(NO_2)_2(CO_2H)_4$ [5:2:6:4:3:1]. Formed by oxidation of di-nitro-ψ-cuminic acid $C_6Me_3(NO_2)_2CO_2H$ [205°] (Nef, *C. J.* 53, 428; *A.* 258, 317). Long silky needles.—Ag_2A'': amorphous pp.

Methyl ether Me_4A^{iv} [180·6°].

Ethyl ether Et_4A^{iv}. [130°].

NITRO-PYROMUCIC ACID $C_5H_3NO_5$ *i.e.* $C_4H_2(NO_2)O.CO_2H$. [184°]. Formed from dehydromucic acid (1 pt.), HNO_3 (10 pts.), and conc. H_2SO_4 (1 pt.) (Klinkhardt, *J. pr.* [2] 25, 51). Got also from $C_4H_2(NO_2)O.CH:CH(NO_2)$ by

oxidation with CrO_3 (Priobs, *B.* 18, 1362). Yellow plates (from water). Yields succinic acid (and not an amido- acid) on reduction with tin and HClAq.—CaA'_2.—PbA'_2.—AgA'.

Ethyl ether EtA'. [101°].

DI-NITRO-PYRROLE $C_4H_2(NO_2)_2NH$. [152°]. Formed by the action of fuming HNO_3 on pyrryl methyl ketone. Formed also, together with an isomeride [173°], by the action of fuming HNO_3 on pyrrole carboxylic acid at 0° (Ciamician a. Silber, *B.* 18, 1462; 19, 1081; *G.* 16, 347). Colourless plates. BaA'_2: yellow needles.

NITRO-PYRROLE CARBOXYLIC ACID $C_4H_2(NO_2)NH(CO_2H)$. [217°]. Formed by saponifying its methyl ether, which is got by nitrating $C_4H_3NH(CO_2Me)$ (Anderlini, *B.* 22, 2505; *Rend. Accad. Linc.* [5] 1, 40). Yellow needles (containing aq), sl. sol. cold water.

Methyl ether MeA'. [197°].

An isomeric acid [161°] may be obtained from its methyl ether [179°] which accompanies the preceding ether. $C_4H(NO_2)_2NH(CO_2Me)$ [115°] is also formed in the nitration.

Nitro-pyrrole carboxylic acid. [146°]. Formed by boiling di-nitro-pyrocoll with potash solution (Ciamician a. Danesi, *G.* 12, 40). Minute needles (containing aq).—NH_4A': prisms or scales.

NITRO-PYRRYLENE-DI-METHYL DIKETONE $C_8H_8N_2O_4$ *i.e.* $C_4H_2(NO_2)N(CO.CH_3)_2$. [149°]. Formed by nitrating pyrrylene di-methyl diketone (Ciamician a. Silber, *G.* 16, 347; *B.* 18, 1467; 19, 1078). Needles (from water).

NITRO-PYRRYL METHYL KETONE. By nitrating $NH<\begin{matrix}CH:CH\\CAc:CH\end{matrix}$ two compounds are formed [197°] and [156°]. Both yield pps. of $C_6H_5N_2O_3Ag$ (Ciamician a. Silber, *B.* 18, 413, 1457). A compound $C_4H_2(NO_2)_2N.CO.CH_3$ [114°] crystallising in yellow needles (containing aq) may also be obtained.

(*B.* 1)-NITRO-QUINOLINE $C_9H_6N_2O_2$ *i.e.* $\begin{matrix}CH:C(NO_2).C.CH:CH\\CH:CH——C.N:CH\end{matrix}$ [72°]. Formed, together with the (*B.* 4)-isomeride, by the nitration of quinoline, especially in presence of fuming H_2SO_4 in the cold (Claus a. Kramer, *B.* 18, 1243; Noelting a. Trautmann, *B.* 23, 3654). Colourless needles (containing aq).

(*B.* 2)-Nitro-quinoline $\begin{matrix}NO_2C\ :CH.C.CH:CH\\CH:CH.C.\ N\ :CH\end{matrix}$ [150°] (La Coste, *B.* 16, 669); [164°] (C. a. K.). Formed by boiling *p*-nitro-aniline (25 pts.), glycerin (60 pts.), nitro-benzene (15 pts.), and H_2SO_4 (50 pts.) for 4 hours. Needles (containing aq).—$B'_2H_2PtCl_6$: small yellow needles.

Methylo-iodide B'MeI. Needles.

(*B.* 3)-Nitro-quinoline $\begin{matrix}CH:CH.C.CH:CH\\NO_2.C\ :CH.C.\ N\ :CH\end{matrix}$ [131·5°]. Formed from *m*-nitro-aniline, picric acid, glycerin, and H_2SO_4 (Claus a. Stiebel, *B.* 20, 3095). Needles.—B'HCl. [225°].—$B'HNO_3$.—$B'_2H_2PtCl_6$: prisms.

(*B.* 4)-Nitro-quinoline $\begin{matrix}CH:CH——C.CH:CH\\CH:C(NO_2).C.\ N\ :CH\end{matrix}$ [89°]. Formed by nitrating quinoline; and also by boiling *o*-nitro-aniline with glycerin, nitrobenzene, and H_2SO_4 (Königs, *B.* 12, 449; La Coste, *B.* 16, 673; Claus, *B.* 18, 1243; Noelting, *B.* 23, 3654). Formed also by heating quinoline (*B.* 4)-sulphonic acid with HNO_3 (Claus a. Küttner, *B.* 19, 2886), and by warming $C_6H_3(NO_2)(OMe).CH:CH.CHO$ with alcoholic ammonia (Miller a. Kinkelin, *B.* 22, 1716). Prisms.—$B'_2H_2PtCl_6$: orange needles.

(*B.* 2, 4)-Di-nitro-quinoline $\begin{matrix}C(NO_2):CH.C.CH:CH\\CH:C(NO_2).C.\ N\ :CH\end{matrix}$ [150°]. Formed by heating (4, 2, 1)-di-nitro-aniline with glycerin, nitro-benzene, and H_2SO_4 (La Coste, *B.* 15, 562). Long slender needles.

By the nitration of quinoline two isomeric di-nitro-quinolines [183°] and [134°] may be got (Claus a. Kramer, *B.* 18, 1243). Their platinochlorides $B'H_2H_2PtCl_6$ form yellow crystals.

NITRO-QUINOLINE-(*Py.* 3)-CARBOXYLIC ACID $C_9H_5(NO_2)(CO_2H)N$. [220°]. Formed by boiling (*Py.* 3)-methyl-quinoline (quinaldine) with nitric acid (S.G. 1·4) (Doebner a. Miller, *B.* 15, 3076). Crystals, sl. sol. cold water.—AgA'.

NITRO-RESORCIN $C_6H_3(NO_2)(OH)_2$[4:3:1]. [115°]. Formed together with a volatile (2, 3, 1)-isomeride [85°], in the preparation of diazoresorcin by the action of nitrous acid on an ethereal solution of resorcin (Weselsky, *A.* 164, 1; *M.* 1, 887). Lemon-yellow needles. When heated with concentrated sulphuric acid it yields $O(C_6H_3(NO_2)OH)_2$ (Hazura, *M.* 4, 610; 5, 188) which forms $Ba(C_{12}H_7N_2O_7)_2$ 2aq and $BaC_{12}H_6N_2O_7$ 5½aq. The isomeride [85°] is converted by the action of nitrous acid into $C_6H_2(OH)O(NOH)(NO_2)$[1:3:4:2] (De la Harpe a. Reverdin, *Bl.* [2] 49, 760).—$BaH_2A''_2$ 5aq.—$BaH_2A''_2$ aq.—$BaH_4A''_3$ 2aq: golden needles.

Methyl ethers $C_6H_3(NO_2)(OH)(OMe)$[4:3:1]. [95°]. Volatile with steam.— $C_6H_3(NO_2)(OMe)(OH)$[4:3:1]. [144°]. Not volatile with steam.

Ethyl ethers $C_6H_3(NO_2)(OEt)(OH)$. [79°]. Volatile with steam. [131°]. Non-volatile.

Di-acetyl derivative $C_6H_3(NO_2)(OAc)_2$. [91°]. Tables (from alcohol) (Errera, *G.* 15, 273).

Di-benzoyl derivative $C_6H_3(NO_2)(OBz)_2$. [111°]. Got by nitration (Schiaparelli a. Abelli, *G.* 13, 257; Errera, *G.* 15, 271).

Di-m-nitro-di-benzoyl derivative [123°].

Di-nitro-resorcin $C_6H_2(NO_2)_2(OH)_2$[4:2:3:1]. [142°]. Formed by the action of nitrous fumes, or of cold HNO_3, upon di-nitroso-resorcin (Benedikt a. Hübl, *M.* 2, 323; Bärr, *B.* 21, 1544; Von Kostanecki, *B.* 21, 3122). Formed also by boiling di-nitro-*m*-amido-phenol with dilute KOHAq (Lippmann a. Fleissner, *M.* 6, 814; 7, 98). Golden leaflets.—K_2A'' ½aq.—BaA''.—Ag_2A'': red pp.

Methyl ether $C_6H_2(NO_2)_2(OMe)(OH)$. [75°]. Needles (Aronheim, *B.* 12, 30).

Di-nitro-resorcin $C_6H_2(NO_2)_2(OH)_2$. [213°]. Formed by nitration of the di-acetyl derivative of resorcin (Typke, *B.* 16, 552). Yellow prisms or needles.—$(NH_4)_2A''$.—$BaH_2A''_2$.—BaA'': red scales with violet lustre, v. sl. sol. water.

Ethers $C_6H_2(NO_2)_2(OMe)_2$: [67°]; $C_6H_2(NO_2)_2(OEt)_2$. [75°]. Obtained by nitration of the ethers of resorcin (Hönig, *B.* 11, 1039; Aronheim, *B.* 12, 32).

Tri-nitro-resorcin $C_6H(NO_2)_3(OH)_2$[6:4:2:3:1]. *Styphnic acid. Oxypicric acid.* Mol. w. 245. [175°]. S. ·64 at 14° (Stenhouse, *Pr.* 19, 410).

Formation.—1. By the action of boiling nitric acid on extract of Brazil wood, or sapan wood, euxanthone, gum ammoniac, asafœtida, galbanum, peucedanin, ostruthin, saganenum, or the aqueous extract of fustic or sandal wood (Chevreul, *A. Ch.* 66, 116; 73, 43; Erdmann, *J. pr.* 37, 409; 38, 355; Böttger a. Will, *A.* 58, 273; Rothe, *J. pr.* 46, 376; Gorup-Besanez, *A.* 183, 336; Stenhouse, *C. J.* 19, 236). Graebe, *B.* 22, 1405).—2. By the action of nitric acid on *m*-nitro-phenol, on γ, δ, or ϵ- di-nitro-phenols, and on β or γ tri-nitrophenol (Bantlin, *B.* 10, 524; 11, 2101; Henriques, *A.* 215, 340).—3. By the nitration of resorcin or of either di-nitro-resorcin (Merz a. Zetter, *B.* 12, 681; Benedikt a. Hübl, *M.* 2, 326; Von Kostanecki, *B.* 21, 3122). 4. By boiling tri-nitro-phenylene-di-methyl diamine with potash (Romburgh, *R. T. C.* 7, 6).—5. Together with three di-nitro-benzoic acids, by adding *o*-nitro-benzoic acid to a mixture of fuming HNO_3 and H_2SO_4 (Griess, *B.* 7, 1224; Salkowski, *B.* 8, 637).

Properties.—Yellow laminæ. Ppd. from its aqueous solution by HCl. V. sol. alcohol and ether.

Salts.—$(NH_4)HA''$.—$(NH_4)_2A''$: monoclinic needles; $a:b:c = 1:1{\cdot}66:2{\cdot}09$; $\beta = 76° 52'$. — Na_2A'' $2\frac{1}{2}$aq. — KHA''aq. —K_2A''.— BaA'' 3aq.— BaA''aq.—SrA'' 2aq.—CaA'' $3\frac{1}{2}$aq.—$Pb_2(OH)_2A''$. —$MnH_2A''_2$ 12aq.—CoA'' $3\frac{1}{2}$aq.—$CaK_2A''_2$4aq.— $NiK_2A''_2$ 3aq. — CuA'' 4aq. — $Cu(NH_4)_2A''_2$ 7aq.— $CuK_2A''_2$ 4aq.—Ag_2A''aq: slender needles.

Methyl ether Me_2A''. [124°]. Formed by nitrating $C_6H_4(OMe)_2$ (Hönig, *B.* 11, 1039).

Di-ethyl ether Et_2A''. [121°]. Yields tri-nitro-*m*-phenylene-diamine on heating with ammonia (Nölting a. Collin, *B.* 17, 259).

NITRO-RESORCIN SULPHONIC ACID $C_6H_2(NO_2)(OH)_2(SO_3H)$. [124°]. Formed by sulphonating nitro-resorcin [115°] (Hazura, *M.* 4, 610). Minute crystals (containing $1\frac{1}{2}$aq).— BaA'''_2 4aq: yellow needles.—BaA''' 2aq: yellow scales.—Ba_3A_2''' 10aq: blood-red needles.

A nitro-resorcin disulphonic acid is formed by oxidising the corresponding nitroso-compound with H_2O_2 (Ulzer, *M.* 9, 1130).

NITRO-SALICYLIC ACID *v.* NITRO-OXY-BENZOIC ACID.

NITROSAMINES. Compounds containing nitrosyl (NO) united to nitrogen. They are described under the amines from which they are derived by displacement of hydrogen by nitrosyl. Nitrosamines are formed by the action of nitrous acid upon secondary bases. They are neutral substances and may be reconverted into the parent base by boiling with tin and HClAq, with zinc and H_2SO_4, with aniline, or with alcoholic potash (Geuther, *A.* 128, 151; Griess, *B.* 7, 218; Witt, *C. J.* 33, 203). Many aromatic nitrosamines are converted into *p*-nitroso- compounds by alcoholic HCl; the nitrosyl entering the benzene nucleus (Fischer a. Hepp, *B.* 20, 1247, 2471).

NITROSATES. This name is given by Wallach (*A.* 241, 288) to compounds formed by the union of nitrogen peroxide with unsaturated hydrocarbons. Thus Guthrie's 'amylene nitrite' (vol. i. p. 210) would be called amylene nitrosate and may be represented as nitroso-amyl nitrate of formula $C_5H_{10}(NO)(O.NO_2)$ or $C_5H_9(NOH)(ONO_2)$. This body reacts with aromatic bases forming $C_5H_9(NOH)NPhH$ [141°], $C_5H_9(NOH)NHC_6H_4Me[1:4]$ [112°], and the isomeric $C_5H_9(NOH)NHC_6H_4Me[1:2]$ [115°], which yield nitrosamines melting at 128°, 148°, and 150° respectively. Amylene 'nitrosate' reacts in like manner with *o*-anisidine, piperidine, and diethylamine, forming bases melting at 139°, 96°, and 72° respectively. These bases are termed 'nitrol-amines' by Wallach.

The term nitrosite is given by Wallach to compounds resulting from the union of N_2O_3 with unsaturated hydrocarbons. Thus terpinene nitrosite $C_{10}H_{16}N_2O_3$ may be viewed as a nitroso-nitrite with formula $C_{10}H_{16}(NO)(ONO)$ or $C_{10}H_{15}(NOH)(ONO)$. They readily exchange O.NO for NHR' or NR'R'' when acted upon by bases, forming nitrolamines. Thus terpinene nitrosite acted upon by ethylamine yields 'terpinene-nitrol-ethylamine' $C_{10}H_{15}(NOH).NHEt$ [131°].

NITROSO-ACETIC ETHER *v.* OXIMIDO-ACETIC ETHER.

NITROSO-ACETOACETIC ETHER $C_6H_9NO_4$ *i.e.* $CH_3.CO.C(NOH).CO_2Et$. [54°]. Formed by the action of nitrous acid on aceto-acetic ether, and on acetyl-malonic ether (V. Meyer a. Züblin, *B.* 11, 320; Wleügel, *B.* 15, 1050; Ceresole, *B.* 15, 1326; Lang, *B.* 20, 1327). Prisms, sl. sol. water, sol. alkalis. Forms $CH_3.C(NOH).C(NOH).CO_2Et$.

Anilide $C_{10}H_{10}N_2O_3$. [100°]. Formed by the action of nitrous acid on the anilide of acetoacetic acid (Knorr, *A.* 236, 80). Prisms.

NITROSO-TRIACETONAMINE *v.* ACETON-AMINE.

NITROSO-ACETONE $C_3H_5NO_2$ *i.e.* $CH_3.CO.CH:NOH$ or $CH_3.CO.CH_2.NO$. *Oxim of pyruvic aldehyde. Oxim of methyl-glyoxal.* [65°]. Formed by the action of nitrous acid on acetoacetic ether (V. Meyer a. Züblin, *B.* 11, 695; Ceresole, *B.* 15, 1326), and by warming acetone with amyl nitrite and HCl (Claisen, *B.* 20, 252). Silvery leaflets or prisms, boiling with decomposition at about 200°. V. sol. water and alcohol, volatile with steam. May be sublimed.

Reactions.—1. Dilute HClAq at 140° forms acetic and formic acids and ammonia (Treadwell and Steiger, *B.* 15, 1059).—2. Tin and HCl give di-methyl-pyrazine.—3. *Hydroxylamine hydrochloride* forms methyl-glyoxim or acetoximic acid (vol. i. p. 38) and a compound, $C_6H_9N_3O_3$, which detonates at 238°–247°, and forms an explosive hydrochloride $C_6H_9N_3O_3HCl$ [113°] (Scholl, *B.* 23, 3578).—4. *Phenyl-hydrazine* yields $CH_3.C(N_2HPh).CH:NOH$ [134°] (Pechmann, *B.* 21, 2994).—5. *Phenyl-methyl-hydrazine* yields $CH_3.C(N_2MePh).CH:NOH$ [118°].

Methyl ether $C_3H_4O(NOMe)$. (115° uncor.). Formed by heating nitroso-acetone with NaOMe (Meyer a. Ceresole, *B.* 15, 3067; 16, 833). Colourless oil.

Ethyl ether $C_3H_4O(NOEt)$. (130°).

Benzyl ether $C_3H_4O(NOC_7H_7)$. [46°].

Di-nitroso-acetone $CH(NOH).CO.CH(NOH)$. [144°]. Formed by the action of nitrous acid on acetone dicarboxylic acid (Pechmann a. Wehsarg, *B.* 19, 2465; 21, 2992). Prisms, sl. sol. cold water, decomposed by boiling water into HCy, CO_2, and water. Explodes when heated.

Phenyl-hydrazide $N_2HPh:C(CH:NOH)_2$. [145°]. Needles. Yields a mono-acetyl derivative [133°].

Phenyl-methyl-hydrazide [137°]. Crystals.

Oxim CH(NOH).C(NOH)CH(NOH). *Tri-nitroso-propane.* [171°]. Crystalline powder.

NITROSO-ACETOPHENONE $C_8H_7NO_2$ *i.e.* C_6H_5.CO.CH:NOH. *Oxim of phenyl-glyoxylic aldehyde.* [128°]. Prepared by the action of amyl-nitrite and NaOEt on acetophenone (Claisen a. Manasse, *B.* 20, 2194; Braun, *B.* 22, 556). Thin, monoclinic plates; $a:b:c = 2{\cdot}762:1:2{\cdot}146$; $\beta = 66°\ 54'$. Sl. sol. cold water, soluble in aqueous Na_2CO_3. On heating with Ac_2O it yields C_6H_5.CO.CN. $SnCl_2$, in HClAq, reduces it to ω-amido-acetophenone and di-phenyl-pyrazine. When its compound with $NaHSO_3$ is boiled with H_2SO_4 it yields C_6H_5.CO.CHO. Hydroxylamine hydrochloride yields $C_{16}H_{13}N_3O_3$ [207°–211°] (Scholl, *B.* 23, 3580).

Oxim v. Oxim of PHENYL-GLYOXAL.

p-**NITROSO-ANILINE** $C_6H_4(NO)(NH_2)$[1:4]. [174°]. Formed by heating nitroso-phenol with NH_4Cl, ammonium acetate, and ammonium carbonate (Fischer a. Hepp, *B.* 20, 2475; 21, 684). Steel-blue needles (from benzene). Decomposed by NaOHAq into NH_3 and nitroso-phenol. Tin and HCl reduce it to phenylene-*p*-diamine. Phenyl-hydrazine hydrochloride forms $C_{12}H_{12}N_4O$ [125°]. Phenyl-methyl-hydrazine yields $C_{13}H_{14}N_4O$ [151°].—$C_6H_5NaN_2O$ 2aq: yellow crystals.

NITROSO-ANTHRONE *v.* ANTHRACENE.

NITROSO-BENZENE ×C_6H_5.NO. On distilling with steam, the product of the action of nitrosyl chloride on $HgPh_2$, there is obtained a pungent green liquid, which yields aniline on reduction (Baeyer, *B.* 7, 1638). By oxidising the di-oxim of quinone with alkaline K_3FeCy_6, there is obtained a golden-yellow pp., probably di-nitroso-benzene $C_6H_4(NO)_2$[1:4]. It yields *p*-phenylene-diamine on reduction, and *p*-di-nitro-benzene on warming with HNO_3. Hydroxylamine hydrochloride converts it into quinone dioxim.

NITROSO-BENZYL-ALLYL-THIO-UREA PhC(NOH).NH.CS.NHC_3H_5. Formed by melting together allyl thiocarbimide and benzamidoxim (Koch, *B.* 24, 399). Fine needles.

ISO-NITROSO-BENZYL-AMINE *v.* BENZENYL-AMIDOXIM.

p-**NITROSO-DI-BENZYL-ANILINE** $C_6H_4(NO).N(CH_2.C_6H_5)_2$. [92°]. Formed by adding amyl nitrite to a solution of di-benzyl-aniline in alcoholic HCl. Thin steel-blue plates, or small green crystals. V. sol. ether and CS_2, m. sol. alcohol. On reduction it gives *u*-di-benzyl-*p*-phenylene diamine (Matzudaira, *B.* 20, 1616).

NITROSO-BENZYL-MALONIC ACID $C_7H_7.C(NO)(CO_2H)_2$. [120°]. Obtained from its ether, which is got from nitroso-malonic ether, NaOEt, and benzyl chloride (Conrad a. Bischoff, *A.* 204, 121; 209, 215). Plates. On fusion, or on boiling with water, it gives benzyl alcohol, CO_2, and HCy.—K_2A''aq (dried at 100°).

NITROSO-BENZYL-TOLYL-THIO-UREA PhC(NOH).NH.CS.NH.C_6H_4Me. [67°]. Formed by melting *p*-tolyl-thio-carbimide with benzamidoxim (Koch, *B.* 24, 397).

NITROSO-BETORCIN $C_8H_9NO_3$ *i.e.* $C_6H(NO)Me_2(OH)_2$[*x*:1:4:3:5]. Obtained by the action of nitrosyl sulphate $SO_3H(NO)$ on a solution of betorcin (Stenhouse a. Groves, *C. J.* 37, 404; Von Kostanecki, *B.* 19, 2323). Red prisms (from HOAc).

p-**NITROSO-ISOBUTYL-ANILINE** $C_6H_4(NO).NHCH_2Pr$. [94°]. Formed from isobutyl-aniline, $NaNO_2$, and HCl (Wacker, *A.* 243, 297). Steel-blue crystals, v. sol. alcohol. Yields $C_6H_4(NH_2).NHCH_2Pr$ on reduction. Boiling alkalis split it up into *p*-nitroso-phenol and isobutylamine. Further treatment with $NaNO_2$ and HCl yields $C_6H_4(NO).N(NO)CH_2Pr$.

α-**NITROSO-*n*-BUTYRIC ACID** $C_4H_7NO_3$ *i.e.* $C_2H_5.C(NOH).CO_2H$. [151°]. Formed by the action of nitrous acid and NaCH upon ethyl-acetoacetic ether (Wleügel, *B.* 15, 1057). Flat prisms.—AgA′: insoluble powder.

β-**Nitroso-butyric acid** $CH_3.C(NOH).CH_2.CO_2H$. [140°]. Obtained from its ether, which is got by the action of hydroxylamine on acetoacetic ether (Westenberger, *B.* 16, 2996).—AgA′: white pp.

(αβ)-**Di-isonitroso-butyric acid** $C_4H_6N_2O_4$ *i.e.* $CH_3.C(NOH).C(NOH).CO_2H$. Obtained from its *ethyl ether* [140°] which is formed, together with the *anhydride* $C_6H_{10}N_4O_7$ [133°], by the action of hydroxylamine on nitroso-acetoacetic ether (Ceresole a. Köckert, *B.* 17, 821). The acid is crystalline and gives the salts $BaA'_2\ 2\frac{1}{2}$aq and AgA′. The anhydride gives $BaA''\ \frac{1}{2}$aq and Ag_2A''.

NITROSO-CARVACROL $C_6H_2(NO)(C_3H_7)(CH_3)(OH)$. [153°]. Yellow prisms (Paterno a. Canzoneri, *B.* 12, 383. Reduced by $SnCl_2$ to amido-carvacrol [304°].

NITROSO-CARVENE *v.* CARVOXIM.

NITROSO-COMPOUNDS. Compounds containing nitrosyl NO. They are usually obtained by the action of nitrous acid. They may be divided into nitrosamines (*q. v.*) in which nitrosyl is attached to nitrogen, and nitroso-compounds proper in which nitrosyl is attached to carbon. Compounds in which nitrosyl is attached to oxygen are called nitrites. Compounds containing the divalent radicle oximidogen NOH are often called isonitroso-compounds, the group C:NOH being isomeric, and often interchangeable, with the group CH.NO. The isonitroso-compounds may be obtained by the action of hydroxylamine on aldehydes, ketones, and ketonic compounds, and may thus be termed oximides, oximes, or oxims of these ketonic bodies. Nitrous acid acting upon the group $.CO.CH_2.$ frequently converts it into .CO.C(NOH).: the new body may be termed either a nitroso-derivative of the original ketone, or a mono-oxim of the diketone .CO.CO.; the latter terminology is that usually employed in this dictionary. Nitrous acid acting upon a secondary amine forms a nitrosamine; with tertiary aromatic amines and with phenols it yields nitroso-compounds, the nitrosyl taking up the *para*-position. When the *p*- position is occupied the nitrosyl can in some cases still enter the benzene nucleus in the *o*- position. The nitroso-phenols $HO.C{<}\begin{matrix}CH{:}CH\\CH.CH\end{matrix}{>}C.NO$ and the oxims of the mono-quinones $CO{<}\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}{>}C{:}NOH$ are identical, and will be described under the quinones. Some aromatic nitrosamines are converted into

the isomeric *p*-nitroso- compounds by the action of alcoholic HCl.

NITROSO-CREATININE *v.* CREATININE.

NITROSO-CRESOL *v. Oxim* of TOLUQUINONE.

DI-NITROSO-CRESORCIN $C_6HMe(NO)_2(OH)_2$ or $C_6HMe(NOH)_2O_2$[1:3:5:2:4]. Formed from cresorcin and HNO_2 (Von Kostanecki, *B.* 20, 3135). Pale-green plates (containing aq). Explodes above 160°. Sl. sol. water. With HNO_3 it yields di-nitro-cresorcin [90°].

DI-NITROSO-CYMENE $C_{10}H_{12}N_2O_2$. [72°]. Formed by oxidising the di-oxim of thymoquinone with alkaline K_3FeCy_6 (Kehrmann a Messinger, *B.* 23, 3560). Greenish-yellow pp., smelling like iodine. After one fusion it melts at 130°.

NITROSO-ETHYL-ACETONE is the (β)-oxim of METHYL ETHYL DIKETONE (*q. v.*).

NITROSO-ETHYL-ANILINE $C_8H_{10}N_2O$ *i.e.* [4:1]$C_6H_4(NO)(NHEt)$. [78°]. Obtained by adding alcoholic HCl to an ethereal solution of the nitrosamine of ethyl-aniline (Fischer a. Hepp, *B.* 19, 2993). Green plates, v. sol. alcohol. Yields $C_6H_4(NH_2)(NHEt)$ (270°) on reduction. On heating with aqueous NaOH it is split up into nitroso-phenol and ethylamine.—B'HCl: needles, v. sol. water.

Nitroso-di-ethyl-aniline [1:4]$C_6H_4(NO).NEt_2$. [84°]. Formed from di-ethyl-aniline and nitrous acid (Kopp, *B.* 8, 621). Green prisms (from ether). Decomposed by boiling dilute NaOH into nitroso-phenol and diethylamine. S a l t s.—$B'_2H_2PtCl_6$.—B'_2I_3. [118·5°] (Dafert, *M.* 4, 506). —B'_3I_2. [127°].—$B'_2H_2SO_4$.—$B'2C_6H_2(NO_2)_3(OH)$. —B'_2HCy. [171°] (Lippmann, *M.* 6, 544). Orange crystals (from alcohol).

NITROSO-DI-ETHYL KETONE *v.* (α)-*Oxim* of METHYL ETHYL DIKETONE.

α-NITROSO-ETHYL-PHENYL-AMINE $C_6H_4(NH_2).CH(NO).CH_3$. Formed by heating $C_6H_4(NH_2).CH_2NO$ with KOH, methyl alcohol, and MeI at 100° (Gabriel a. Meyer, *B.* 14, 2339). Yellowish oil.—B'HCl: prisms.

A c e t y l   d e r i v a t i v e $C_6H_4(NHAc).CH(NO).CH_3$. [109°].

NITROSO-ETHYL-*o*-TOLUIDINE $C_9H_{12}N_2O$ *i.e.* $C_6H_3Me(NO).NHEt$. [140°]. Green plates (Fischer, *B.* 19, 2994).

NITROSO-ETHYL-*o*-XYLIDINE $C_{10}H_{14}N_2O$ *i.e.* $C_6H_2(NO)Me_2(NHEt)$ [1:2:3:4]. [124°]. Green crystals (Menton, *A.* 263, 327).—B'HCl: needles.

NITROSO-FORMANILIDE *v.* FORMIC ACID.

α-NITROSO-GLUTARIC ACID $CO_2H.C(NOH).CH_2.CH_2.CO_2H$. [152°]. Produced by boiling furazyl-propionic acid $O\langle{}^{N:CH}_{N:C.CH_2.CH_2.CO_2H}$ [86°] with potash, the semi-nitrile $CN.C(NOH).CH_2.CH_2.CO_2H$ [87°] being formed at the same time (Wolff, *A.* 260, 112). Prisms. Yields amido-glutaric acid on reduction.—$BaA''1\frac{1}{2}aq$: needles, v. sl. sol. water.

A m i d o x i m $CO_2H.CH_2.CH_2.C(NOH).C(NOH).NH_2$. [158°]. Formed by the action of hydroxylamine on the semi-nitrile [87°]. Needles, sl. sol. water.

NITROSO-GUANIDINE *v.* GUANIDINE.

NITROSO-HEXOIC ETHER $CH_3.C(NOH).CHEt.CO_2Et$. Formed from ethyl-acetoacetic ether and hydroxylamine (Westenberger, *B.* 16, 2997). Oil.

Nitroso-hexoic acid $CH_3.C(NOH).CMe_2.CO_2H$. [97°]. By the action of amyl nitrite and nitric acid on tri-methyl-ethylene there is formed a compound $CMe_2(ONO_2).C(NOH).CH_3$ which when heated with alcoholic KCy yields the nitrile $CH_3.C(NOH).CMe_2.CN$ [100°] (230°) which forms on saponification the corresponding amide [164°] and acid [97°] (Wallach, *A.* 248, 166). The acid is split up by heat into CO_2 and the oxim of methyl isopropyl ketone.

NITROSO-INDOXYL *v.* ψ-ISATIN OXIM.

NITROSO-MALONIC ACID $CH(NO)(CO_2H)_2$ or $C(NOH)(CO_2H)_2$. *Oxim of mesoxalic acid.*

Formation.—1. By treating barbituric acid with nitrous acid and warming the resulting violuric acid with potash (Baeyer, *A.* 131, 292). 2. From its ether, which is got by passing nitrous fumes into sodium-malonic ether (Conrad a. Bischoff, *B.* 13, 599; *A.* 209, 211).—3. By the action of hydroxylamine on mesoxalic acid (Meyer a. Müller, *B.* 16, 608).

Properties.—Needles. Decomposes at 126° with violence. At 40° its aqueous solution gives off CO_2 and HCy. Sodium-amalgam reduces it to amido-malonic acid.

S a l t s.—$K_2A''\frac{1}{2}aq$.—PbA'' aq.—$AgA'\frac{1}{2}aq$.

E t h y l   e t h e r Et_2A''. S.G. $\frac{15}{15}$ 1·149. Oil.

NITROSO-MESITYL OXIDE $CMe_2:CH.CO.CH:NOH$. [102°]. Prisms (Claisen a. Manasse, *B.* 22, 526).

NITROSO-METHYL-ACETONE *v. Oxim* of DI-METHYL-DIKETONE.

NITROSO-DI-METHYL-*p*-AMIDO-BENZOIC ACID $C_6H_2(NOH)(NMe_2).CO_2H$. [224°]. Formed by the action of nitrous acid on $C_6H_4(NMe_2)CO_2H$ (Bischoff, *B.* 22, 342). Plates (from alcohol). Yields $C_6H_4(NMe_2)CO_2H$ on reduction with $SnCl_2$ and HCl. S a l t s.—$B'H_2C_2O_4$. [178°–181°].—$B'C_6H_2(NO_2)_3OH$. [168°]. — B'HCl: slender needles.

M e t h y l   e t h e r $MeA'6\frac{1}{2}aq$. [101°].—B'HCl. —$B'C_6H_2(NO_2)_3OH$. Golden-yellow needles.

NITROSO-DI-METHYL-AMIDO-BENZOPHENONE $C_6H_5.CO.C_6H_2(NOH).NMe_2$. Oil (Bischoff, *B.* 22, 340).

Nitroso-tetra-methyl-diamido-benzophenone *v.* p. 263.

***p*-NITROSO-METHYL-ANILINE** $C_7H_8N_2O$ *i.e.* $C_6H_4(NO).NMeH$. [118°]. Formed by adding alcoholic HCl to an ethereal solution of the nitrosamine $C_6H_5.NMe(NO)$ (Fischer a. Hepp, *B.* 19, 2991). Steel-blue prisms (from water). Decomposed by NaOHAq into *p*-nitroso-phenol and methylamine. Yields $C_6H_4(NH_2)(NMeH)$ on reduction. Nitrous acid forms the nitrosamine $C_6H_4(NO).NMe.NO$ [101°]. Nitric acid (S.G. 1·13) yields the nitro-compound $C_6H_4(NO_2).NMe.NO$ [104°].

Nitroso-di-methyl-aniline $C_6H_4(NO)NMe_2$ or $C_6H_4\langle{}^{NMe_2}_{N}\rangle O$. Mol. w. 150. [85°]. Formed by the action of nitrous acid on di-methyl-aniline hydrochloride (Baeyer a. Caro, *B.* 7, 963; Schraube, *B.* 8, 616; Wurster, *B.* 12, 523, 1825; Meldola, *C. J.* 39, 37). Green plates (from ether).

Reactions.—1. Reduced by *tin* and HClAq to $C_6H_4(NH_2)(NMe_2)$.—2. Resolved by boiling *alkali* into nitroso-phenol and dimethylamine. — 3. K_3FeCy_6 oxidises it to $C_6H_4(NO_2)(NMe_2)$.— 4. *Alcoholic potash* forms $N_2O(C_6H_4NMe_2)_2$.— 5. HClAq at 105° yields $C_6H_4(NH_2)(NMe_2)$,

$C_6H_2Cl_2(NH_2)(NMe_2)$ and $C_6H_2Cl_2(NH_2)_2$ (Möhlau, *B.* 19, 2010). — 6. *Phenyl-hydrazine acetate* yields $C_{14}H_{16}N_4O$ [103°]. This base is also formed by the action of diazobenzene on nitroso-dimethylaniline (O. Fischer, *B.* 21, 2610; 22, 623). Phenyl-methyl-hydrazine yields the compound $C_{15}H_{18}N_4O$ [141°].

Salts.—$B'HCl$: yellow needles.—$B'H_2SO_4$.—$B'H_2C_2O_4$ 2aq.—$B'H_2C_2O_4$.—$B'_2H_4FeCy_6$ aq.—$B'_3H_3FeCy_6$ 2½aq.—B'_2AgNO_3.—B'_2HCy. [222°]. (Lippmann a. Fleissner, *M.* 6, 537).

Combinations.—B'_2I_3. [116°] (Dafert, *M.* 4, 506).—B'_3I_2. [124°].—B'_2PhNH_2: steel-blue crystals.—$B'_2NH_2.C_6H_4Me$ [1:4].—B'_2PhOH.—$B'C_6H_6$: dark-green crystals.—$B'_2HCyC_6H_6$.—$B'_2HCyC_6H_5NO_2$.—$B'_2HCyC_7H_8$.—$(B'_2HCy)_3(PhN_2)_2$.

NITROSO-METHYL-OXINDOLE *v. Oxim of* METHYL-ISATIN.

NITROSO-METHYL-o-TOLUIDINE $C_6H_3Me(NO)(NHMe)$ [1:5:2]. [151°]. Formed by the action of HCl on the isomeric nitrosamine $C_6H_4Me(NMe.NO)$ (Kock, *A.* 243, 308). Green plates. Split up by boiling NaOHAq into nitroso-o-cresol and methylamine. $KMnO_4$ oxidises it to nitro-methyl-*o*-toluidine.—$B'H_2Cl_2$ aq. [110°]. Yellow cubes.

Nitroso-di-methyl-*m*-toluidine $C_6H_3Me(NO)NMe_2$ [1:2:5]. [92°]. Formed by the action of nitrous acid on di-methyl-*m*-toluidine (Wurster a. Riedel, *B.* 12, 1796; 13, 126). Light-green needles. Decomposed by boiling NaOHAq into NMe_2H and the oxim of *m*-toluquinone.—$B'HCl$.—$B'_2H_4FeCy_6$ aq.—$B'_2H_3FeCy_6$ 2aq: yellow needles.

NITROSO-METHYL-o-XYLIDINE $C_6H_2Me_2(NO)(NHMe)$ [1:2:6:3]. [161°]. Green needles, sl. sol. water (Menton, *A.* 263, 323).—$B'HCl$: crystalline meal.

NITROSO-NAPHTHALENE $C_{10}H_7(NO)$. [89°]. Formed from $Hg(C_{10}H_7)_2$ and NOBr in CS_2 (Baeyer, *B.* 7, 1639; 8, 615). Yellow crystals.

Di-nitroso-naphthalene $C_{10}H_6(NO)_2$ [1:4]. Formed by the action of alkaline K_3FeCy_6 on the dioxim of (α)-naphthoquinone (Nietzki a. Guitermann, *B.* 21, 433). Pale-yellow powder, exploding at 120°. Insol. water and alcohol.

Di-nitroso-naphthalene $C_{10}H_6(NO)_2$ [1:2]. [126°]. Formed from (β)-naphthoquinone dioxim and K_3FeCy_6 (Leuckart, *B.* 19, 174). Needles, m. sol. alcohol.

NITROSO-NAPHTHOL *v. Oxim* of NAPHTHOQUINONE.

NITROSO-(β)-NAPHTHOL SULPHONIC ACID $C_{10}H_5(NO)(OH)SO_3H$ or $C_{10}H_5(NOH)O(SO_3H)$ [1:2:3] or [1:3:2]. Formed from ammonium (β)-naphthol sulphonate, $NaNO_2$, and HCl (Meldola, *C. J.* 39, 41). Very soluble orange crystals. Its solution gives with phenol in HOAc a blue colour, becoming red on dilution, and with diphenylamine a blue colour, remaining blue on dilution. Tin and HCl reduce it to the amido- acid.—BaA'_2 aq: orange needles.—$BaC_{10}H_5NSO_5$ 2aq: green needles.—$Ag(NH_4)A''$.—$(NH_4)_2A''$ aq: green.—MgA''3aq: orange.—ZnA''3aq.—PbA''aq.

An isomeric acid, obtained by reducing benzene-azo-(β)-naphthol sulphonic acid with aqueous ammonium sulphide, crystallises in sparingly soluble grey needles (Griess, *B.* 14, 2042).

NITROSO-DI-(α)-NAPHTHYL-AMINE $C_{10}H_6(NO).NHC_{10}H_7$. [169°]. Formed from $(C_{10}H_7)_2N.NO$ and alcoholic HCl (Fischer a. Hepp, *B.* 20, 1248; Wacker, *A.* 243, 301). Dark-red needles. With boiling dilute H_2SO_4 it yields the mono-oxim of (α)-naphthoquinone and (α)-naphthylamine.—$B'HCl$: green needles.

Nitroso-(β)-naphthylamine $C_{10}H_6(NO)NH_2$ [1:2]. [152°]. Formed by heating the (α)-oxim of (β)-naphthoquinone with NH_4Cl and NH_4OAc (Ilinski, *B.* 17, 391; Harden, *A.* 255, 150). Dark-green needles (from dilute alcohol. Yields naphthylene o-diamine on reduction and the di-oxim of (β)-naphthoquinone on treatment with hydroxylamine.—$B'HCl$.—$B'_2H_2PtCl_6$.—$B'H_2SO_4$ aq.

(α) - **NITROSO - (β) - NAPHTHYL-ETHYL-AMINE** $C_{10}H_6(NO).NHEt$. [121°]. Formed by the action of alcoholic HCl at 6° on the nitrosamine $C_{10}H_7.NEt(NO)$, and also by the action of ethylamine on the (α)-oxim of (β)-naphthoquinone (Fischer a. Hepp, *B.* 20, 2471; 21, 686). Green crystals. Yields a crystalline nitrosamine $C_{12}H_{11}N_3O_2$, decomposing at 105°.

(α)-Nitroso-(α)-naphthyl-ethyl-amine $C_{12}H_{12}N_2O$ *i.e.* $C_{10}H_6(NO)NHEt$ [1:4]. [133°]. Formed in like manner (Kock, *A.* 243, 310). Brown pp. Reduced by stannous chloride to $C_{10}H_6(NH_2)(NHEt)$. Yields ethylamine and $C_{10}H_6(NOH)O$ when boiled with NaOHAq.—$B'HCl$.—Picrate $C_{18}H_{15}N_5O_8$. [174°].—$C_{12}H_{13}N_2O_2Na$: white spangles, v. sol. water.

Tetrahydride $C_6H_8<\begin{matrix}C(NHEt):CH\\C(NO)=CH\end{matrix}$. [119°]. Formed from the isomeric nitrosamine and alcoholic HCl (Bamberger a. Helwig, *B.* 22, 1314). Needles.—$B'HCl$: golden crystals. Nitroso-naphthyl-di-ethyl-amine $C_{10}H_6(NO).NEt_2$. [165°]. Formed by adding $NaNO_2$ to a well-cooled solution of the base (B. E. Smith, *C. J.* 41, 182). Reddish-golden scales. Gives a blue colour with H_2SO_4.

NITROSO-NITRATES *v.* NITROSATES.

NITROSO-NITRO-ANTHRONE $C_{14}H_8N_2O_4$. [263°]. Formed by the action of alkalis on 'hydro-anthracene nitrite' (Liebermann, *B.* 14, 467; *cf.* vol. i. p. 277).

NITROSO-NITRO-BUTANE $C_4H_8N_2O_3$ *i.e.* $CH_3.C(NO)(NO_2).C_2H_5$. *Pseudobutylnitrole.* [58°]. Formed by the action of KOH, KNO_2, and dilute H_2SO_4 on β-nitro-butane (Meyer a. Locher, *A.* 180, 136) and of NO_2 on $CH_3.C(NOH).C_2H_5$ (Scholl, *B.* 21, 508). White prisms (from chloroform), yields a blue liquid on fusion. Insol. water and alkalis.

The isomeric $Pr.CH(NO)(NO_2)$ and $PrCH(NO)(NO_2)$ are oils (Demole, *B.* 7, 790; Züblin, *B.* 10, 2084).

NITROSO-NITRO-PENTANE $Et_2C(NO)(NO_2)$. [63°]. Formed from $Et_2C:NOH$ and N_2O_4 (Scholl, *B.* 21, 509).

NITROSO-NITRO-PROPANE $C_3H_6N_2O_3$ *i.e.* $CH_3.C(NO)(NO_2).CH_3$. [76°]. Formed from acetoxim and N_2O_4 (Scholl, *B.* 21, 508). The isomeric compound $CH_3.CH_2.CH(NO)NO_2$ or $CH_3.CH_2.C(NOH).NO_2$ melts at 60° (Meyer, *A.* 175, 114).

NITROSO-NITRO-RESORCIN $C_6H_4N_2O_5$ *i.e.* $C_6H_2(OH)(NO_2)O(NOH)$ [1:2:3:4]. Formed from nitro-resorcin [85°] and nitrous acid (De la Harpe a. Reverdin, *B.* 21, 1405). Brown needles, not melted at 200°, explodes at a higher temperature.

NITROSO-ORCIN $C_6H_2Me(NO)(OH)_2$. Formed from orcin, NaOHAq, and amyl nitrite (Krämer, *B.* 17, 1883). Dark-red prisms. When heated with orcin and H_2SO_4 it gives the dyestuff $C_{14}H_{11}NO_3$.

Di-nitroso-orcin $C_6HMe(NO)_2(OH)_2$ [1:2:4:3:5]. Formed by adding H_2SO_4 containing N_2O_3 to a solution of orcin (Stenhouse a. Groves, *C. J.* 31, 544). Yellow prisms. Blackens about 140° without melting. Alcoholic hydroxylamine hydrochloride at 100° yields $C_6HMe(NOH)_4$, whence Ac_2O forms $C_6HMe(N_2O)_2$ [47°] (Goldschmidt, *B.* 20, 1607). The compound $C_6HMe(NOH)_4$ yields, on oxidation by potassium ferricyanide, the product $C_6HMe(NO)_4$ [103°], crystallising in pale-yellow needles.

NITROSO - OXANTHRANOL $C_{14}H_9NO_3$. Formed by boiling 'hydro-anthracene nitrite' with alkalis (Liebermann, *B.* 14, 471). Orange flakes, sol. alkalis.

NITROSO-OXINDOLE *v.* Isatin oxim.

NITROSO-OXY-METHYL-QUINOLINES $C_5H_3N{:}C_4HMe(NO)(OH)$. The following crystalline compounds have been obtained by the action of nitrous acid on the oxy-methyl-quinolines (Noelting a. Trautmann, *B.* 23, 3665):— (*B.* 3)-nitroso-(*B.* 4)-oxy-(*B.* 1)-methyl-quinoline; (*B.* 1)-nitroso-(*B.* 4)-oxy-(*B.* 2)-methyl-quinoline; (*B.* 4)-nitroso-(*B.* 1)-oxy-(*B.* 2)-methyl-quinoline; (*B.* 1)-nitroso-(*B.* 4)-oxy-(*B.* 3)-methyl-quinoline; and (*B.* 2)-nitroso-(*B.* 1)-oxy-(*B.* 4)-methyl-quinoline. Friedländer and Müller (*B.* 20, 2014) have obtained in like manner (*Py.* 1,3)-nitroso-oxy-(*Py.* 4)-methyl-quinoline crystallising in red needles.

NITROSO-OXY-DI-PHENYL-AMINE $C_6H_3(NO)(OH).NHPh$ [4:3:1]. Formed from $C_6H_4(OH).NPh(NO)$ and alcoholic HCl (Kohler, *B.* 21, 909). Red needles, m. sol. alcohol.

NITROSO-(*B.* 4)-OXY-QUINOLINE $C_9H_5(NO)(OH)N$. Formed from o-oxy-quinoline and nitrous acid (Lippmann a. Fleissner, *M.* 10, 794). Yellow needles. The isomeric nitroso-(*B.* 2)-oxy-quinoline crystallises from HOAc in golden needles (Mathëus, *B.* 21, 1886).

(*Py.* 2)-Nitroso-(*Py.* 1,3) di-oxy-quinoline $C_6H_4\Big\langle\begin{matrix}CO.C(NOH)\\ N{:}C(OH)\end{matrix}$. [208°]. Formed by the action of nitrous acid on (*Py.* 1,3)-di-oxy-quinoline (oxycarbostyril (Baeyer a. Homolka, *B.* 16, 2216). Orange prisms. Decomposed by conc. HClAq into isatin and hydroxylamine. $SnCl_2$ yields tri-oxy-quinoline.

NITROSO-PHENOL *v. Mono-oxim* of Quinone.

NITROSO-PHENYL-ACETIC ACID *v. Oxim* of Phenyl-glyoxylic acid.

p-**NITROSO-DI-PHENYL-AMINE** $C_6H_4(NO).NPhH$. [143°]. Formed from di-phenyl-nitrosamine and alcoholic HCl (O. Fischer a. Hepp, *B.* 19, 2991; 21, 677, 2614). Green plates (from benzene). With phenyl-hydrazine hydrochloride it yields a compound $C_{18}H_{16}N_4O$ [112°]. Free phenyl-hydrazine in ether yields amido-diphenylamine [75°] and $C_{24}H_{20}N_4O$ [173°]. *p*-Bromo-aniline yields $C_{36}H_{25}Br_4N_5$ [243°]. Tin and HCl reduce it to $C_6H_4(NH_2)(NPhH)$ [65°] (Ikuta, *A.* 243, 274). Aqueous NaOH yields aniline and quinone-oxim.—B'HCl: bronze tables or needles.

Acetyl derivative [97°]. Red prisms.

Nitrosamine $C_6H_4(NO).NPh(NO)$. [98°].

NITROSO-PHENYL-BENZYL-THIO-UREA $PhC(NOH).NH.CS.NHPh$. [172°]. Crystals (from alcohol) (Koch, *B.* 24, 394).

NITROSO-PHENYL-(α)-NAPHTHYL-AMINE $C_{10}H_6(NO).NHPh$. [150°]. Formed from phenyl-naphthyl-nitrosamine and alcoholic HCl (Fischer a. Hepp, *B.* 20, 1247). Brownish-yellow crystals. Yields $C_{10}H_6(NH_2).NHPh$ on reduction. Boiling dilute H_2SO_4 splits it up into aniline and quinone oxim.—B'HCl: green plates.

TRI-NITROSO-PHLOROGLUCIN $C_6(NO)_3(OH)_3$. Prepared by the action of KNO_2 and HOAc on phloroglucin (Benedikt, *B.* 11, 1374). Needles, sol. water and alcohol.—K_3A''': needles, exploding above 130°.

TRI-NITROSO-PROPANE *v. Oxim* of Di-nitroso-acetone.

NITROSO-PROPIONIC ACID *v. Oxim* of Pyruvic acid.

NITROSO-PROPYL-ANILINE $C_9H_{12}N_2O$ *i.e.* $C_6H_4(NO).NPrH$. [59°]. Formed from the isomeric $C_6H_5.NPr(NO)$ and alcoholic HCl (Wacker, *A.* 243, 291). Steel-blue needles, v. sol. alcohol. Yields $C_6H_4(NH_2).NPrH$ on reduction, and quinone-oxim and $NPrH_2$ on boiling with alkalis. $NaNO_2$ and HCl yield $C_6H_4(NO).NPr(NO)$ [69°].

Nitroso - di - propyl - aniline $C_6H_4(NO).NPr_2$. [42°]. Formed from di-propyl-aniline (241°) and HNO_2 (Mandl, *M.* 7, 99). Green trimetric crystals, $a{:}b{:}c = {\cdot}576{:}1{:}\,{\cdot}277$. Yields quinone-oxim and dipropylamine on warming with potash. HCy forms $C_{25}H_{37}N_5O_2$. [140°].

NITROSO-PROPYL-CRESOL $C_{10}H_{13}NO_2$ *i.e.* $C_6H_2MePr(NO)(OH)$. *Cymoquinone oxim* [140°] is formed from propyl-cresol, KNO_2, and HOAc (Mazzara, *G.* 12, 167). The isomeric $C_6H_2MePr(NO)(OH)$ melts at 167°.

NITROSO-RESORCIN $C_6H_3(NO)(OH)_2$ [4:3:1]. *Oxy-quinone oxim.* Formed from $C_6H_4(OH)(ONa)$ and amyl nitrite (Fèvre, *Bl.* [2] 39, 585; *C. R.* 96, 790). Golden crystals (containing aq), turning brown at 112°. Its solution is turned deep green by a ferrous salt. $SnCl_2$ reduces it to amido-resorcin. H_2O_2 yields nitroresorcin (Ulzer, *M.* 9, 1128).—NH_4A' 2aq.—KA' aq.—NaA'.—AgA': brown needles.

Methyl ether MeA' (Aronheim, *B.* 12, 30).

Ethyl ether EtA'. Yellow flakes.

Di-nitroso-resorcin $C_6H_2(NO)_2(OH)_2$[4:2:3:1]. Formed by the action of nitrous acid on resorcin (Fitz, *B.* 8, 631; Kostanecki, *B.* 22, 1345). Yellowish plates (containing aq). Explodes at 115°. Forms coloured lakes. Yields di-amido-resorcin on reduction.—NH_4A'.—NaA': dark-green powder.

NITROSO-RESORCIN DISULPHONIC ACID. The salt $C_6H_2(NO)(OH)(OK)SO_3K$ is formed by the action of KNO_2 and HOAc on potassium resorcin disulphonic acid (Ulzer, *M.* 9, 1127). It forms violet crystals.

NITROSO-SUCCINIC ACID $C_4H_5NO_5$ *i.e.* $CO_2H.CH_2.C(NOH).CO_2H$. Obtained from its mono-ethyl ether, which is got by allowing di-nitroso-succino-succinic ether to stand with water (Ebert, *A.* 229, 65). Crystals, decomposing below 126°.—CaA'' 4aq.

Mono-ethyl ether EtHA''. [111°].—NH_4EtA''.—$CaEt_2A''_2$ 2aq.—$CaC_6H_7NO_5$ 2aq.—$BaC_6H_7NO_5$ aq.—$Zn(EtA'')_2$.—AgEtA''.

An isomeric ether EtHA'' [54·7°] is obtained by the action of NaOEt on the oxim of oxalacetic

ether (Piutti, *C. C.* 1888, 1460; 1890, 938; Hantzsch, *B.* 23, 11).

Di-ethyl ether Et_2A''. Oil. Identical with the oxim of oxalacetic ether.

Di-nitroso-succinic acid $CO_2H.C(NOH).C(NOH).CO_2H$. [130°]. Formed from carboxy-tartronic acid and hydroxylamine (Müller, *B.* 16, 2985). Prisms.—Ag_2A'': explosive pp.

NITROSOSULPHATES and **NITROSO-SULPHURIC ACIDS** *v.* SULPHATES and SULPHURIC ACID in vol. iv.

NITROSO-THIOGLYCOLLIC ACID $HS.C(NOH).CO_2H$. Formed by boiling nitroso-thiohydantoïn with baryta-water (Maly a. Andreasch, *M.* 1, 168; *B.* 13, 601). Crystals, v. sol. ether. Gives a blue colour with $FeCl_3$. Decomposed by boiling water or alcohol into CO_2, hydrogen sulphocyanide, and H_2O.—BaA'' aq.

NITROSO - THIOHYDANTOÏN $C_3H_3N_3OS$. Formed from thiohydantoïn and HNO_2 (Maly, *B.* 12, 967). Crystalline powder, sl. sol. water.

NITROSO - THYMOL *v. Oxim* of THYMO-QUINONE.

DI - NITROSO - TOLUENE $C_6H_3Me(NO)_2$ [6:3:2or1]. [c. 144°]. Formed by oxidising toluquinone dioxim with K_3FeCy_6 (Nietzki, *B.* 21, 432; Mehne, *B.* 21, 734). Amorphous insoluble powder, volatile with steam. Gasified on fusion. Reconverted by hydroxylamine into toluquinone dioxim.

NITROSO-*o*-TOLUIDINE $C_7H_8N_2O$ *i.e.* $C_6H_3Me(NO)(NH_2)$ [1:5:2]. [116°]. Formed by heating toluquinone mono-oxim (nitroso-o-cresol, with acetate and chloride of ammonium (Mehne) *B.* 21, 731). Small green needles with blue reflex. Yields NH_3 and nitroso-o-cresol on heating with aqueous NaOH. Hydroxylamine yields toluquinone dioxim.

Nitroso-*m*-toluidine $C_6H_3Me(NO)(NH_2)$ [1:2:5]. [178°]. Formed in like manner from nitroso-*m*-cresol. Resembles its isomeride and yields the same dioxim on treatment with hydroxylamine.

α-NITROSO-VALERIC ACID is the *Oxim* of PROPYL-GLYOXYLIC ACID.

γ-Nitroso-valeric acid $CH_3.C(NOH).CH_2.CH_2.CO_2H$. *Oxim* of *acetyl-propionic acid.* [96°]. Formed from β-acetyl-propionic acid (levulic acid) and hydroxylamine (Müller, *B.* 16, 1617). Prisms. Yields levulic acid on treatment with tin and HCl. H_2SO_4 at 100° forms methyl-succinimide (Bredt, *A.* 251, 316; *cf.* Rischbieth, *B.* 20, 2671).—BaA'_2 2aq.—AgA': white pp.

Ethyl ether EtA'. Oil.

γδ-Di-nitroso-valeric acid $CH(NOH).C(NOH).CH_2.CH_2.CO_2H$. [136°]. Formed from glyoxyl-propionic acid and hydroxylamine (Wolff, *A.* 260, 93). Prisms. Converted by conc. H_2SO_4 at 70° into furazyl-propionic acid $O<\begin{array}{l}N:CH\\N:C.CH_2.CH_2.CO_2H\end{array}$. [86°]. —$BaA'_2$ 3aq: thin needles.

NITROSO-XYLENOL *v. Oxim* of XYLO-QUINONE.

ISO-NITRO-STEARIC ACID $C_{18}H_{35}(NO_2)O_2$. Formed by boiling stearic acid (100 g.) with HOAc (1500 c.c.) and HNO_3 (250 g. of S.G. 1·48) for four days (Claus, *J. pr.* [2] 43, 161). Yellowish buttery mass, v. sol. ether and alcohol, insol. water and ligroïn. Yields stearic acid on reduction. It is therefore not a true nitro- compound. —K_2A''.—$K_2A''KHCO_3$.—Na_2A'': granular mass, insol. ether.—SrA''.—CuA'_2.—CuA'': light-green.

NITRO-STRYCHNINE *v.* STRYCHNINE.

NITRO-STYRENE. The o, *m*, and *p*- isomerides $C_6H_4(NO_2).CH:CH_2$, melting at 14°, −5°, and 29° respectively, are formed by boiling the acids $C_6H_4(NO_2).CHBr.CH_2.CO_2H$ with aqueous Na_2CO_3 (Einhorn, *B.* 16, 2213; Prausnitz, *B.* 17, 597; Basler, *B.* 16, 3005). The corresponding dibromides $C_6H_4(NO)_2.CHBr.CH_2Br$ melt at 52°, 79°, and 73° respectively.

ω-Nitro-styrene $C_6H_5.CH:CH.NO_2$. [58°]. (250°-260°). Formed by heating benzoic aldehyde with nitro-methane and $ZnCl_2$ for 8 hours at 160° (Priebs, *A.* 225, 319). Formed also by boiling styrene with HNO_3 (Simon, *A.* 31, 269; Blyth a. Hofmann, *A.* 53, 297). Yellow crystals, yielding benzoic acid on oxidation. When freshly prepared it is soluble in NaOHAq, but the solution slowly decomposes, yielding benzoic aldehyde and resin. Diluted H_2SO_4 yields benzoic aldehyde, hydroxylamine, and CO. Conc. HClAq yields hydroxylamine and $PhCHCl.CO_2H$ [78°].

ωo-Di-nitro-styrene $C_6H_4(NO_2).CH:CH(NO_2)$. [107°]. Formed, together with the ω*p*-isomeride, by nitration of ω-nitro-styrene (Priebs). Yellow needles (from alcohol).

ω*p*-Di-nitro-styrene. [199°]. Formed as above, and also by the action of HNO_3 and H_2SO_4 on *p*-nitro-cinnamic acid at 0° (Friedländer a. Mähly, *A.* 229, 224; *B.* 16, 851). Yellow crystals, sol. KOHAq. Dilute H_2SO_4 decomposes it into *p*-nitro-benzoic aldehyde, hydroxylamine, and CO.

ω*m*-Di-nitro-styrene. [122°]. Formed from *m*-nitro-cinnamic acid, HNO_3, and H_2SO_4 at 0° (Friedländer a. Lazarus, *A.* 229, 233). Yellowish plates (from water). Conc. H_2SO_4 at 100° gives CO and *m*-nitro-benzaldoxim.

o-NITRO-STYRYL-ACROLEÏN $C_{11}H_9NO_3$ *i.e.* $C_6H_4(NO_2).CH:CH.CH:CH.CHO$. [153°]. Formed from o-nitro-cinnamic aldehyde, aldehyde, and very dilute NaOH (Einhorn, *B.* 17, 2026). Pale-yellow crystals (from dilute alcohol).

o-NITRO-STYRYL-ACRYLIC ACID $C_6H_4(NO_2).CH:CH.CH:CH.CO_2H$. [218°]. Formed from o-nitro-cinnamic aldehyde, Ac_2O, and sodium acetate, and obtained also by oxidising $C_6H_4(NO_2).C_4H_4.CO.CH_3$ with aqueous NaOCl (Diehl a. Einhorn, *B.* 18, 2331). Slender folted needles, v. sol. hot alcohol.

o-NITRO-STYRYL-GLYOXYLIC ACID $C_6H_4(NO_2).CH:CH.CO.CO_2H$. [136°]. Formed from o-nitro-benzoic aldehyde, pyruvic acid, and HClAq (Baeyer a. Drowson, *B.* 15, 2862). Crystals. Converted by alkalis into indigo.

DI-*m*-NITRO-DI-STYRYL KETONE. [232°]. Sparingly soluble flakes (Von Miller a. Rohde, *B.* 22, 1838).

o-NITRO-STYRYL METHYL KETONE $C_6H_4(NO_2).CH:CH.CO.CH_3$. [60°]. Formed, together with tho *p*- isomerido [110°], by nitration of styryl mothyl ketone (Baeyer a. Drowson, *B.* 15, 2858; 16, 1953). Formed also by boiling $C_6H_4(NO_2).CH(OH).CH_2.CO.CH_3$ with Ac_2O, or $C_6H_4(NO_2).CH:CH.CO.CH_2.CO.CH_3$ with dilute

H_2SO_4 (Fischer a. Kuzel, *B.* 16, 35). Long needles, sol. alcohol.

m-**NITRO-STYRYL-QUINOLINE** $C_{17}H_{12}N_2O_2$ *i.e.* $C_6H_4{:}C_3H_2N.CH{:}CH.C_6H_4(NO_2)$. [132°]. Formed by heating methyl-quinoline (lepidine) with *m*-nitro-benzoic aldehyde and $KHSO_4$ at 160° (Heymann a. Königs, *B.* 21, 1429). Needles (from alcohol).

An isomeride [139°] is formed from (*Py.* 3)-methyl-quinoline and *m*-nitro-benzoic aldehyde (Wallach, *B.* 16, 2009; Wartanian, *B.* 23, 3646). It gives the crystalline salts $B'HCl$.—$B'HNO_3$.—$B'C_6H_2(NO_2)_3OH$.—$B'_2H_2PtCl_6$ 1½aq.

p-**Nitro-styryl-quinoline.** [165°]. Formed from (*Py.* 3)-methyl-quinoline and *p*-nitro-benzoic aldehyde (Bulach, *B.* 20, 2047; 22, 285). Needles. Yields a dibromide $C_{17}H_{12}N_2O_2Br_2$ [276°] which turns brown at 230°.

NITRO-DI-STYRYL-DI-VINYL-KETONE *v.* NITRO-PHENYL-BUTINYL PHENYL-BUTINYL KETONE.

NITRO-*o*-SULPHO-BENZOIC ACID $C_7H_5NSO_7$ *i.e.* $C_6H_3(NO_2)(SO_3H)(CO_2H)$ [4:2:1]. [110°]. Formed by oxidising nitro-toluene sulphonic acid (Hart, *Am.* 1, 350; Hedrick, *Am.* 9, 411; Kastle, *Am.* 11, 177). White needles (from hot water).—KHA''aq: long needles.—K_2A''.—BaA''.

Chloride $C_6H_3(NO_2)(SO_2Cl)(COCl)$. [60°].

Amide $C_6H_3(NO_2)(SO_2NH_2)(CO_2H)$. [172°]. Formed by oxidising *p*-nitro-toluene sulphonic amide with K_3FeCy_6 or alkaline $KMnO_4$ (Noyes, *Am.* 8, 171; 11, 161). Small granules (from hot water), melting at 177° when slowly heated, but at 172° when quickly heated. Changes slowly when kept at 180° into the anhydride $C_6H_3(NO_2){<}\substack{SO_2\\CO}{>}NH$ [209°] which yields the salts $KC_7H_3N_2SO_5$, S. ·96 at 18·5°, $Ba(C_7H_3N_2SO_5)_2$ 3aq, and $AgC_7H_3N_2SO_5$. The free amic acid yields the salts $Ba(C_7H_5N_2SO_6)_2$ aq, $AgC_7H_5N_2SO_6$ ½aq, and $Ag_2C_7H_4N_2SO_6$ aq.

Nitro-*m*-sulphobenzoic acid $C_6H_3(NO_2)(SO_3H)(CO_2H)$ [*x*:3:1]. Formed by nitrating *m*-sulphobenzoic acid (Limpricht a. Uslar, *A.* 106, 27). Crystalline.—BaA'' 3aq.—BaA'' 1½aq.—$BaH_2A''_2$ 4aq: radiating prisms.

Nitro-*p*-sulphobenzoic acid $C_6H_3(NO_2)(SO_3H)(CO_2H)$ [2:4:1]. Formed by oxidising (2, 1, 4)-nitro-toluene sulphonic acid (Hart, *Am.* 1, 352).—KHA''.—BaA'' 2aq: granules.

Nitro-*p*-sulphobenzoic acid $C_6H_3(NO_2)(SO_3H)(CO_2H)$ [3:4:1]. [131°]. Formed by nitrating *p*-sulphobenzoic acid (Hart, *Am.* 1, 342; Remsen, *A.* 178, 288). Prisms.—KHA'' 1½aq.—BaA'' 4aq. — $BaH_2A''_2$ 6aq. — CaA'' 5aq. — CuA'' 5aq: bluish-green crystals.

NITRO-SULPHO-TOLUIC ACID $C_8H_7NSO_7$ *i.e.* $C_6H_2Me(NO_2)(SO_3H)(CO_2H)$ [1:6:4:3]. Formed by oxidation of nitro-*m*-xylene-sulphonic acid $C_6H_2Me_2(NO_2)(SO_3H)$ [1:3:6:4] with $KMnO_4$ (Limpricht, *B.* 18, 2191).—$A'K$ ½aq: fine white silky needles.

NITRO-SULPHYDRO-CINNAMIC ACID $C_6H_4(NO_2).CH{:}C(SH).CO_2H$. [240°]. Formed from $C_6H_5.CH{:}C(SH).CO.SCN$, nitric acid, and H_2SO_4 (Bondzynski, *M.* 8, 355). Crystals (from alcohol).—BaA'_2: long needles.

NITRO-α-SULPHYDRO-CINNAMOYL SULPHOCYANIDE $C_6H_4(NO_2).CH{:}C(SH).CO.SCN$. The *o*- compound [189°] is formed, together with the *p*- derivative [251°] by nitrating sulphydro-cinnamoyl sulphocyanide. These bodies may also be got from thioglycollyl sulphocyanide and the corresponding nitro-benzoic aldehyde (Bondzynski, *M.* 8, 355). Both are crystalline.

NITRO-SULPHYDRO-METHYL-IMIDAZOLE. *Methyl derivative* $C_3H_2Me(NO_2)SMe$. [85°]. Formed from $NMe{<}\substack{CH\,=\,CH\\C(SMe){:}N}$ and dilute HNO_3 (Wohl a. Marckwald, *B.* 22, 1358). Yellow needles, sl. sol. cold water.—$B'_2H_2PtCl_6$. [197°].

NITRO-SULPHYDRO-PHENYL-IMIDAZOLE. *Methyl derivative* $C_3HN_2Ph(NO_2)(SMe)$. [116°]. Formed from $NPh{<}\substack{CH{:}CH\\C(SMe)}{>}N$ and dilute HNO_3 (Wohl a. Marckwald, *B.* 22, 1357).

NITROSYL BROMIDE and **CHLORIDE** *v.* *Nitrogen oxybromides* and *oxychlorides*, under NITROGEN, p. 569.

NITRO-TEREPHTHALIC ACID $C_8H_5NO_6$ *i.e.* $C_6H_3(NO_2)(CO_2H)_2$[2:4:1]. [270°]. Formed by nitrating terephthalic acid (De la Rue a. Müller, *A.* 121, 90; Burkhardt, *B.* 10, 145). Crystalline. —Ag_2A'': powder (Skraup, *M.* 7, 148).

Methyl ether Me_2A''. [70°]. Prisms (Ahrens, *B.* 19, 1636).

Amide $C_6H_3(NO_2)(CONH_2)_2$. Prisms.

NITRO-TEREPHTHALIC ALDEHYDE $C_6H_3(NO_2)(CHO)_2$. [86°]. Formed from terephthalic aldehyde, KNO_3, and H_2SO_4 at 110° (Löw, *A.* 231, 364). Large needles (by sublimation). With acetone and NaOH at 60° it gives the indigo-reaction.

NITRO-THIENOL $C_4H_2S(NO_2)(OH)$. [116°]. Formed by treating a dilute H_2SO_4 solution of amido-thiophene with nitrous acid and boiling for some time. Colourless needles. Sol. water and ether. Dissolves in alkalis with a yellow colour (Stadler, *B.* 18, 2319).

NITRO-(α)-THIENYL-GLYOXYLIC ACID $C_4H_2(NO_2)S.CO.CO_2H$. [92°]. Formed by oxidation of nitro-thienyl methyl ketone [123°] (Peter, *B.* 18, 541). Crystals.

NITRO-(α)-THIENYL METHYL KETONE $C_4H_2(NO_2)S.CO.CH_3$. Two isomerides [86°] and [123°] are formed by nitrating (α)-thienyl methyl ketone with fuming HNO_3 at −8° (Peter, *B.* 17, 2646; 18, 541). They both yield the same di-nitro-thienyl methyl ketone [167°].

m-**NITRO-THIOBENZOIC ALDEHYDE** $(C_6H_4(NO_2).CHS)_x$? A grey powder formed by passing H_2S into an alcoholic solution of *m*-nitro-benzoic aldehyde (Bertagnini, *A.* 79, 269). Insol. ordinary solvents.

NITRO-THIONYL-ANILINE $C_6H_4(NO_2).N(SO)$. Formed from nitro-aniline and thionyl chloride (Michaelis a. Hümme, *B.* 24, 755). The *m*- compound melts at 63·5°; the *p*- isomeride at 70°. Decomposed by hot water.

NITRO-THIOPHENE $C_4H_3(NO_2)S$. [44°]. (225° cor.). Prepared by passing air charged with thiophene vapour through fuming HNO_3 (Meyer a. Stadler, *B.* 17, 2648; 18, 533). Pale-yellow monoclinic prisms.

Di-nitro-thiophene $C_4H_2(NO_2)_2S$. [52°]. (290°). Formed, together with the isomeride [78°], by further nitration of nitro-thiophene (Meyer a. Stadler, *B.* 17, 2648, 2779; 18, 530, 1778). Yellow monoclinic plates, m. sol. water. Converted by repeated steam-distillation into the isomeride [78°]. A drop of KOHAq added to the alcoholic solution gives a splendid red colour, destroyed by excess of KOH. Forms the

double compounds $C_4H_2(NO_2)_2SC_{10}H_8$ [50°] and $C_4H_2(NO_2)_2SC_{14}H_{10}$ [162°].

Di-nitro-thiophene [78°]. Formed as above. Yellow needles, volatile with steam.

NITRO-THIOPHENE SULPHONIC ACID $C_4H_2(NO_2)(SO_3H)S$. Formed from nitro-thiophene and fuming H_2SO_4 (Stadler, *B.* 18, 534). White hygroscopic crystals.—AgA′.

Chloride. Oil.

Amide $C_4H_2(NO_2)S(SO_2NH_2)$. [173°].

NITRO-(α)-THIOPHENIC ACID $C_5H_3NSO_4$ *i.e.* $C_4H_2S(NO_2)(CO_2H)$. [146°]. Formed from (α)-thiophenic acid and conc. HNO_3 at 50° (Römer, *B.* 20, 116). Needles, slowly changed by water into a variety melting at about 125°. A little NaOH colours its alcoholic solution magenta. CuA'_2.—AgA′: needles.

Ethyl ether EtA′. [71°].

NITRO-THYMOL $C_6H_2Me(C_3H_7)(NO_2)(OH)$. [140°]. Formed by oxidation of nitroso-thymol (R. Schiff, *B.* 8, 1501; Liebermann, *B.* 10, 612).

Di-nitro-thymol [55°]. Formed by nitration of thymol or its sulphonic acid (Lallemand, *A. Ch.* [3] 49, 152). Crystalline. — KA′. — BaA'_2 3aq.—CaA'_2 5aq.—AgA′: lemon-yellow pp.

Ethyl ether EtA. [53°]. Tables (from alcohol) (Ladenburg a. Engelbrecht, *B.* 10, 1218).

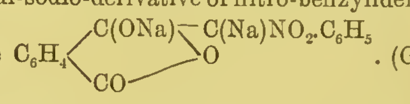
Tri-nitro-thymol. [111°]. Got by nitrating di-nitro-thymol. Yields a methyl ether [92°] (Atcherley, *Z.* 1871, 415).

NITRO-TOLUAMIDOXIM $C_8H_9N_3O_3$ *i.e.* $C_6H_3Me(NO_2).C(NOH)(NH_2)$ [4:2:1]. [161°]. Formed by heating nitro-toluic nitrile with alcoholic hydroxylamine (Weise, *B.* 22, 2430). Needles.—B′HCl: white crystalline mass.

o-NITRO-TOLUENE $C_6H_4Me(NO_2)$ [1:2]. Mol. w. 137. (218°). S.G. $\frac{15}{}$ 1·168 (Streng, *B.* 24, 1987). S.V. 142·3 (Lossen, *A.* 254, 73). Formed, together with the *p*- isomeride, by nitration of toluene (Glénard a. Boudault, *C. R.* 19, 505; Hofmann a. Muspratt, *A.* 53, 221; Kekulé, *Z.* [2] 3, 225; Rosenstiehl, *A. Ch.* [4] 27, 433). Formed also by elimination of NH_2 from (2, 1, 4)-nitro-*p*-toluidine (Beilstein a. Kuhlberg, *A.* 155, 1; 158, 348). Liquid; solidifies at −10·5°. After administration to dogs it appears in the urine as o-nitro-benzoic acid and crystalline $C_{14}H_{19}N_3O_{10}$ $2\frac{1}{2}$aq (Jaffé, *Russ. Zeit. Pharm.* 1878, 513; Noyes, *Am.* 5, 99). Long boiling with alkaline K_3FeCy_6 yields o-nitro-benzoic acid. Zinc-dust and alcoholic NaOH reduce it to o-azoxy-toluene [59°] (Guitermann, *B.* 20, 2016). Its product of sulphonation differs from that of *p*-nitro-toluene in giving no red colour when boiled with alkalis (Reverdin a. Harpe, *Bl.* [2] 50, 44).

m-**Nitro-toluene** $C_6H_4Me(NO_2)$ [1:3]. [16°]. (230°). S.G. $\frac{22}{}$ 1·168. S.V. 144·0. Occurs in small quantity in crude nitro-toluene (Monnet, Reverdin, a. Nölting, *B.* 12, 445; 18, 1337). Prepared from o- or *p*-toluidine by successive acetylation, nitration, saponification, diazotisation, and boiling with alcohol (Beilstein a. Kuhlberg, *A.* 155, 24; 158, 346; Buchka, *B.* 22, 829). Yields *m*-nitro-benzoic acid on oxidation. $SnCl_2$ in HClAq reduces it to pure *m*-toluidine, while zinc-dust and HClAq yield chloro-*m*-toluidine also. Boiling with KOH in MeOH forms $(C_6H_4Me)_2N_2O$ [39°].

p-**Nitro-toluene** $C_6H_4Me(NO_2)$ [1:4]. [54°]. (234°) (Streng). S.V.S. 121·7 (Schiff, *A.* 223, 261). Formed, together with the *o*- isomeride, by nitration of toluene. Trimetric crystals. Much less volatile with steam than o-nitro-toluene. Oxidised by boiling alkaline K_3FeCy_6 to *p*-nitro-benzoic acid (Noyes, *B.* 16, 52). Reduced by iron and HClAq to pure *p*-toluidine, while zinc and HClAq yield chlorinated toluidine. Zinc-dust and NaOH reduce it to $(C_6H_4Me)_2N_2$ [144°], two azoxy- compounds $(C_6H_4Me)_2N_2O$ [75°] and [70°] and $(C_6H_4Me)_2N_2H_2$ [126°] (Janovsky a. Reimann, *B.* 22, 40). CrO_2Cl_2 followed by water yields nitro-toluquinone (Étard, *C. R.* 87, 989). NaOMe yields a brownish-red product reduced by $SnCl_2$ to $C_2H_2(C_6H_4NH_2)_2$ (Bender a. Schultz, *B.* 19, 3237).

ω-**Nitro-toluene** $C_6H_5.CH_2(NO_2)$. *Phenyl-nitro-methane.* Formed by the action of acids upon the di-sodio-derivative of nitro-benzylidene-phthalide  . (Gabriel a. Koppe, *B.* 18, 1254; 19, 1145). Liquid, boiling with decomposition at 226°. Reduced by tin and HCl to benzylamine. By heating with fuming HCl at 150° it yields benzoic acid and hydroxylamine. Gives a white crystalline sodium derivative.

Di-nitro-toluene $C_6H_3Me(NO_2)_2$ [1:2:4]. Mol. w. 182. [70°]. (300°). S.V.S. 137·5 (Schiff). S. (CS_2) 2·19 at 17°. Obtained by nitration of toluene (Deville, *A.* 44, 307; Cahours, *C. R.* 24, 555; Nölting a. Witt, *B.* 18, 1336) and o- or *p*-nitro-toluene. Obtained also by eliminating NH_2 from di-nitro-toluidine [195°] (Staedel, *A.* 259, 220). Monoclinic needles, sl. sol. cold alcohol. Yields tolylene-*m*-diamine on reduction (Baeyer, *B.* 7, 1638). By partial reduction with ammonium sulphide the *p*-nitro- group is reduced, giving $C_6H_3Me(NO_2)(NH_2)$ [1:2:4] of melting-point [78°]. On the other hand, by alcoholic $SnCl_2$ (3 mols.) the o-nitro- group is first reduced, giving $C_6H_3Me(NH_2)(NO_2)$ [1:2:4] of melting-point [107°] (Anschütz a. Heusler, *B.* 19, 2161).

s-**Di-nitro-toluene** $C_6H_3Me(NO_2)_2$ [1:3:5]. [93°]. Formed by eliminating NH_2 from di-nitro-o-toluidine [208°] or di-nitro-*p*-toluidine [166°] (Staedel, *B.* 14, 901; *A.* 217, 189; Nevile a. Winther, *C. J.* 41, 416; Hübner, *A.* 222, 75). Yellow needles (from HOAc mixed with benzene), v. sol. benzene and alcohol. Volatile with steam. Yields di-nitro-benzoic acid [204°] on oxidation.

Di-nitro-toluene $C_6H_3Me(NO_2)_2$ [1:2:3]. [63°]. Formed by heating (2, 3, 1, 4)-di-nitro-toluic acid with dilute HClAq (Rozanski, *B.* 22, 2681). Hair-like needles (from dilute HOAc).

Di-nitro-toluene $C_6H_3Me(NO_2)_2$ [1:2:5]. [48°] (N. a. L.); [52·5°] (R.). Formed by heating (1, 4, 3, 6)-di-nitro-toluic acid with dilute HClAq at 250° (Rozanski, *B.* 22, 2679). Formed also from toluquinone dioxim and HNO_3 (Nietzki a. Guitermann, *B.* 21, 428). Yellow crystals (from ligroïn). Appears also to occur among the products of the nitration of toluene (Limpricht, *B.* 18, 1402).

Di-nitro-toluene $C_6H_3Me(NO_2)_2$ [1:2:6]. [61°]. Formed by eliminating NH_2 from di-nitro-*p*-toluidine [168°] (Staedel, *A.* 217, 206; 225, 384). Formed also by nitration of toluene. Needles (from alcohol).

Di-nitro-toluene $C_6H_3Me(NO_2)_2$ [1:3:4]? [60°]. S. (CS_2) 2·188 at 17°. A product of nitration of *m*-nitro-toluene (Beilstein a. Kuhlberg). Long needles (from CS_2).

(*α*)-**Tri-nitro-toluene** $C_6H_2Me(NO_2)_3$ [1:2:4:6]. Mol. w. 227. [82°]. S. (CS_2) ·386 at 17°. Formed by nitration of toluene (Wilbrand, *A.* 128, 178). Flat needles, v. sol. hot alcohol. Forms with aniline a compound $C_6H_2Me(NO_2)_3PhNH_2$ [84°] (Hepp, *A.* 215, 365).

(*β*)-**Tri-nitro-toluene** $C_6H_2Me(NO_2)_3$. [112°]. Formed, together with the (*γ*)-isomeride, by nitration of *m*-nitro-toluene (Hepp). Triclinic prisms (from acetone).

(*γ*)-**Tri-nitro-toluene** $C_6H_2Me(NO_2)_3$. [104°]. Formed as above (Hepp). Trimetric plates; $a:b:c = ·937:1:·672$. V. sl. sol. cold alcohol.

NITRO-TOLUENE-ω-PHOSPHONIC ACID $C_6H_4(NO_2).CH_2.PO(OH)_2$. Formed by dissolving toluene ω-phosphonic acid in fuming HNO_3 (Litthauer, *B.* 22, 2144). Yellow needles, decomposing at 217° without melting. The acid $(C_6H_4(NO_2).CH_2)_2PO.OH$ melts at 212°.

NITRO-TOLUENE SULPHINIC ACID $C_6H_3Me(NO_2).SO_2H$. Formed by reduction of $C_6H_3Me(NO_2).SO_2Cl$ by sodium amalgam (Otto a. Grüber, *A.* 145, 24). Crystalline.—NaA′ ½aq.

Di-nitro-toluene sulphinic acid $C_6H_2(CH_3)(NO_2)_2.SO_2H$. Formed by reduction of di-nitro-toluene-sulphonic chloride with zinc-dust (Perl, *B.* 18, 71). V. sol. water and alcohol.

Salts.—A′K.—A′₂Ba.—A′₂Pb 3aq: minute prisms.

o-**NITRO-TOLUENE SULPHONIC ACID** $C_6H_3Me(NO_2)(SO_3H)$ [1:2:5]. Formed from $C_6H_2Me(NO_2)(NH_2)(SO_3H)$ [1:2:4:5] by heating its diazo- derivative with alcohol at 100° (Foth, *A.* 230, 305).

Chloride $C_6H_3Me(NO_2)(SO_2Cl)$. [50°].

Amide [133·5°]. Long needles.

o-**Nitro-toluene sulphonic acid** $C_6H_3Me(NO_2)(SO_3H)$[1:2:4]. Formed by sulphonating o-nitro-toluene or by nitrating toluene *p*-sulphonic acid (Beilstein a. Kuhlberg, *A.* 155, 18; Engelhardt a. Bck, *Z.* [2] 5, 209; Kornatzki, *A.* 221, 180).

Salts.—BaA'_2 2aq. S. (of BaA'_2) ·58 at 19·5°.—PbA'_2 2aq. S. (of PbA'_2) ·77 at 18°.

Chloride. Oil (Otto a. Grüber, *A.* 145, 23).

Amide [128°] (O. a. G.); [139°] (K.); [144°] (Neale, *A.* 203, 73). Yields a benzoyl derivative $C_6H_3Me(NO_2).SO_2NHBz$ [130°] whence the salts $C_6H_3Me(NO_2).SO_2NKBz$, $Ca(C_{14}H_{11}N_2SO_5)_2$ 2aq and $Ba(C_{14}H_{11}N_2SO_5)_2$ may be prepared, and whence PCl_5 produces $C_6H_3Me(NO_2).SO_2N:CClPh$ [125°] from which ammonium carbonate forms $C_{14}H_{13}N_3SO_4$ [123°] (Anna Wolkoff, *Z.* 1871, 422; *B.* 5, 141).

p-Toluide. [131°]. Crystals.

o-**Nitro-toluene sulphonic acid** $C_6H_3Me(NO_2)(SO_3H)$ [1:2:3, 5 or 6]. Formed from (2, 1, 4)-nitro-toluidine by sulphonating and eliminating NH_2 (Foth). Its salts are v. e. sol. water.

Chloride [50°]. Thick prisms.

Amide [133°]. Needles.

o-**Nitro-toluene sulphonic acid** $C_6H_3Me(NO_2)(SO_3H)$[1:2 or 6:3]. Formed from *p*-toluidine sulphonic acid by nitration and elimination of NH_2 (Pechmann, *A.* 173, 214; Foth, *A.* 230, 308).—BaA'_2 2aq: plates, sl. sol. cold water.

Chloride $C_6H_3Me(NO_2)SO_2Cl$. [58·5°].

Amide $C_6H_3Me(NO_2)SO_2NH_2$. [163·5°].

m-**Nitro-toluene sulphonic acid.** Formed by sulphonating *m*-nitro-toluene (B. a. K.). — BaA'_2 2aq. S. (of BaA'_2) 1·145 at 17·5°. — PbA'_2 2½aq. S. (of PbA'_2) 3·62 at 18°.

p-**Nitro-toluene sulphonic acid** $C_6H_3Me(NO_2)(SO_3H)$[1:4:2]. [134°]. S. 210 at 23°; 250 at 28°. Formed by sulphonating *p*-nitro-toluene (Javorsky, *Z.* 1865, 222; B. a. K.; Jenssen, *A.* 172, 230; Hart a. Remsen, *B.* 10, 1046; *Am.* 1, 349; Schwanert, *A.* 186, 351; Noyes, *Am.* 8, 168; Hausser, *Bl.* [3] 3, 797). Trimetric crystals (containing 2½aq). NaOHAq yields an azoxy- compound reduced by zinc-dust to di-amido-stilbene disulphonic acid.

Salts.—NH_4A': long prisms, not decomposed by H_2SO_4 at 100°.—NaA′ 2aq.—KA′. S. 2·62 at 16°.—BaA'_2 3aq. S. 3·34 at 18·5.—CaA'_2 4aq.—CaA'_2 aq.—CaA'_2 6aq.—PbA'_2 3aq. S. (of PbA'_2) 15·3 at 19°.—PbA'_2 2aq.

Chloride [44°]. Tablets (from ether).

Amide [187°]. Needles.

Nitro-toluene exo-sulphonic acid [1:4]$C_6H_4(NO_2).CH_2.SO_3H$. Formed by nitration of $C_6H_5.CH_2SO_3H$ (Mohr, *A.* 221, 217).

Chloride. Oil. When gently distilled it gives SO_2 and $C_6H_4(NO_2).CH_2Cl$[1:4] [71·5°].

Amide [204°]. Prisms. Accompanied by an isomeride [140°–160°].

Nitro-toluene disulphonic acid $C_6H_2Me(NO_2)(SO_3H)_2$. Formed by boiling *p*-bromo-toluene disulphonic acid with fuming HNO_3 (Kornatzki, *A.* 221, 198).—K_2A''. The same, or an isomeric acid, is obtained by displacing Br by H and nitrating the product; it gives the salts K_2A'' and BaA'' 3aq.

Di-nitro-toluene exo-sulphonic acid $C_6H_3(NO_2)_2.CH_2SO_3H$. Formed from the acid $C_6H_4(NO_2).CH_2.SO_3H$ and a mixture of H_2SO_4 (2 pts.) and fuming HNO_3 (1 pt.) (Mohr, *A.* 221, 225).—KA′.—BaA'_2 4aq.—PbA'_2 4aq.

Di-nitro-toluene sulphonic acid $C_6H_2Me(NO_2)_2SO_3H$ [1:2:6:4]. [165°]. Formed by nitrating toluene *p*-sulphonic acid (Schwanert, *B.* 10, 28; *A.* 186, 342). Trimetric prisms (containing 2aq).—KA′. S. ·52 at 14·5°. S. (94 p.c. alcohol). ·09 at 22°.—NH_4A'. S. 4·2 at 18°.—BaA'_2 4aq. S. 3 at 17°.—CaA'_2 2aq.—PbA'_2 2aq.—PbA'_2 3aq. S. (of PbA'_2) 2·64 at 14·5° (B. a. K., *Z.* [2] 6, 796).

Chloride. [125°]. Crystals (from ether).

Amide. [203°]. Laminæ.

(*α*)-**NITRO-o-TOLUIC ACID** $C_8H_7NO_4$ *i.e.* $C_6H_3Me(NO_2)(CO_2H)$[2:5:1]. [179°]. Formed, together with the (*β*)-acid, by nitration of *o*-toluic acid; and, together with the (*γ*)- acid by oxidation of nitro-o-xylene with dilute HNO_3 (Jacobsen, *B.* 16, 1957; 17, 162). Small crystals, v. sl. sol. water. Yields amido-toluic acid [196°] and oxy-toluic acid [172°].—KA′ aq.—CaA'_2 2aq.—BaA'_2 2aq: slender needles.

(*β*)-**Nitro-o-toluic acid** $C_6H_3Me(NO_2).CO_2H$ [2:3:1]. [145°]. Formed as above. Long needles. Yields oxy-toluic acid [183°].—BaA'_2 2aq.—CaA'_2 2aq.

(*γ*)-**Nitro-*o*-toluic acid** $C_6H_3Me(NO_2).CO_2H$ [2:4:1]. [152°]. Formed as

above. Long needles. Yields oxy-toluic acid [179°].—BaA'_2 5aq: easily soluble prisms.

(α)-Nitro-*m*-toluic acid $C_6H_3Me(NO_2).CO_2H$ [3:6:1]. [219°]. Formed, together with a small quantity of its (3, 2, 1)-isomeride [182°], by nitration of *m*-toluic acid (Jacobsen, *B.* 14, 2353; Ahrens, *Z.* 1869, 183; Krausler, *Z.* 1866, 370; Panaotovic, *J. pr.* [2] 33, 64). Monoclinic prisms.—BaA'_2 2aq.—CaA'_2 4aq: m. sol. water.

(β)-Nitro-*m*-toluic acid $C_6H_3Me(NO_2)CO_2H$ [3:2:1]. [182°]. Formed as above (Jacobsen).

s-Nitro-*m*-toluic acid $C_6H_3Me(NO_2)CO_2H$ [3:5:1]. [167°]. Formed by oxidation of *s*-nitro-*m*-xylene with $KMnO_4$ and acetic acid (Thöl, *B.* 18, 360). Silky needles, v. sol. water.—BaA'_2 4aq. S. ·308 at 15°. Needles.

Nitro-*m*-toluic acid $C_6H_3Me(NO_2)CO_2H$ [3:4:1]. [214°]. Formed by oxidation of crude nitro-xylene (Beilstein a. Kreusler, *A.* 144, 168; Remsen a. Kuhara, *Am.* 3, 426) and of nitro-isocymene (Kelbe, *A.* 221, 161). — NH_4A' 2aq. — MgA'_2 7aq.— CaA'_2 2aq. — BaA'_2 4aq: very soluble needles.

Ethyl ether EtA'. [55°] (B. a. K.).

Amide. [151°] (B. a. K.].

Nitrile $C_6H_3Me(NO_2).CN$. [80°].

Nitro-*p*-toluic acid $C_6H_3Me(NO_2)(CO_2H)$ [4:3:1]. [190°]. Formed by boiling cymene or *p*-toluic acid with fuming HNO_3 (Noad, *A.* 63, 297; Fittica, *A.* 172, 309; Fittig, *A.* 168, 251; Ahrens, *Z.* [2] 5, 102). Monoclinic prisms, sl. sol. cold water.—BaA'_2 4aq.—CaA'_2 3aq.—CuA'_2 4aq.—$Cu_3A'_4(OH)_2$.—$Cu_3A'_5(OH)$ aq (Noyes, *Am.* 10, 472).—$Pb(OH)A'$.—AgA'. The *ethers* MeA' and EtA' are crystalline.

Nitro-*p*-toluic acid $C_6H_3Me(NO_2)(CO_2H)$ [4:2:1]. [161°]. Obtained by heating its nitrile with HClAq at 195°. Long needles.—BaA'_2 4aq.—BaA'_2 5aq (Noyes, *Am.* 10, 472).—CaA'_2 2aq.—CuA'_2 aq.—AgA': needles.

Amide. [153°]. Slender needles.

Nitrile $C_6H_3Me(NO_2)CN$. [99°] (G.; W.); [101°] (N.). Formed from (3, 1, 4)-nitro-*p*-toluidine by Sandmeyer's reaction (Glock, *B.* 21, 2662; Weise, *B.* 22, 2429; Von Niementowski, *J. pr.* [2] 40, 4; 21, 1535, 1992). Needles (from alcohol). Yields on reduction with tin and HCl the compounds $(C_6H_3MeCy)_2N_2O$ [182°] and $C_6H_3Me(NH_2)CN$ [94°]. Does not form an imido-ether when treated with alcoholic HCl (Pinner, *B.* 23, 2919).

A nitro-toluic acid [218°] was obtained by Ahrens together with the acids [219°] and [190°] by the action of HNO_3 on crude xylene.

Di-nitro-o-toluic acid $C_6H_2Me(NO_2)_2CO_2H$ [2:5:3:1]. [206°]. Formed by nitrating o-toluic acid (Jacobsen a. Wierss, *B.* 16, 1957; Racine, *A.* 239, 77). Needles. Yields di-nitro-phthalic acid [226°] on oxidation.—BaA'_2 2aq: v. e. sol. water.

Methyl ether MeA'. [74°]. Needles.

Di-nitro-*p*-toluic acid $C_6H_2Me(NO_2)_2CO_2H$ [4:3:5:1]. [158°]. Formed by nitrating *p*-toluic acid (Brückner, *B.* 8, 1678). Plates (from hot water).—KA' 2aq.—CaA'_2 2aq.—BaA'_2 2aq.—AgA'.

Di-nitro-*p*-toluic acid $C_6H_2Me(NO_2)_2CO_2H$ [4:2:5:1]. [188°]. Formed, together with the isomeride [249°], by nitrating (2, 4, 1)-nitro-toluic acid (Rozansky, *B.* 22, 2676). Radiating needles. Yields (1, 4, 3)-di-nitro-toluene on heating with dilute HCl at 250°.—NaA' 3aq.—BaA'_2 2½aq.—CaA'_2 2aq.

Di-nitro-*p*-toluic acid $C_6H_2Me(NO_2)_2CO_2H$ [4:2:3:1]. [249°]. Formed as above (R.). Trimetric prisms.—CaA'_2 aq.—BaA'_2 4aq: long needles.

NITRO-*m*-TOLUIC ALDEHYDE $C_8H_7NO_3$ *i.e.* $C_6H_3Me(NO_2)CHO$. An oil, formed as well as di-nitro-*m*-toluic aldehyde [112°], by nitrating *m*-toluic aldehyde (Bornemann, *B.* 17, 1473).

NITRO-o-TOLUIDINE $C_6H_3Me(NH_2)(NO_2)$ [1:2:3]. [97°]. Obtained from acetyl-*o*-toluidine by nitration and saponification (Lellmann a. Würthner, *A.* 228, 240), and also by heating its sulphonic acid with dilute H_2SO_4 at 180° (Nietzki a. Pollini, *B.* 23, 138). Prisms (from dilute alcohol).

Acetyl derivative. [158°]. Plates.

Nitro-o-toluidine $C_6H_3Me(NH_2)(NO_2)$ [1:2:4]. [107°]. Obtained by nitrating o-toluidine (1 pt.) dissolved in H_2SO_4 (10 pts.) (Nölting a. Collin, *B.* 17, 268) and by reduction of (4, 2, 1)-di-nitro-toluene [70·5°] (Graeff, *A.* 229, 343; Limpricht, *B.* 18, 1400; Anschütz, *B.* 19, 2161). Orange monoclinic prisms. Sweet taste.—$B'_2H_2SO_4$: plates, decomposed by water.

Acetyl derivative [151°]. Needles.

Nitro-o-toluidine $C_6H_3Me(NH_2)(NO_2)$ [1:2:5]. [128°]. Obtained from its acetyl derivative which is got by nitrating acetyl o-toluidine (Beilstein a. Kuhlberg, *A.* 158, 345). Small lemon-yellow needles (from water).

Acetyl derivative [197°]. Needles.

Nitro-o-toluidine $C_6H_3Me(NH_2)(NO_2)$ [1:2:6]. [92°]. Formed by reduction of (6, 2, 1)-di-nitro-toluene (Cunerth, *A.* 172, 223; Ullmann, *B.* 17, 1957). Formed also, together with the (1, 2, 4)-isomeride, by nitrating o-toluidine in presence of a large excess of H_2SO_4 (Green a. Lawson, *priv. com.*). Bright yellow slender needles.—B'HCl.

Acetyl derivative [158°]. Needles.

Benzoyl derivative [167°].

Nitro-*m*-toluidine $C_6H_3Me(NH_2)(NO_2)$ [1:3:6]. [134°]. Formed from its acetyl derivative, which is got by nitrating acetyl-*m*-toluidine (Beilstein a. Kuhlberg, *A.* 158, 348). Obtained also by heating the ethyl ether [54°] of nitro-cresol [129°] with NH_3Aq at 150° (Staedel, *A.* 259, 214). Needles, v. sol. alcohol. Yields tolylene-*p*-diamine [64°] on reduction (Fileti a. Crosa, *G.* 18, 298).

Acetyl derivative [102°]. Cubes.

Nitro-*m*-toluidine $C_6H_3Me(NH_2)(NO_2)$[1:3:4]. [109°]. Formed by heating the ethyl ether [51°] of nitro-cresol [56°] with NH_3Aq for 8 hours at 150° (Staedel, *A.* 259, 225). Golden plates, m. sol. alcohol.

s-Nitro-*m*-toluidine $C_6H_3Me(NH_2)(NO_2)$[1:3:5]. [98°]. Formed from *s*-di-nitro-toluene (Becker, *B.* 15, 1138; Nevile a. Winther, *C. J.* 41, 416; Staedel, *A.* 217, 199). Needles.—B'HCl. [56°]. Prisms.

Benzoyl derivative. [177°].

Nitro-*m*-toluidine $C_6H_3Me(NH_2)(NO_2)$ [1:3:2]. [53°]. Formed by reducing (2, 3, 1)-di-nitro-toluene (Limpricht, *B.* 18, 1401).—B'HCl.—$B'_2H_2SO_4$: tables, v. sol. hot water.

Acetyl derivative [136°]. Needles.

Nitro-*p*-toluidine $C_6H_3Me(NH_2)(NO_2)$ [1:4:3].

[116°]. Formed from acetyl-*p*-toluidine by nitration and hydrolysis (Beilstein a. Kuhlberg, *A.* 155, 23; Lorenz, *A.* 172, 177; Hübner, *A.* 208, 313; Cosack, *B.* 13, 1088; Ehrlich, *B.* 15, 2009; Gattermann, *B.* 18, 1483; Lellmann, *A.* 221, 7; Nölting, *B.* 17, 263). Formed also by heating nitro-*p*-cresol with NH_3Aq at 180° (Barr, *B.* 21, 1543). Red monoclinic prisms, $a:b:c = 1{\cdot}358:1:1{\cdot}755$; $\beta = 54°\ 51'$ (Panebianco, *G.* 9, 358).—B'HCl.—B'HNO_3: crystals, decomposed by water.

Acetyl derivative [95°]. Needles. Reduced by means of ammonium sulphide at 0° to $\{C_6H_3Me(NHAc)\}_2N_2O$ [196°] and the compound $C_6H_3Me{<}^{N}_{NH.CMe}{>}O$ [234°], whence B'HCl, $B'_2H_2PtCl_6$, and B'HNO_3 (Bankievitch, *B.* 22, 1396).

Trichloroacetyl derivative [55°].

Valeryl derivative [88°]. Yields on reduction $C_6H_3Me{<}^{N}_{NH}{>}C.C_4H_9$ [145°].

Benzoyl derivative [143°]. Needles.

Nitro-*p*-toluidine $C_6H_3Me(NH_2)(NO_2)$ [1:4:2]. [77·5°]. Formed by reduction of (4, 2, 1)-di-nitro-toluene (B. a. K.) and, together with a small quantity of the preceding isomeride, by the action of nitric acid on a solution of *p*-toluidine in H_2SO_4 (Hubner, *B.* 10, 1716; Nölting a. Collin, *B.* 17, 263; Foth, *A.* 230, 299). Monoclinic needles.—B'HCl. [220°].—B'HNO_3.—$B'_2H_2SO_4$ 2aq: stellate needles.—B'_4AgNO_3. [132°]. Greenish-yellow crystals (Mixter, *Am.* 1, 241).

Acetyl derivative. [144·5°]. Needles (Wallach, *A.* 234, 353).

Benzoyl derivative [172°]. Pale-yellow prisms (Bell, *C. N.* 30, 202).

Di-nitro-o-toluidine $C_6H_2Me(NH_2)(NO_2)_2$ [1:2:3:5]. [208°]. Formed from di-nitro-o-cresol and its ethers by the action of NH_3 (Staedel, *B.* 14, 900; *A.* 217, 185, 203; Van Romburgh, *R. T. C.* 3, 398; Barr, *B.* 21, 1543). Yellow prisms (from xylene).

Di-nitro-*m*-toluidine $C_6H_2Me(NH_2)(NO_2)_2$ [1:3:4:6]. [193°]. Formed from the ethyl ether of di-nitro-*m*-cresol and NH_3Aq at 100° (Staedel, *A.* 259, 220), and from $C_6H_2MeBr(NO_2)_2$ and NH_3 (Jackson, *B.* 22, 1232). Formed also by reducing (γ)-tri-nitro-toluene (Hepp, *A.* 215, 368). Yellow crystals, yielding di-nitro-toluene [71°] on elimination of NH_2.

Di-nitro-*p*-toluidine $C_6H_2Me(NH_2)(NO_2)_2$ [1:4:3:5]. [168°]. S. (CS_2) ·32 at 18°. Formed by nitration of acetyl or benzoyl *p*-toluidine and hydrolysis of the product (Beilstein, *B.* 13, 242; Hubner, *A.* 222, 73). Formed also by the action of ammonia on the ethers of di-nitro-*p*-cresol (Staedel, *A.* 217, 183). Needles, sl. sol. alcohol. Yields chrysanisic acid on oxidation.

Acetyl derivative [195°]. Needles. Yields on reduction an azoxy-compound [236°], an azo-compound [244°], and $C_9H_9N_3O_3$ [256°]. The compounds $C_6H_2Me(NO_2){<}^{N}_{NH}{>}CMe$ [246°] and $C_6H_2Me(NH_2){<}^{NH.CMe}_{N}{>}O$ [266°] may also be got by reduction (Bankievitch, *B.* 21, 2404).

Trichloroacetyl derivative [142°]. Prisms or needles (Friederici, *B.* 11, 1975).

Benzoyl derivative [186°]. Needles.

An isomeric body [203°] is got by nitrating benzoyl-(2,1,4)-nitro-toluidine (Cunerth, *A.* 172, 229).

Di-nitro-*p*-toluidine $C_6H_2Me(NH_2)(NO_2)_2$ [1:4:2:6]. [168°]. Formed from tri-nitro-toluene [82°] and ammonium sulphide (Tiemann, *B.* 3, 218; Beilstein, *B.* 13, 242; Staedel, *A.* 225, 384). Needles, v. sol. alcohol.

Di-nitro-*p*-toluidine $C_6H_2Me(NH_2)(NO_2)_2$. [94°]. Formed by heating (β)-tri-nitro-toluene with alcoholic NH_3 at 100° (Hepp). Golden needles (from HOAc).

Tri-nitro-*m*-toluidine $C_6HMe(NH_2)(NO_2)_3$ [1:3:2:4:6]. [136°]. Formed by the action of NH_3 on the ethyl ether of tri-nitro-*m*-cresol (Nölting a. Salis, *B.* 15, 1864; *A. Ch.* [6] 4, 128; Staedel, *A.* 259, 222). Small cubes, sol. alkalis, forming a red solution.

NITRO-*p*-TOLUIDINE SULPHONIC ACID $C_6H_2Me(NH_2)(NO_2)(SO_3H)$ [1:4:2:5]. S. ·1603 at 15°. Formed by sulphonating nitro-*p*-toluidine (Limpricht, *B.* 18, 2183; Foth, *A.* 230, 298).—KA'aq.—BaA'_2 4aq.—PbA'_2 $3\frac{1}{2}$aq?

DI-NITRO-TOLYL-ACETIC ACID $C_6H_2Me(NO_2)_2.CH_2.CO_2H$. [173°]. Formed by nitration (Senkowsky, *M.* 9, 856). Yields the *ethers* MeA' [41°] and EtA' [68°] crystallising in needles.

NITRO-*p*-TOLYL-AMIDO-ACETIC ACID [1:3:4] $C_6H_3Me(NO_2).NH.CH_2.CO_2H$. [190°]. Formed from nitro-*p*-toluidine and bromo-acetic acid (Plöchl, *B.* 19, 9; Leuckhart, *B.* 20, 24). Prisms.—NH_4A'.—BaA'_2 $2\frac{1}{2}$aq.—PbA'_2: purple-red needles.

Ethyl ether EtA'. [65°]. Needles.

NITRO-o-TOLYLAMIDO-BENZOIC ACID [3:4:1] $C_6H_3(NO_2)(NHC_7H_7).CO_2H$. [211°]. Formed by heating o-toluidine with bromo-nitro-benzoic acid (Heidensleben, *B.* 23, 3451). Brown needles.—NaA'*x*aq: red needles.

Ethyl ether EtA'. [106°]. Leaflets.

***m*-Nitro-*p*-tolyl-amido-benzoic acid** $C_6H_4Me.NH.C_6H_3(NO_2).CO_2H$. [257°]. Formed from *p*-toluidine and bromo-nitro-benzoic acid (Schöpff, *B.* 22, 3288; H.).—NaA': dark-red needles.

Ethyl ether EtA'. [115°]. Leaflets.

NITRO-DI-*p*-TOLYL-AMINE $NH(C_7H_7)(C_7H_6NO_2)$. [85°]. The *benzoyl derivative* [167°] is formed, together with that of di-nitro-di-tolyl-amine [191°], by nitrating benzoyl-di-*p*-tolyl-amine (Lellmann, *B.* 15, 831).

Hexa-nitro-di-*p*-tolyl-amine $NH(C_7HMe(NO_2)_3)_2$. [258°]. Formed from di-tolyl-nitrosamine and fuming HNO_3 (Lehne, *B.* 13, 1545). Trimetric crystals.

NITRO-TOLYL-ISOBUTYRIC ACID [1:3:6] $C_6H_3Me(NO_2).CH_2.CHMe.CO_2H$. [139°]. Formed from iodo-isobutyl-toluene and dilute HNO_3 (S.G. 1·12) at 200° (Effront, *B.* 17, 2326).—AgA': colourless plates.

NITRO-TOLYLENE-DIAMINE $C_7H_9N_3O_2$ *i.e.* $C_6H_2Me(NO_2)(NH_2)_2$ [1:*x*:2:6]. [154°]. Obtained from its *acetyl derivative* [253°], which is got by nitrating di-acetyl-tolylene-diamine (Tiemann, *B.* 3, 9; Ladenburg, *B.* 8, 1211). Needles, with violet reflex. Yields a *di-benzoyl derivative* [245°] (Ruhemann, *B.* 14, 2656).

Nitro-tolylene-diamine. *Benzoyl derivative* $C_6H_2Me(NO_2)(NH_2)(NHBz)$ [1:2:5:4]. [139°].

Formed by reducing benzoyl-di-nitro-toluidine (Hübner, *A.* 208, 317). Red needles (from water).

Nitro-tolylene-diamine $C_6H_2Me(NO_2)(NH_2)_2$ [1:6:4:2] ? [132°]. Formed by reducing (6,4,2,1)-tri-nitro-toluene (Tiemann, *B.* 3, 218). Red prisms (from water).

Tri-nitro-tolylene-diamine $C_6Me(NO_2)_3(NH_2)_2$ [1:2:4:6:3:5]. [222°]. Formed from $C_6Me(NO_2)_3Br_2$ and alcoholic NH_3 (Palmer, *B.* 21, 3501). Small yellow prisms.

NITRO-TOLYLENE-TETRA-METHYL-DI-AMINE $C_6H_2Me(NO_2)(NMe_2)_2$. [63°]. Formed by nitration (Niementowski, *B.* 20, 1888). Prisms.

DI-NITRO-DI-TOLYL-ETHYLENE-DIAMINE $C_2H_4(NH.C_6H_3Me.NO_2)_2$. [195°]. Formed from (3,1,4)-nitro-toluidine and ethylene bromide. (Gattermann a. Hager, *B.* 17, 779). Red plates.

NITRO-TOLYL-HYDRAZINE SULPHONIC ACID $C_6H_2Me(NO_2)(N_2H_3)(SO_3H)$ [1:2:4:5]. Formed from nitro-*p*-diazo-toluene sulphonic acid and a cooled solution of $SnCl_2$ (Limpricht, *B.* 18, 2194). Tables.—BaA'_2 4aq: yellow prisms.

NITRO-TOLYL-METHYLENE-PHTHALIDE

$$C_6H_4\begin{cases} C{=}C(NO_2).C_7H_7 \\ CO.O \end{cases}$$ [144°]. Formed from tolyl-methylene-phthalide by the action of nitrous acid, the resulting $C_6H_4\begin{cases} C(NO_2).CH(NO_2)C_7H_7 \\ CO.O \end{cases}$ [133°] being boiled with dilute alcohol (Heilmann, *B.* 23, 3163). Needles.

NITRO-TOLYL-METHYLENE-PHTHALIMIDINE $C_6H_4\begin{cases} C{=}C(NO_2).C_7H_7 \\ CO.NH \end{cases}$. [159°]. Formed from tolyl-methylene-phthalimidine and nitrous acid (Heilmann, *B.* 23, 3161). Needles (from alcohol).

NITRO-*m*-TOLYL-PROPIONIC ACID $C_6H_3Me(NO_2)C_2H_4CO_2H$. [130°–136°]. Formed from (2,5,1)-iodo-isobutyl-toluene and HNO_3 (S.G. 1·25) at 200° Effront, *B.* 17, 2327). Needles (from water).

DI-NITRO-DI-TOLYL-PROPIONIC ACID $(C_6H_3MeNO_2)_2CMe.CO_2H$. [129°]. Formed, together with the tetra-nitro- acid [225°] by nitrating di-tolyl-propionic acid (Haiss, *B.* 15, 1476). Yellowish crystals.

DI-NITRO-DI-o-TOLYL-SULPHAZIDE $C_{14}H_{14}N_4O_6S$ *i.e.* [2:4:1] $C_6H_3Me(NO_2).NH.NH.SO_2.C_6H_3(NO_2)Me$ [1:4:2] ? [142°]. Obtained by the action of alcoholic SO_2 upon nitro-o-diazo-toluene (Limpricht, *B.* 20, 1241). Small yellow prisms.

NITRO-TOLYL-THIOCARBAMIC ETHER [1:2:4] $C_6H_3Me(NO_2).NH.CS.OEt$. [96°]. Formed by boiling with alcohol nitro-tolyl-thiocarbimide, which is produced by the action of Ac_2O on phenyl-nitro-tolyl-thio-urea (Steudemann, *B.* 16, 2337). Needles, v. sol. alcohol.

NITRO-TOLYL-THIO-UREAS. The following compounds have been prepared by Steudemann (*B.* 16, 2337) from $C_6H_3Me(NO_2)(NH_2)$ [1:2:4]:

$NH_2.CS.NH.C_6H_3Me(NO_2)$. [176°].

[4:1] $C_6H_4Me.NH.CS.NH.C_6H_3Me(NO_2)$. [169°].

$CS(NH.C_6H_3Me(NO_2))_2$. [207°].

DI-NITRO-DI-*p*-TOLYL-UREA $CO(NH.C_7H_6.NO_2)_2$. [c. 233°]. Formed from di-*p*-tolyl-guanidine, alcohol, and HNO_3 (S.G. 1·4) (A. G. Perkin, *C. J.* 37, 698). Needles (from xylene).

NITRO-URACIL *v.* NITRO-DI-OXY-PYRIMIDINE.

NITRO-URAMIDO-BENZOIC ACIDS. The three following acids are obtained by boiling the three di-nitro-uramido-benzoic acids with aqueous NH_3 (Griess, *B.* 5, 193):—

$C_6H_3(NO_2)(NH.CO.NH_2).CO_2H$ [6:3:1]. Crystals.

$C_6H_3(NO_2)(NH.CO.NH_2)CO_2H$ [4:3:1]. Needles.

$C_6H_3(NO_2)(NH.CO.NH_2)CO_2H$ [2:3:1]. Plates.

The isomeric $C_6H_3(NO_2)(NH.CO.NH_2)CO_2H$[5:3:1] is formed, together with nitro-di-uramido-benzoic acid, by the action of potassium cyanate on nitro-amido-benzoic acid (Griess, *B.* 17, 2184). It yields the salt BaA'_2 5aq.

Nitro-diuramido-benzoic acid $(NH_2.CO)_2N.C_6H_3(NO_2)CO_2H$ forms crystals (containing 2aq), and yields the salt BaA'_2 $7\frac{1}{2}$aq. Three crystalline di-nitro-*m*-uramido-benzoic acids are got by nitrating *m*-uramido-benzoic acid. A di-nitro-*p*-uramido-benzoic acid is formed by nitrating *p*-uramido-benzoic acid.

NITROUS ACID *v.* NITROGEN, p. 567.

NITROUS ETHER *v.* ETHYL NITRITE.

NITRO-UVITIC ACID $C_6H_2Me(NO_2)(CO_2H)_2$ [1:*x*:3:5]. [227°]. Formed, together with an isomeride $C_9H_7NO_6$ $\frac{1}{2}$aq [250°] by nitrating uvitic acid (Böttinger, *B.* 9, 804; *A.* 189, 171). Prisms (containing 2aq).—K_2A'' aq.—BaA''aq.—CaA'' 3aq: needles, m. sol. hot water.

NITRO-VALERIC ACID $C_4H_8(NO_2).CO_2H$. Formed by the action of nitric acid on isovaleric acid and on di-isoamyl ketone (Dessaignes, *A.* 79, 374; Bredt, *B.* 15, 2319; Brazier a. Gossleth, *A.* 75, 262; Schmidt, *B.* 5, 602). Monoclinic tables.—AgA': prisms (from hot water).

DI-NITRO-VINYL-FURFURANE $C_4H_2(NO_2)O.CH:CH.NO_2$. [144°]. Formed by nitrating vinyl-furfurane (Priebs, *B.* 18, 1362). Yellow needles. Yields a dibromide [111°].

NITRO-VINYL-PHENOL. *Methyl derivative* $C_6H_3(NO_2)(CH:CH.NO_2)OMe$ [3:1:4]. [163°]. Formed from the methyl derivative of *p*-coumaric acid and HNO_3 (Einhorn a. Grabfield, *A.* 243, 369). Yellow needles (from alcohol).

o-NITRO-o-XYLENE $C_6H_3Me_2(NO_2)$ [1:2:4]. Mol. w. 151. [29°]. (258°). S.G. $\frac{30}{30}$ 1·139. Formed by nitration of o-xylene (Jacobsen, *B.* 17, 160). Long yellow prisms.

c-**Nitro-o-xylene** $C_6H_3Me_2(NO_2)$ [1:2:3]. (250° i.V. at 739 mm.). S.G. $\frac{15}{15}$ 1·147. Formed, together with the preceding isomeride, by the action of H_2SO_4 and HNO_3 on o-xylene (Nölting a. Forel, *B.* 18, 2669). Liquid.

c-**Nitro-*m*-xylene** $C_6H_3Me_2(NO_2)$ [1:3:2]. (225°) at 745 mm. S.G. $\frac{15}{}$ 1·112. Formed from nitro-xylidine [78°] by eliminating NH_2 (Grevingk, *B.* 17, 2430), and, together with the (1,3,4)-isomeride, by nitration of *m*-xylene with HNO_3 and H_2SO_4 at 0° (N. a. F.). Liquid.

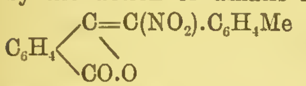
i-**Nitro-*m*-xylene** $C_6H_3Me_2(NO_2)$ [1:3:4]. (244° cor.). S.V. 164·5. Formed by nitrating *m*-xylene (Harmsen, *B.* 13, 1558) or its dihydride (Wallach, *A.* 258, 330), and by eliminating NH_2 from nitro-xylidine [123°] (G.). Liquid.

s-**Nitro-*m*-xylene** $C_6H_3Me_2(NO_2)$ [1:3:5]. [75°]. (263° i.V.) at 739 mm. Formed by eliminating NH_2 from nitro-xylidine [70°] (Wroblewsky, *A.* 207, 94; *Bl.* [2] 34, 332; Thöl,

B. 18, 360; Nölting a. Forel, *B.* 18, 2678). Needles, volatile with steam.

Nitro-*p*-xylene $C_6H_3Me_2(NO_2)$ [1:4:2]. (239° i.V.) at 739 mm. S.G. $\frac{15}{}$ 1·132. Formed by nitration of *p*-xylene (Jannasch, *A.* 176, 55; N. a. F.). Liquid.

ω-Nitro-*m*-xylene $C_6H_4Me(CH_2.NO_2)$. Formed by the action of alkalis followed by HCl_2 on



(Heilmann, *B.* 23, 3164). Oil, with irritating odour.

Di-nitro-*m*-xylene $C_6H_2Me_2(NO_2)_2$ [1:3:4:2]. Mol. w. 196. [82°]. Formed, together with the isomeride [93°], by nitrating *m*-xylene with HNO_3 and H_2SO_4 at 5° (Grevingk, *B.* 17, 2422). Plates, v. sol. alcohol.

Di-nitro-*m*-xylene $C_6H_2Me_2(NO_2)_2$ [1:3:4:6]. [93°]. Formed by nitrating *m*-xylene or its di-hydride (Luhmann, *A.* 144, 274; Fittig, *A.* 148, 5; Wallach, *A.* 258, 332). Crystals (from alcohol).

Di-nitro-*p*-xylene $C_6H_2Me_2(NO_2)_2$ [1:4:2:3]. [93°]. Formed, together with the isomeride [124°], by nitrating *p*-xylene (Rammer, *Bl.* [2] 9, 434; Fittig, *A.* 136, 307; 147, 17; Jannasch, *A.* 171, 79; Nölting, *B.* 19, 144; Lellmann, *A.* 228, 252). Monoclinic crystals. Yields xylylene-diamine [75°].

Di-nitro-*p*-xylene $C_6H_2Me_2(NO_2)_2$ [1:4:2:6]. [124°]. Needles.

Di-nitro-*p*-xylene $C_6H_2Me_2(NO_2)_2$ [1:4:2:5]. Formed in small quantity by nitrating *p*-xylene (L.). Long yellow needles (from alcohol).

Tri-nitro-*m*-xylene $C_6HMe_2(NO_2)_3$ [1:3:2:4:6]. Mol. w. 241. [c. 182°]. Formed by nitration of *m*-xylene or its dihydride (Luhmann; Grevingk; Tilden, *C. J.* 45, 416; Wallach, *A.* 258, 333). Crystals, insol. hot alcohol.

Tri-nitro-*p*-xylene $C_6HMe_2(NO_2)_3$ [1:4:2:3:5]. [140°]. Formed by nitration of *p*-xylene (Fittig; Nölting, *B.* 19, 145). Crystals (from benzene).

NITRO-*m*-XYLENE PHOSPHONIC ACID $C_6H_2Me_2(NO_2)PO(OH)_2$. Two acids of this formula, [100°] and [182°], are formed by nitrating *m*-xylene (α)-phosphonic acid (Weller, *B.* 20, 1722; 21, 1492). From *m*-xylene (β)-phosphonic acid an isomeric acid [107°] is obtained, and another isomeride [224°] may be obtained from *p*-xylene phosphonic acid.

NITRO-*m*-XYLENE SULPHONIC ACID $C_6H_2Me_2(NO_2)(SO_3H)$ [1:3:6:4]. [132°]. Formed by sulphonating nitro-*m*-xylene and by nitrating *m*-xylene (α)-sulphonic acid (Harmsen, *B.* 13, 1558; Limpricht, *B.* 18, 2191; Claus a. Schmidt, *B.* 19, 1418). Crystals. NaA′aq.—NaA′ 2aq.—KA′.—NH_4A'.—BaA'_2 3½aq.—CaA'_2 6aq. S. 6·35 at 18°.—MgA'_2 9aq.—CuA'_2 6aq.—PbA'_2 4aq.—AgA′ aq.

Amide [179°] (L.); [187°] (C. a. S.).

Chloride [98°] (L.).

Nitro-*m*-xylene sulphonic acid $C_6H_2Me_2(NO_2)(SO_3H)$ [1:3:5:4]. [100°]. Formed, with the preceding and succeeding acid, by nitrating (1,3,4)-xylene sulphonic acid (C. a. S.). Plates.—KA′.—NaA′aq.—BaA'_2 1½aq.—CaA'_2 6aq.—PbA'_2 aq.—CuA'_2 6aq.—AgA′ aq: needles, v. sol. water.

Amide [108°]. Needles.

Chloride [97°].

Nitro-*m*-xylene sulphonic acid $C_6H_2Me_2(NO_2)SO_3H$ [1:3:2:4]. [144°]. Formed as above (C. a. S.). Plates (containing aq).—KA′ ½aq.—NaA′ aq.—BaA'_2.—CaA'_2.—PbA'_2.—CuA'_2 2aq.—AgA′ ½aq.

Chloride [96°]. Needles.

Amide [172°]. Needles.

Di-nitro-xylene sulphonic acid $C_6HMe_2(NO_2)_2SO_3H$ [1:3:6:5:4]. [70°]. Formed, as well as the following isomeride, by nitrating *m*-xylene sulphonic acid (Claus a. Schmidt, *B.* 19, 1425). Plates.—KA′.—NaA′ aq.—BaA'_2 ½aq.—BaA'_2 2½aq.—CaA'_2 5aq.—PbA'_2 4½aq.—CuA'_2 4aq: pale-green plates.

Chloride [118°]. Crystals.

Amide [158°]. Needles.

Di-nitro-xylene sulphonic acid $C_6HMe_2(NO_2)_2SO_3H$ [1:3:6:2:4]. Needles (containing 2aq) (Limpricht, *B.* 18, 2192; C. a. S.).—NaA′ aq.—KA′.—BaA'_2 3aq.—CaA'_2 3½aq.—CuA'_2 2½aq.—PbA'_2 3½aq: prisms.

Chloride [123°]. Prisms.

Amide [193°]. Prisms.

NITRO-*m*-XYLENOL $C_8H_9NO_3$ *i.e.* $C_6H_2Me_2(NO_2)(OH)$ [1:3:*x*:4]. [68·5°]. Formed by nitrating *m*-xylenol (Lako, *A.* 182, 32). Needles.—KA′ 3aq: dark-red plates.

Nitro-*m*-xylenol $C_6H_2Me_2(NO_2)(OH)$. [95°]. Formed by the action of nitrous acid on the nitro-xylidine obtained by partial reduction of di-nitro-*m*-xylene (Pfaff, *B.* 16, 616, 1136). Needles.—KA′ 2aq: red crystals.

Methyl ether MeA′. [57°]. Needles.

(α)-Nitro-*p*-xylenol $C_6H_2Me_2(NO_2)(OH)$ [1:4:6:3]. [115°] (O.); [122°] (G. a. S.). Formed by oxidising nitroso-*p*-xylenol (the oxim of phlorone) with alkaline K_3FeCy_6 (Oliveri, *G.* 12, 162; Goldschmidt a. Schmid, *B.* 18, 569). Needles, sol. hot water.

(β)-Nitro-*p*-xylenol $C_6H_2Me_2(NO_2)(OH)$. (236°). Formed by nitrating *p*-xylenol (O.). Oil.—BaA'_2: purple scales.

(γ)-Nitro-*p*-xylenol. [89°]. Formed by heating *p*-xylenol sulphonic acid with fuming HNO_3 (O.). Light-yellow scales.—KA′ aq.—BaA'_2 aq: light-yellow scales.

Nitro-*p*-xylenol $C_6H_2Me_2(NO_2)(OH)$ [1:4:3:5]. [91°]. Formed by the action of nitrous acid on the corresponding nitro-xylidine (Von Kostanecki, *B.* 19, 2320). Buff-coloured plates; perhaps identical with the preceding isomeride.

Nitro-*p*-xylenol. *Ethyl ether* $C_6H_2Me_2(NO_2)(OEt)$. [85°]. Formed from *p*-xylidine by nitration and treatment with nitrous acid (Nölting, Witt, a. Forel, *B.* 18, 2667).

Di-nitro-*o*-xylenol $C_6HMe_2(NO_2)_2(OH)$[1:2:3:5:4]. [128°]. Formed as a by-product by nitrating o-xylene (Nölting a. Pick, *B.* 21, 3158). Obtained also from (1, 2, 4)-xylidine. Needles, sl. sol. cold water.

Di-nitro-*o*-xylenol $C_6HMe_2(NO_2)_2(OH)$ [1:2:3:4:6]. [82°]. Obtained by nitrating and diazotising (1, 2, 3)-xylidine (N. a. P.). Orange-yellow needles, m. sol. water.

Di-nitro-*p*-xylenol [121°]. Formed from *p*-xylenol, H_2SO_4, and HNO_3 (Kostanecki, *B.* 19, 2321). Yellow plates (from water).

NITRO-*m*-XYLENOL SULPHONIC ACID $C_6HMe_2(NO_2)(OH)(SO_3H)$[1:3:*x*:6:4]. Formed from nitro-xylidine sulphonic acid by the diazo-reaction (Limpricht a. Sartig, *B.* 18, 2190; *A.*

230, 340).—BaA'_2 3aq.—PbA'_2 3aq. The *ethyl derivative* forms $C_6HMe_2(NO_2)(OEt)(SO_3K)$ aq, crystallising in plates.

NITRO-*m*-XYLIDINE $C_8H_{10}N_2O_2$ *i.e.* $C_6H_2Me_2(NO_2)(NH_2)$ [1:3:5:4]. [76°]. Formed from acetyl-*m*-xylidine by nitration and saponification (Wroblewsky, *A.* 207, 91; Nölting a. Forel, *B.* 18, 2677). Orange needles.

Acetyl derivative. [173°]. Needles.

Nitro-*m*-xylidine $C_6H_2Me_2(NO_2)(NH_2)$ [1:3:6:4]. [123°]. Formed by reduction of di-nitro-*m*-xylene (Fittig, *A.* 147, 18; Wallach, *A.* 258, 332) and by nitration of (1,3,4)-*m*-xylidine (1 pt.) dissolved in H_2SO_4 (10 pts.) (Nölting a. Collin, *B.* 17, 265). Orange needles.—$B'HCl$.—$B'_2H_2SO_4$.—$B'_2H_2C_2O_4$.

Acetyl derivative. [160°].

Diacetyl derivative. [116°].

Nitro-*s*-*m*-xylidine $C_6H_2Me_2(NO_2)(NH_2)$ [1:3:4:5]. [54°]. Formed by nitration of *s*-*m*-xylidine dissolved in 10 pts. of conc. H_2SO_4 (Nölting a. Forel, *B.* 18, 2679). Yellow needles. Volatile with steam.

Nitro-*m*-xylidine $C_6H_2(CH_3)_2(NO_2)(NH_2)$ [1:3:2:4] or [1:3:4:2]. [78°]. Formed by reduction of di-nitro-*m*-xylene [82°] with alcoholic ammonium sulphide (Grevingk, *B.* 17, 2425). Yellow needles, sol. hot water.

Acetyl derivative. [149°]. White needles.

Nitro-*p*-xylidine $C_6H_2Me_2(NO_2)(NH_2)$ [1:4:5:2]. [142°]. Formed by nitration of acetyl-*p*-xylidine and saponification, or by nitration of *p*-xylidine dissolved in conc. H_2SO_4 (Nölting, Witt, a. Forel, *B.* 18, 2666). Formed also by reducing di-nitro-*p*-xylene (Kostanecki, *B.* 19, 2318). Brownish-yellow crystals. On reduction it gives the *para*-diamine [147°].

Acetyl derivative. [166°]. Needles.

Nitro-*p*-xylidine $C_6H_2Me_2(NO_2)(NH_2)$ [1:4:3:5]. [96°]. Formed by reduction of di-nitro-*p*-xylene [123°] (Fittig, *A.* 147, 22; Kostanecki, *B.* 19, 2320). Needles (from alcohol).

Acetyl derivative. [180°]. Needles.

Di-nitro-*p*-xylidine $C_6HMe_2(NO_2)_2(NH_2)$ [1:4:3:5:2]. [203°]. Formed from tri-nitro-*p*-xylene and alcoholic NH_3 (Nölting, *B.* 19, 145). Needles (from HOAc).

Di-nitro-xylidine [192°]. Formed by reduction of tri-nitro-xylene (Bussenius a. Eisenstuck, *A.* 113, 165; Beilstein, *A.* 133, 45). Yellow needles.

NITRO-XYLIDINE SULPHONIC ACID $C_6HMe_2(NO_2)(NH_2)SO_3H$ [1:3:*x*:6:4]. S. ·0818 at 8°. Formed by nitrating xylidine sulphonic acid (Limpricht a. Sartig, *B.* 18, 2189; *A.* 230, 338). Needles. — KA' $1\frac{1}{2}$aq. — BaA'_2 $1\frac{1}{2}$aq. — PbA'_2 aq: yellow silky needles.

NITRO-XYLYLENE-DIAMINE $C_8H_{11}N_3O_2$ *i.e.* $C_6HMe_2(NO_2)(NH_2)_2$. [215°]. Formed by reducing tri-nitro-*m*-xylene (Bussenius a. Eisenstuck, *A.* 113, 159; Fittig, *A.* 148, 6; Wallach, *A.* 258, 333). Red prisms. With EtI at 105° it yields crystalline $C_6HMe_2(NO_2)(NEt_2)(NHEt)$.—$B''HCl$.—$B''H_2Cl_2$. — $B''H_2PtCl_6$ 3aq. — $B''H_2SO_4$ 2aq.—$B''(H_2SO_4)_2$ 2aq.—$B''_2H_2SO_4$.

NITRYL CHLORIDE *v.* *Nitrogen oxychlorides*, under NITROGEN, p. 570.

NOBLE METALS. The elements *Gold, Ruthenium, Rhodium, Palladium, Iridium, Osmium,* and *Platinum* are sometimes classed together as the *noble metals.* The application of the term *noble* to metals is a survival of the alchemical notion of a close connexion between physical and moral properties. Gold was regarded by the alchemists as the purest metal, as that which most nearly approached their ideal element. As gold did not change when heated in air, and did not dissolve in any single acid, these two properties came to be looked on as characteristic; and when these properties were found to belong also to certain other metals these other metals were placed in the same class as gold. Silver dissolves in nitric acid, but it does not change by heating in air; hence Ag was often classed with Au as a noble metal. The term *noble* is applied in this article to the seven metals named above, as a convenient form of expressing the fact that these metals have many properties in common. The seven metals are all found uncombined in nature; they are all very lustrous, heavy, generally ductile and malleable, hard (except Au); some are not oxidised by heating in air, others combine with O at high temperatures.

Au has been known from prehistoric times. Pt was discovered about 1750; and the other Pt metals from 1803 to 1845. The name platinum is said to be derived from *platina del Pinto* (*platina* = diminutive of *plata* = silver), a name by which the natural alloy of the metal was known in New Granada, from whence it was first obtained. The names palladium and rhodium were given by Wollaston, who separated these metals from Pt ore, in 1803, the first suggested by the planet Pallas discovered about that time, and the second from ῥόδον = a rose, in allusion to the colour of solutions of the salts of the metal. Tennant discovered two other metals in Pt ore, in 1803; he called one iridium, because of its many-coloured salts (ἶρις = the rainbow), and the other osmium, because of the peculiar smell of its volatile oxide (ὀσμή = a smell). In 1845, Claus separated a sixth metal from Pt ore from the Ural, and called it ruthenium, in allusion to Russia.

Ru, Rh, Pd; and Ir, Os, Pt, form the second and third sections or families of Group VIII. in the periodic classification of the elements; the first family of this group is composed of Fe, Ni, and Co. Au belongs to Group I.; it is a member of the family Cu, Ag, Au. As Cu follows immediately after Fe, Ni, Co in the *long period* beginning with K and ending with Br, and as Ag follows Ru, Rh, Pd, in the *long period* Rb to I, so Au is placed in immediate succession to Os, Ir, Pt in the *long period* which, when it is complete, will begin with an alkali metal resembling Cs and end with a halogen more or less like I. Looking at the position of Au in the periodic scheme of classification (*v.* Table, p. 204, vol. ii.) one may say that the relations of this element to Os, Ir, and Pt will be found very similar to the relations of Ag to Ru, Rh, and Pd, and also to the relations of Cu to Fe, Ni, and Co.

The table on page 629 presents some of the important properties of the metals Ru, Rh, and Pd.

These three metals form *oxides* MO and MO_2; Ru and Rh also form M_2O_3; Ru forms a volatile oxide RuO_4; Rh forms RhO_3; and Pd_2O is known. The oxides MO are basic, forming salts

	RUTHENIUM	RHODIUM	PALLADIUM
Atomic weights	101·4	102·7	106·3
	The only compound of these elements which has been gasified is RuO_4. The S.H. of each has been determined directly. Molecular weights unknown.		
Spec. gravities (approx.)	12·3	12·1	11·4
$\frac{\textit{Atomic weight}}{\textit{spec. gravity}}$	8·5	8·6	9·3
Melting points (approx.)	above 2000°	2000°	1500°–1600°
Spec. heats	·061	·058	·06
Occurrence and preparation	The metals Rh, Ru, and Pd, occur in small quantities in many Pt ores; they are usually separated in the form $2NH_4Cl.MCl_4$; on strongly heating these double chlorides, the metals remain.		
Physical properties	White, lustrous, hard, brittle, crystalline; less ductile and malleable than Pd; fuses in O-H flame.	Greyish-white, very hard, malleable, not very ductile; may be fused in O-H flame, and is thus obtained in crystals.	White, hard, lustrous; ductile and malleable; most fusible of the Pt metals. Crystallises in octahedral and also in hexagonal forms.
Chemical properties	Oxidised by heating powdered metal in air; also by heating with KOH or K_2CO_3, forming K_2RuO_4 which is sol. water. Combines with Cl at red heat; dissolves very slowly in *aqua regia*.	Oxidised at red heat, when in powder; combines with Cl at red heat; unacted on by any acid; but when alloyed with Pb, Cu, &c., dissolves in *aqua regia*. Fused with $KHSO_4$, forms a soluble Rh-K sulphate. Absorbs H rapidly. When in very fine powder, decomposes H_2CO_2 to H and CO_2, and C_2H_6O to H and C_2H_4O.	Oxidises superficially at moderate temp.; at higher temps. the oxide is reduced. Absorbs H rapidly, probably forming a definite compound. Dissolves in hot conc. HClAq or H_2SO_4; also sol. HNO_3 and *aqua regia*.

$MX(X = SO_4$ &c.). Ru_2O_3 and Rh_2O_3 are also basic; the corresponding salts are M_23X. A few salts corresponding with RuO_2 have been isolated, but none derivable from RhO_2 or PdO_2 has been prepared. RhO_3 has not yet been proved to be basic. RuO_3 is not known, but a few salts (*ruthenates*) have been isolated in which RuO_3 forms the negative radicle, *e.g.* K_2RuO_4. An acid $HRuO_4$ is known; the K salt ($KRuO_4$) is said to be isomorphous with $KClO_4$ and $KMnO_4$. RuO_4 is a solid melting at c. 26°; it is very volatile; easily reduced to lower oxides; explodes at c. 108° giving RuO_2 and O; with KOHAq it forms K_2RuO_4. The *chlorides* generally correspond with the oxides MO, M_2O_3, and MO_2; the chlorides form double chlorides with more positive chlorides; the salts $MCl_4.2XCl$ are best regarded as salts of the acids H_2MCl_6 (*e.g.* K_2PdCl_6 and $(NH_4)_2RuCl_6$). The *cyanides* MCy_2 form double salts; an acid H_4RuCy_6 is known. The *sulphides* generally correspond with the oxides MO, M_2O_3, and MO_2; PdS_2 forms thio- salts, Na_2PdS_3, &c.; Rh_2S_3 dissolves in alkali sulphides: the sulphides M_2S_3 and MS_2 are therefore more or less acidic. The three metals form many *ammoniacal compounds*, which are best regarded as salts of various radicles obtained by replacing H in two or more NH_4 molecules by Ru, Rh, or Pd.

In the table on page 630 are presented some of the more important properties of the metals Os, Ir, Pt, and Au.

Au differs considerably in its chemical properties from Os, Ir, and Pt. The oxides of Os, Ir, and Pt are MO and MO_2; M_2O_3, represented by Os_2O_3 and Ir_2O_3; OsO_4. Very few salts of Os have been prepared as yet; OsO and Os_2O_3 are probably basic. OsO_3 is not known, but osmates, *e.g.* K_2OsO_4, have been isolated. OsO_4 is solid, with low melting and boiling points; it is slowly soluble in water, seems to form very unstable salts with alkalis, but does not decompose carbonates. Os forms a peculiar acid $H_2N_2Os_2O_6$; perhaps $HO.OsO_2.N{:}N.OsO_2.OH$; it also forms ammoniacal bases, in which OsO seems to replace H_2 in N_2H_8, and OsO_2 to replace H_4 in N_4H_{16}. The acid H_4OsCy_6 is known. Very few salts of Ir are known; Ir_2O_3 is basic. The chloride $IrCl_4$, corresponding to IrO_2, is known; and also such salts as $IrO.SO_3$, in which an acid radicle seems to replace O in IrO_2. Some iridates have been obtained, *e.g.* $K_2O.2IrO_3$. The acid H_3IrCy_6, and salts of this acid, exist. Some ammoniacal bases are known, in which Ir seems to replace H_2 of N_2H_8. A few salts corresponding with PtO are known, but they have been but little studied; PtO_2 forms salts such as $Pt(SO_4)_2$. PtO_2 also combines with some positive oxides to form salts $xPtO_2.yRO$, *e.g.* $3PtO_2.Na_2O$. PtO_2 also combines with acidic and basic oxides to form complex salts, *e.g.* $PtO_2.10MoO_3(\text{or } 10WO_3).4Na_2O.xH_2O$. A very large number of salts of complex ammoniacal

	Osmium	Iridium	Platinum	Gold
Atomic weights	190·3	192·5	194·3	197
	The only compound of these elements which has been gasified is OsO_4. The S.H. of each has been determined directly. Molecular weights are unknown.			
Spec. gravities (approx.)	22·5	22·4	21·4	19·5
$\frac{\textit{Atomic weight}}{\textit{Spec. gravity}}$	8·5	8·6	9	10·1
Melting-points (approx.)	Infusible at full white heat.	1900°	1800°	1200°
Spec. heats	·0311	·0326	·0324	·0324
Occurrence and preparation	The three metals Os, Ir, and Pt, occur in small quantities, associated (? alloyed) with each other, and frequently with Ru, Rh, and Pd. They are usually separated as $2NH_4Cl.MCl_4$, and are obtained by strongly heating these compounds.			Occurs native, generally alloyed with Ag. Prepared by removing earthy impurities; or by crushing auriferous quartz, forming an amalgam of Au and Hg, and removing Hg by heat; sometimes by smelting, or by treatment with Cl &c.
Physical properties	White, with tinge of blue; very hard; crystalline; brittle; also a black, amorphous, powder. Os does not melt at the highest temp. of the O-H flame; it is the heaviest substance known.	White; lustrous; hard; crystalline; brittle, but fairly malleable at red heat; also a hard black powder. Melts in O-H flame.	Silver-white; very lustrous; fairly hard; very malleable and ductile; expands by heat less than any other metal. Melts in O-H flame.	Very lustrous, yellow metal; crystallises in octahedra; good conductor of heat and electricity; most malleable of all metals; very ductile. Also obtained as a lustreless, brown-yellow, powder.
Chemical properties	Oxidised readily, to OsO_4, by heating finely powdered metal in air; also oxidised by HNO_3, when in fine powder. Oxidised by fusion with KOH or KNO_3. Combines directly with Cl.	When finely divided, oxidises slowly when heated in air, and dissolves in *aqua regia*; in compact form is insol. in all acids. Oxidised by fusion with KOH and KNO_3. Combines directly with Cl.	Not oxidised by heating in air or O, but by fusion with KOH. Dissolves in *aqua regia*. Combines directly with Cl. Absorbs H rapidly, and gives it off again at red heat.	Not oxidised by heating in air. Dissolves in *aqua regia*. Combines directly with Cl, Br, and I. Compounds are easily decomposed, yielding Au.

bases, containing Pt, are known. Pt is rather remarkable for the number of compounds which it forms with H and acidic radicles; these compounds are acids, and corresponding with each is a series of salts; the acids in question are H_2PtCl_4, H_2PtCl_6, H_2PtI_6; $H_3Pt(NO_2)_4Cl_2$, $H_2Pt(NO_2)_4$; H_2PtCy_4, $H_2PtCy_4Cl_2$, $H_2Pt(SCN)_6$; $H_2Pt_4S_6$ (salts of $H_4Pt_3S_6$ exist).

Au forms three oxides, Au_2O, AuO, and Au_2O_3; Au_2O is slightly sol. cold water; a few salts corresponding with Au_2O_3 are known, *e.g.* $Au(NO_3)_3$; $AuSO_4$ corresponds with AuO. Au_2O_3 forms aurates, *e.g.* $KAuO_2$, by reacting with alkalis. The sulphides, Au_2S and AuS, form thio- salts with the alkali sulphides, *e.g.* NaAuS; but these thio- salts have been examined very slightly. The chlorides are AuCl and $AuCl_3$; the acids $HAuCl_4$, $HAuBr_4$, and $HAuCy_4$, and salts of the form M^IAuI_4, are known. The compounds of Au are easily decomposed with separation of Au.

The Pt metals fall into two families: (1) Ru, Rh, Pd, and (2) Os, Ir, Pt. The elements, as a group, possess the physical characters of metals very distinctly marked; but the existence of acidic oxides and sulphides points to the non-metallic nature of these elements. Au is physically more metallic, and chemically more non-metallic, than any of the other noble metals. For the relations of Au to Cu and Ag, and

the relations o this family to the members of Group VIII. (Fe, Ni, Co, Ru, Rh, Pd, Os, Ir, Pt), and also to the other members of Group I. (Li, Na, K, Rb, Cs), *v.* COPPER GROUP OF ELEMENTS, vol. ii. p. 250; *v.* also IRON GROUP OF ELEMENTS, this vol. p. 65. For details about the individual noble metals, *v.* GOLD, vol. ii. p. 647; IRIDIUM, this vol. p. 46; OSMIUM, PALLADIUM, in this vol.; PLATINUM, RHODIUM, and RUTHENIUM in vol. iv.

M. M. P. M.

NOMENCLATURE. The nomenclature of chemistry is based on the system introduced by Lavoisier, De Morveau, Berthollet, and De Fourcroy in 1787. The leading principles laid down by the French chemists were (1) that every substance is to be regarded as an element until it is proved to be otherwise; (2) that the name of a compound is to exhibit the elements, and as far as possible the relative proportions of the elements, of which it is composed. The names given to elements are not based on any uniform principle; some are known by the names given them for centuries; more recently discovered elements are named, sometimes from the names of compounds of them well known before the elements were discovered, sometimes from the localities where the material was found from which the element was prepared for the first time, sometimes from a characteristic property of the element, sometimes from fanciful considerations, and sometimes to express the pride of the discoverer in his own nationality. To all more recently discovered metals have been given names ending in *um.* Binary compounds are designated by names ending in *ide*, this termination being applied to the name of the more negative element; thus all binary compounds of O are called oxides. As Cl is more negative than S, it is better to call S_2Cl_2 sulphur chloride than chlorine sulphide. When two oxides, chlorides, &c., of an element exist, they are generally distinguished by throwing the name of the more positive element into adjectival form, and using the termination *ic* to indicate more of the negative element, and *ous* to denote less of the negative element, relatively to a fixed quantity of the more positive element; thus the compounds $FeCl_2$ and $FeCl_3$ are known as ferrous chloride and ferric chloride respectively. When more than two oxides, chlorides, &c., of an element are known, it is customary either to use prefixes *di-* (or *bi-*), *tri-* (or *ter-*), &c., or to indicate the relative proportions of the elements by such prefixes as *hypo-* and *per.* It is also customary to give names to certain oxides for the purpose of indicating their acidic character. Thus the five oxides of N have been named as follows at different times:

N_2O. Nitrous oxide; nitrogen monoxide (might also be called hyponitrous anhydride).

NO. Nitric oxide; nitrogen dioxide.

N_2O_3. Nitrogen trioxide; nitrogen sesquioxide; nitrous anhydride.

N_2O_4. Nitrogen dioxide; nitrogen tetroxide; nitroso-nitric anhydride; nitrogen peroxide.

N_2O_5. Nitrogen pentoxide; nitric anhydride; nitrogen peroxide.

The same name—nitrogen dioxide—has been given to two different compounds, NO and NO_2; and the name peroxide has been used for NO_2 and N_2O_5. This illustrates a difficulty. The prefixes *mono-*, *di-*, &c. are sometimes employed to designate the first, second, third, &c., members of a series of oxides, chlorides, &c. of the same element, without implying anything as to the number of O, Cl, &c. atoms in the molecules of the various compounds; but the same prefixes are employed sometimes to imply one, two, &c. atoms of O, Cl, &c. On both systems of naming N_2O is called monoxide; on the first system NO is called dioxide, but on the second system it must be called monoxide; hence the second system of naming gives the same name to two different compounds. To get over this difficulty N_2O may be called dinitrogen monoxide, and NO mononitrogen monoxide; but such names are cumbersome. The prefix *per-* is generally employed to designate the highest compound of a series, *i.e.* the one with relatively most negative element; but a higher compound may be discovered; in such a case the prefix, if used at all, must be moved from the older to the more recently discovered substance. Salts are named from the acids of which they are metallic derivatives. If there are two acids containing the same elements, to that with relatively more of the negative radicle is given a name ending in *-ic*, and its salts are called *-ates*; to the other acid is given a name ending in *-ous*, and its salts are called *-ites.* By the use of prefixes *per-*, *hypo-*, &c., four or five acids and their salts may be named, *e.g.*

HClO. Hypochlorous acid.
$HClO_2$. Chlorous acid.
$HClO_3$. Chloric acid.
$HClO_4$. Perchloric acid.

Compounds which probably contain the OH group are generally called hydroxides, and those containing the SH group are called hydrosulphides or sulphydrates. These names more or less imply a special view of the structure of the compounds; as the same view is not always held by all chemists, it seems preferable to call a commonly occurring compound, such as KOH, potash, rather than potassium hydroxide. The nomenclature of organic chemistry must be based on certain conceptions regarding the structure of carbon compounds. These compounds are so numerous, and many of them show such small differences in empirical composition, while not a few are identical in composition, that it would be impossible to frame a systematic nomenclature without the help of the conceptions of molecular structure which lie at the root of organic chemistry. In other words, names cannot be found for the vast variety of carbon compounds without considering the properties and functions of these compounds as well as their composition; but the only way we have of expressing, at present, the chemical properties of carbon compounds is in terms of the molecular and atomic theory. For complicated examples *v.* AZO- COMPOUNDS, vol. i. p. 369; for some simpler cases *v.* HYDROCARBONS, vol. ii. p. 715.

No attempt is made in this article to trace the historical development of chemical nomenclature, nor to discuss fully the present systems of naming used in the science. Chemical nomenclature is a subject the details of which must be

learned gradually by studying chemical substances and their reactions. The article NOMENCLATURE in the first edition of this Dictionary contains references to the more important older memoirs on the subject. In addition to these should be added a report on chemical nomenclature by a committee of the British Association (*B. A.* 1884. 39). Reference should also be made to the suggestions of the Council of the Chemical Society (*C. J.* 35, 277). M. M. P. M.

NONADECANE *v.* ENNDECANE.

NONANE *v.* ENNANE.

NONAPHTHENE C_9H_{18}. (136° cor.). S.G. $\frac{20}{20}$ ·763. H.C.v. 1,380,900. H.C.p. 1,383,400. Occurs in Russian petroleum (Markownikoff, *J. R.* 15, 331; Ossipoff, *J. R.* 20, 645). It is ψ-cumene hexahydride as it yields ψ-cumene sulphonic acid on treatment with H_2SO_4 (Konovaloff, *C. C.* 1887, 1133; *J. R.* 22, 4, 118). Br and $AlBr_3$ yield tri-bromo-ψ-cumene. Nitric acid (S.G. 1·4) yields $C_8H_{15}NO_2$ (219°), which on reduction yields $C_8H_{15}NH_2$ (172°–177°), S.G. $\frac{0}{}$ ·873, smelling like coniine. Chlorine yields $C_9H_{17}Cl$ (186°), whence $C_9H_{17}I$ (110° at 200 mm.), $C_9H_{17}OAc$ (209°), and $C_9H_{17}OH$ (191°), S.G. $\frac{20}{20}$ ·8972 may be successively derived. Nonaphthyl iodide is converted by Ag_2O into $(C_9H_{17})_2O$ (301°), S.G. $\frac{20}{20}$ ·866. Nonaphthylene C_9H_{16} (136°), S.G. $\frac{0}{}$ ·807 may be obtained from nonaphthyl chloride.

Isononaphthene C_9H_{18}. (151°). H.C.v. 1,381,700. H.C.p. 1,384,200. Occurs also in Russian petroleum.

NONIC ACID $C_{10}H_{16}O_3$. [187°]. Formed by the action of bromine and alcoholic potash on isopropyl-isovaleric acid (Wohlbrück, *B.* 20, 2336). Plates.

NONOÏC ACID *v.* ENNOÏC ACID.

NONYL. The radicle C_9H_{19}, called ENNYL in this Dictionary.

Di-nonyl is OCTODECANE.

NONYL ALCOHOL *v.* ENNYL ALCOHOL.

NONYLENE *v.* ENNYLENE.

NONYLENIC ACID *v.* ENNENOIC ACID.

NONYLIC ACID *v.* ENNOIC ACID.

NORMETHYLHEMIPIC ACID *v. Methyl derivative* of DI-OXY-PHTHALIC ACID.

NORMETHYLNITROHEMIPIC ACID *v. Methyl derivative* of NITRO-DI-OXY-PHTHALIC ACID.

NORNARCOTINE *v.* NARCOTINE.

NOROPIANIC ACID *v.* OPIANIC ACID.

NORWEGIUM Ng. (?) At. w. c. 219. This name was given by Dahll to a substance separated by him from *nickel-glance* from the Norwegian island of Osterö and ranked by him among the elements (*B.* 12, 1731; 13, 250). According to Prochazka (*A. C. J.* 2, 213) the element exists in some specimens of unrefined Pb (along with Bi, Cu, and Ni). The claim of Ng to rank as an element cannot be regarded as yet satisfactorily established. Ng is said to show great resemblances to Bi; to melt at c. 254°; to form a fusible oxide resembling Bi_2O_3. The hydroxide is soluble in KOHAq, also in a large excess of NH_4 or Na carbonate solution. If the oxide is Ng_2O_3, the at. w. is approximately 219; if the oxide is NgO, the at. w. is approximately 146. M. M. P. M.

NOTATION. The expression of the composition, and, as far as possible, the properties, of compounds by the use of symbols and formulæ. The subject is discussed sufficiently in the articles EQUATIONS, CHEMICAL (*q. v.* vol. ii. p. 433), FORMULÆ (*q. v.* vol. ii. p. 572), and ISOMERISM (*q. v.* this vol. p. 79). M. M. P. M.

NUCIN *v.* JUGLONE.

NUCITANNIN. Occurs in walnuts (Phipson, *C. N.* 20, 116). Decomposed by dilute acid into sugar and red amorphous rufic acid $C_{14}H_{12}O_7$, which yields the salts $CaC_{28}H_{24}O_{15}$ and $PbC_{14}H_{12}O_8$.

NUCLEIN *v.* PROTEÏDS, *Appendix C.*

NUCLEO-ALBUMIN *v.* PROTEÏDS, *Appendix C.*

NUCLEO-PROTEÏDS *v.* PROTEÏDS, *Appendix C.*

NUMBERS, LAW OF EVEN. Laurent (*A. Ch.* [3] 18, 266) said that the sum of the monovalent, trivalent, and pentavalent elements contained in any well-defined and stable compound is always an even number. This *law of even numbers* was long an article of belief among orthodox chemists. If by an *n*-valent element is meant one the atom of which combines directly with *n* other atoms to form a molecule, then there are several exceptions to the so-called law; *e.g.* the molecules $InCl_2$, $InCl_3$, and probably InCl exist as gases; so do the molecules $FeCl_2$ and $FeCl_3$, the molecules WCl_5 and WCl_6, &c. M. M. P. M.

NUPHARIN $C_{18}H_{24}N_2O_2$. An amorphous substance in the rhizome of *Nuphar luteum* (Grüning, *J.* 1882, 1156).

NUX VOMICA *v.* STRYCHNINE.

O

n-**OCTADECANE** $C_{18}H_{38}$. [28°]. (317°). S.G. $\frac{20}{4}$ ·775; $\frac{40}{4}$ ·768. Occurs in paraffin from brown coal. Formed by reduction of stearic acid with HI and P and by the action of Na on ennyl iodide (Krafft, *B.* 15, 1703; 16, 1723; 19, 2221; 21, 2261). Hexagonal tables.

OCTADECINENE $C_{18}H_{34}$. [30°]. (184° at 15 mm.). S.G. $\frac{30}{4}$ ·8016. Formed by heating $C_{18}H_{36}Br_2$ with alcoholic potash (Krafft, *B.* 17, 1374). Plates.

OCTADECOIC ACID $(C_8H_{17})_2CH.CO_2H$. [39°]. (above 300°). Prepared by heating di-octyl-malonic acid (Conrad a. Bischoff, *B.* 13, 597). White crystals.

OCTADECYL ALCOHOL $C_{18}H_{37}.OH$. [59°]. (210° at 15 mm.). S.G. $\frac{70}{4}$ ·8048; $\frac{99}{4}$ ·7849. Occurs in crude cetyl alcohol, and is prepared by reducing stearic aldehyde with zinc-dust and acetic acid (Krafft, *B.* 16, 1722; 17, 1627).

Acetyl derivative [c. 31°]. (223° at 15 mm.).

OCTADECYL-BENZENE $C_{18}H_{37}.C_6H_5$. [36°]. (249° at 15 mm.). Formed from octadecyl iodide, iodo-benzene, and sodium (Krafft, *B.* 19, 2984). Yields a solid sulphonic acid.

OCTADECYLENE $C_{18}H_{36}$. [18°]. (179° at 15 mm.). S.G. $\frac{18}{4}$ ·7910; $\frac{22}{4}$ ·7881. Formed by distilling octadecyl palmitate (Krafft, *B.* 16, 3024).

Octadecylene $C_{18}H_{36}$. *Anthemene.* [64°]. S.G. $\frac{15}{}$ ·942. V.D. 127 (H = 1). Obtained from *Anthemis nobilis* by extracting the blossoms with ligroïn (Naudin, *Bl.* [2] 41, 483). Minute needles.

OCTADECYLENE BROMIDE *v.* DI-BROMO-OCTADECANE.

OCTADECYL IODIDE $C_{18}H_{37}I$. [33·5°] (K.); [43°] (S.). From the alcohol, I, and P (Krafft, *B.* 19, 2984; Schweizer, *Ar. Ph.* [3] 22, 753).

OCTADECYL-PHENOL $C_{18}H_{37}.C_6H_4.OH$. [84°]. (277° at 15 mm.). Formed by fusing octadecyl-benzene sulphonic acid with potash (Krafft, *B.* 19, 2985). Plates (from alcohol).

***n*-OCTANE** C_8H_{18}. Mol. w. 114. (125°). S.G. $\frac{0}{4}$ ·7188. V.D. 4·03 (Lemoine, *Bl.* [2] 41, 163). C.E. (0°–10°) ·001186; (0°–100°) ·001331 (Thorpe, *C. J.* 37, 217). S.V. 186·3. Occurs in American petroleum (Pelouze a. Cahours, *A.* 127, 197; Schorlemmer, *C. J.* 15, 419). Formed by the action of zinc and HClAq on sec-octyl iodide (Schorlemmer, *C. J.* 27, 1029), by the action of sodium-amalgam on *n*-octyl iodide (Zincke, *A.* 152, 15), and by the action of sodium on *n*-butyl iodide (Schorlemmer, *A.* 161, 280). Obtained also by distilling whale oil under pressure (Engler, *B.* 22, 595). Oil.

Iso-octane Pr.CH_2.CH_2.Pr. *Di-isobutyl.* (108°). S.G. $\frac{0}{}$ ·709; $\frac{20}{}$ ·693 (W.); $\frac{0}{4}$ ·711 (Thorpe). C.E. (0°–10°) ·001205; (0°–100°) ·001401. μ_D = 1·3943 at 16° (W.). R_D = 64·47. S.V. 184·5 (Schiff, *A.* 220, 88). V.D. 3·94. Formed by electrolysis of potassium isovalerate (Kolbe, *A.* 69, 261; *C. S. Mem.*, 3, 378; *C. J.* 2, 157). Formed also by the action of sodium on isobutyl iodide and on a mixture of isoamyl and isopropyl iodides (Wurtz, *A.* 93, 112; 96, 364; Schorlemmer, *Pr.* 16, 37; *A.* 144, 188; W. C. Williams, *C. J.* 31, 541; 35, 125). Occurs also among the products of the distillation of whale oil under pressure (Engler, *B.* 22, 595). Oil.

Octane C_2Me_6. *Hexa-methyl-ethane.* [97°]. (106°). Formed from tert-butyl iodide and sodium (Lwow, *Bl.* [2] 35, 169).

Octane C_8H_{18} (119°). V.D. 3·97 (obs.). S.G. $\frac{11}{}$ ·712. Formed by reduction of coniïne, coniceïne, or conhydrine by prolonged heating with HI and P (Hofmann, *B.* 18, 12).

OCTANE DICARBOXYLIC ACID $C_{10}H_{18}O_4$. [184°–194°]. A product of the action of sodium on bromo-methyl-ethyl-acetic ether (Pagenstecher, *A.* 195, 121). Crystals (from water).

Octane dicarboxylic acid $CO_2H.CH_2.CHMe.[CH_2]_5.CO_2H$. [44°]. *Methyl-azelaïc acid.* Formed by heating the tetra-carboxylic acid (Perkin, jun., *C. J.* 51, 218). Crystals.—Ag_2A''. *Ethyl ether* Et_2A''. Oil.

Octane tetracarboxylic ether $(CO_2Et)_2CH.CHMe.(CH_2)_4.CH(CO_2Et)_2$. (275° at 60 mm.). A product of the action of di-bromo-methyl-pentamethylene on malonic ether (Perkin, *C. J.* 53, 217). Syrup.

Octane tetradeca-carboxylic ether $CO_2Et.CH_2.[C(CO_2Et)_2]_6.CH_2.CO_2Et$. Formed from chloro-butane heptacarboxylic ether and sodium butane heptacarboxylic ether (Bischoff, *B.* 21, 2116). Viscid oil.

OCTENE *v.* OCTYLENE.

OCTENOIC ACID $C_8H_{14}O_2$ *i.e.* Pr.CH_2.CH:CH.CH_2.CO_2H. (231°). Formed by distilling isobutyl-paraconic acid (Fittig, *B.* 21, 920; *A.* 255, 103). Oil.

Octenoic acids are also formed by oxidation of octenoic aldehyde (Fossek, *M.* 2, 622), and by reduction of suberene-carboxylic acid $C_8H_{12}O_2$ (Spiegel, *A.* 211, 119). They are volatile with steam.

OCTENOIC ALDEHYDE $C_8H_{14}O$. (150° at 18 mm.). Formed by heating isobutyric aldehyde with conc. NaOAcAq at 150° (Fossek, *M.* 2, 614). Liquid, volatile with steam. Forms a mirror with ammoniacal $AgNO_3$, and a crystalline compound with $NaHSO_3$. Yields acetic and isobutyric acids on oxidation.

Octenoic aldehyde PrCH:CEt.CHO. (173°). Formed from butyric aldehyde and aqueous NaOH or NaOAc (Raupenstrauch, *M.* 8, 108). Oil. Reacts with phenyl-hydrazine. Yields $C_8H_{16}O$ (161°) on reduction with iron and HOAc.

Octenoic aldehyde $C_8H_{14}O$. (230° i.V.). S.G. $\frac{0}{}$ ·958. Formed by passing dry HCl into isobutyric aldehyde (Oeconomides, *Bl.* [2] 36, 209). Oil, resinified by potash. Reduces ammoniacal $AgNO_3$ forming a mirror.

OCTENYL ALCOHOL $C_8H_{16}O$ *i.e.* CH_2:CH.CH_2.CEt_2OH. *Di-ethyl-allyl-carbinol.* (156°). S.G. $\frac{0}{0}$ ·889. C.E. (0°–33°) ·00104. Formed from di-ethyl ketone, allyl iodide, and zinc (Schirokoff a. Saytzeff, *A.* 196, 113). Oil. Yields di-ethyl-ketone and propionic acid on oxidation. With HOCl it forms a compound converted by caustic potash into tri-oxy-octane. $KMnO_4$ yields $CEt_2(OH).CH_2.CO_2H$. Dilute H_2SO_4 at 100° yields octinene (c. 123°) (Reformatsky, *J. pr.* [2] 30, 217).

Octenyl alcohol CMePr(C_3H_5)(OH). (160°). S.G. $\frac{0}{0}$ ·8486; $\frac{20}{0}$ ·8345. Formed from methyl propyl ketone, allyl iodide, and zinc (Semljanitzin, *J. pr.* [2] 23, 263; Reformatsky, *J. pr.* [2] 40, 412). Yields CMePr(OH).CH_2.CO_2H on oxidation.

OCTENYL CHLORIDE C_6H_{13}.CH:CHCl. (168°). S.G. $\frac{0}{}$ ·927. Formed from $C_8H_{16}Cl_2$ and alcoholic potash (Béhal, *A. Ch.* [6] 15, 278). Liquid, smelling like carrots.

OCTINENE C_8H_{14} *i.e.* CH_3.C⫶C.C_5H_{11}. *Methyl-amyl-acetylene.* (133°). S.G. $\frac{0}{}$ ·771. Formed by the action of alcoholic potash on octylene bromide (derived from octylene got by dehydrating octyl alcohol) (Rubien, *A.* 142, 299; Béhal, *Bl.* [2] 47, 33; 48, 704; 50, 359, 629; *A. Ch.* [6] 15, 274, 428). Mobile liquid. Does not react with ammoniacal Cu_2Cl_2. On dissolving in cold H_2SO_4 and pouring into ice-cold water it yields the ketone $C_8H_{16}O$ (171°), S.G. $\frac{0}{}$ ·835 which forms hexoic and acetic acids on oxidation.

Octinene C_8H_{14} *i.e.* CH⫶C.CH_2.C_5H_{11}. (125°–133°). Obtained by heating the preceding isomeride with sodium at 110° (Béhal). Liquid. Forms a yellow pp. with ammoniacal cuprous chloride.

Octinene C_8H_{14}. *Conylene.* (125°). V.D. 55·6 (H=1). Obtained by dry distillation of di-methyl-coniine methylo-hydroxide and by heating 'azoconhydrine' with P_2O_5 (Wertheim, *A.* 123, 170; Hofmann, *B.* 14, 710). Oil. Forms a di-bromide (*v.* DI-BROMO-OCTYLENE).

Octinene C_8H_{14}. *Diisocrotyl.* [5°]. (125°–130°). Formed from CMe_2:CHBr and sodium (Pribytek, *J. R.* 20, 506). Oil, rapidly absorbing oxygen.

Octinene CH_2:CMe.CH_2.CH_2.CMe:CH_2. (114°). Formed from CH_2:CMe.CH_2Cl and sodium (Przybytek, *B.* 20, 3240).

Octinene C_8H_{14}. (c. 123°). S.G. $\frac{0}{0}$ ·7734; $\frac{15·4}{}$ ·7588. R_∞ 62·12. Formed by heating octenyl alcohol CH_2:CH.CH_2.CEt_2OH with dilute H_2SO_4 at 100° (Reformatsky, *J. pr.* [2] 30, 217). Mobile liquid, absorbing oxygen from the air. Combines with bromine. Oxidised to acetic and propionic acids by chromic acid mixture. Yields $C_8H_{14}Br_4$.

Isomeride: Xylene tetrahydride.

OCTINOIC ACID *v.* DI-ALLYL-ACETIC ACID.

OCTINYL ALCOHOL $C_8H_{14}O$ *i.e.* (CH_2:CH.CH_2)$_2$CMe(OH). *Methyl-di-allyl-carbinol.* (158° cor.). S.G. $\frac{0}{0}$ ·864; $\frac{13}{0}$ ·852. H.C. 1,201,400 (Longuinine, *A. Ch.* [5] 23, 388). Formed from allyl iodide, acetic ether, and zinc (Saytzeff a. Sorokin, *B.* 9, 33, 277; *A.* 185, 169). Yields oxy-methyl-glutaric acid on oxidation.

Acetyl derivative (177° cor.).

OCTODECANE *v.* OCTADECANE.

***n*-OCTOIC ACID** $C_8H_{16}O_2$ *i.e.* $CH_3(CH_2)_6.CO_2H$. *Caprilic acid.* Mol. w. 144. [17°]. (237° i.V.). S.G. $\frac{0}{0}$ ·927 (Zander, *A.* 224, 71); $\frac{15}{15}$ ·913; $\frac{25}{25}$ ·908. M.M. 8·565 at 18·5°. S. ·25 at 100°. H.C. 1,138,694 (Louguinine, *A. Ch.* [6] 11, 221); 1,145,600 (Stohmann, *J. pr.* [2] 43, 18). C.E. (0°–10°) ·00092. S.V. 197·8. Occurs as glyceryl ether in butter (Lerch, *A.* 49, 214) in cocoa-nut oil (Fehling, *A.* 53, 399; Renesse, *A.* 171, 380), and in Limburg cheese (Iljenko, *A.* 55, 85). It occurs also in fusel oil from various sources. Formed by oxidation of *n*-octyl alcohol (Zincke, *A.* 152, 9) and by saponifying its nitrile which is formed by the action of bromine and NaOH on the amide of ennoic acid (Hofmann, *B.* 17, 1408). Formed also by oxidising di-oxy-stearic acid with alkaline $KMnO_4$ (Spiridonoff, *J. pr.* [2] 40, 248). White crystals, insol. cold water.

Salts.—BaA'$_2$. S. ·62 at 20°.—CaA'$_2$aq.—ZnA'$_2$. [136°].—PbA'$_2$. [84°].—CuA'$_2$. [266°].—AgA': white curdy pp.

Methyl ether MeA'. (193°). S.G. $\frac{0}{0}$ ·8942. S.V. 220·1. C.E. (0°–10°) ·00094 (Gartenmeister, *A.* 233, 286).

Ethyl ether EtA'. Mol. w. 172. (206°). S.G. $\frac{0}{0}$ ·8842. S.V. 245·9. C.E. (0°–10°) ·00098.

Propyl ether PrA'. (225°). S.G. $\frac{0}{0}$ ·8805. S.V. 270·3. C.E. (0°–10°) ·00092.

Butyl ether C_4H_9A'. (240·5°). S.G. $\frac{0}{0}$ ·8797. S.V. 295·9. C.E. (0°–10°) ·00094.

Heptyl ether C_7H_{15}A'. (290°). S.G. $\frac{0}{0}$ ·8754. S.V. 377·0. C.E. (0°–10°) ·00086.

n-Octyl ether C_8H_{17}A'. (306°). S.G. $\frac{0}{0}$ ·8755. S.V. 404·3. C.E. (0°–10°) ·00084.

Phenyl ether PhA'. (300°).

Amide $C_8H_{15}O.NH_2$. [106°]. S. ·454 at 100°. Plates.

Anhydride $(C_8H_{15}O)_2O$. (c. 285°). (Chiozza, *A.* 85, 229).

Nitrile C_7H_{15}.CN. (195°) (F.); (199°) (Hofmann, *B.* 17, 1410). S.G. $\frac{13}{}$ ·82 (Felletar, *Z.* [2] 4, 665).

Iso-octoic acid $C_8H_{16}O_2$. (219°). S.G. $\frac{0}{4}$ ·926; $\frac{20}{4}$ ·911. S. ·15 at 15°. Formed by oxidising iso-octyl alcohol (W. C. Williams, *C. J.* 31, 542; 35, 129). Liquid.—NaA'.—KA'.—MgA'$_2$ 2aq.—AgA'. Crystallises from hot water.

Ethyl ether EtA'. (175°).

Iso-octyl ether C_8H_{17}A'. (c. 280°).

Octoic acid CH_2Pr.CH_2.CHMe.CO_2H. (c. 215°). Formed by oxidation of isodibutol $C_8H_{16}O$ (Butlerow, *A.* 189, 70). Liquid. Probably identical with the preceding acid.

Octoic acid CMe_3.CMe_2.CO_2H ? (210°–230°). Formed, in small quantity, by passing CO over a mixture of NaOMe and NaOAc at 200° (Geuther a. Fröhlich, *A.* 202, 313).

Octoic acid Pr_2CH.CO_2H.

Di-n-propyl-acetic acid. (220°). S.G. $\frac{0}{4}$ ·9215. Obtained by boiling di-propyl-acetoacetic ether with alcoholic potash or by heating di-propyl-malonic acid (Burton, *Am.* 3, 389; Fürth, *M.* 9, 317).—CaA'$_2$ 2aq. S. 9·57 at 0°; 1·65 at 80°.—BaA'$_2$.—AgA'. S. ·123.

Ethyl ether EtA'. (183°).

Octoic acid CH_2Pr.CMe_2.CO_2H. [18°]. (215°). Obtained from its ether, which is formed by the action of sodium on isobutyric ether (Brüggemann, *A.* 246, 149). Large hexagonal plates.

OCTOIC ALDEHYDE $C_8H_{16}O$. (171°). Occurs among the products of the distillation of castor oil soap (Limpricht, *A.* 93, 242; Bouis, *A. Ch.* [3] 48, 99; Städeler, *J. pr.* 72, 241; Dachauer, *A.* 106, 270; Béhal, *Bl.* [2] 47, 33, 163). Formed also by distilling a mixture of calcium octoate and calcium formate. Liquid. Combines with $NaHSO_3$. Yields a mirror with ammoniacal $AgNO_3$.

Oxim (222°).

Octoic aldehyde C_4H_9CHEt.CHO. (161°). Formed by reduction of octenoic aldehyde (Raupenstrauch, *M.* 8, 108). Oil. Volatile with steam. Reduces ammoniacal $AgNO_3$.

OCTO-ICOSONOIC ALDEHYDE $C_{28}H_{50}O$ *i.e.* C_6H_{13}.CH:C(C_5H_{11}).CH:C(C_5H_{11}).CH:C(C_5H_{11}).CHO. (c. 335°). A product of the action of alcoholic potash or of Ac_2O on heptoic aldehyde (œnanthol) (Perkin, *C. J.* 43, 66). Oil. Yields a mixture of heptoic and hexoic acids on fusion with potash.

OCTONAPHTHENE C_8H_{16}. (119°). Occurs in Russian petroleum (Markownikoff, *B.* 20, 1851). Yields a very little tri-nitro-*m*-xylene on treatment with H_2SO_4 and HNO_3. H_2SO_4 yields a sulphonic acid, the amide of which crystallises in needles [220°].

OCTYL. The radicle C_8H_{17}, which is also called CAPRYL.

Di-octyl *v.* HEXADECANE.

OCTYL ACETATE *v. Acetyl derivative* of OCTYL ALCOHOL.

DI-OCTYL-ACETONE *v.* METHYL HEPTADECYL KETONE.

***n*-OCTYL ALCOHOL** $C_8H_{18}O$. Mol. w. 130. (195·5° i.V.). S.G. $\frac{0}{0}$ ·8375 (Z.); $\frac{15}{15}$ ·8301; $\frac{25}{25}$ ·8249 (P.). C.E. (0°–10°) ·00080. M.M. 8·880 at 20° (Perkin). S.V. 190·6 (Zander, *A.* 224, 84); 197·3 (Ramsay). Obtained from its acetyl derivative which occurs in the volatile oil of cow-

parsnep (*Heracleum Sphondylium*), and in the oil of *H. giganteum* (Zincke, *A.* 152, 1; *B.* 4, 822; Möslinger, *A.* 185, 26). The butynyl derivative occurs in the ripe fruits of *Pastinaca sativa* (Renesse, *A.* 166, 80). Heated with ammoniacal $ZnCl_2$ at 280° it yields a mixture of mono- di- and tri- octyl-amines, the yield of mixed bases amounting to 70 per cent. of the alcohol used (Merz a. Gasiorowski, *B.* 17, 629).

Acetyl derivative $C_8H_{17}OAc$. (212° cor.). S.G. $\frac{0}{0}$ ·8847 (G.); $\frac{15}{15}$ ·8744; $\frac{25}{25}$ ·8678 (P.). C.E. (0°–10°) ·00094. S.V. 245·8 (Gartenmeister). M.M. 10·601 at 16·1° (Perkin, *C. J.* 45, 421).

Benzoyl derivative $C_8H_{17}OBz$. (306°).

Ethyl ether $C_8H_{17}OEt$. (183°). S.G. $\frac{17}{}$ ·79.

Sec-**Octyl alcohol** $C_6H_{13}.CH(OH).CH_3$. *Capryl alcohol. Methyl-hexyl-carbinol.* (179·5° cor.). S.G. $\frac{15}{15}$ ·8236; $\frac{25}{25}$ ·8178. M.M. 9·004 at 12·4° (Perkin). S.V. 191·3 (Schiff, *A.* 220, 103). μ_β = 1·4297. R_∞ = 65·57 (Brühl, *A.* 203, 28). Formed by distilling sodium ricinoleate with NaOH (Bouis, *A.* 97, 34; Moschinin, *A.* 87, 111; *A. Ch.* [3] 44, 140; Limpricht, *A.* 93, 242; Neison, *C. J.* 27, 837; Schorlemmer, *Pr.* 16, 376; *C. J.* 27, 1029). Obtained also from *n*-octane viâ octyl chloride and octyl acetate (Schorlemmer, *A.* 152, 152). Yields methyl hexyl ketone on oxidation.

Acetyl derivative $C_8H_{17}OAc$. (193°).

Octyl alcohol $C_8H_{18}O$. *Di-isobutyl hydrate.* (180°). S.G. $\frac{0}{4}$ ·841. Formed by chlorinating $CH_2Pr.CH_2Pr$, converting the resulting octyl chloride into octyl acetate, and boiling this with KOHAq (W. C. Williams, *C. J.* 35, 127). Yields an octoic acid on oxidation.

Octyl alcohol $C_8H_{18}O$. (c. 162°). S.G. $\frac{15}{4}$ ·820. Formed at the same time as the preceding (W.). Yields on oxidation a ketone $C_4H_9.CO.C_3H_7$ (160°).

Octyl alcohol $CHEt_2.CH(OH).C_2H_5$. (164°–168°). Formed from $CH_2Br.COBr$ and $ZnEt_2$ followed by water (Winogradoff, *A.* 191, 125). Sl. sol. water.

Octyl alcohol $C_8H_{18}O$. (174°–178°). S.G. $\frac{0}{}$ ·811. Obtained from octylene, by treatment with HI, the resulting octyl iodide being converted into octyl acetate by AgOAc (De Clermont, *C. R.* 66, 1211; *A.* 149, 38; *Bl.* [2] 12, 212). Yields a ketone $C_8H_{16}O$ on oxidation, and, on further oxidation, acetic and hexoic acids. Is probably identical with methyl-hexyl-carbinol.

Acetyl derivative. (c. 176°).

Tert-**Octyl alcohol** $Pr_2CMe(OH)$. (161·5° cor.). S.G. $\frac{20}{0}$ ·8236; $\frac{30}{0}$ ·8151. Formed from di-propyl ketone, MeI, and zinc, followed by water (Saytzeff, *J. pr.* [2] 31, 320; *Bl.* [2] 45, 257). Yields acetic, propionic, and butyric acids on oxidation.

Acetyl derivative. (c. 175°). S.G. $\frac{20}{0}$ ·8554. (160·5°). S.G. $\frac{20}{}$ ·838.

Tert-**Octyl alcohol** $CEt_2Pr(OH)$. Formed from butyryl chloride or EtCOPr and $ZnEt_2$ followed by water (Butlerow, *Bl.* [2] 5, 17; Sokoloff, *J. R.* 1887, 595). Yields butyric, propionic, and acetic acids on oxidation.

Acetyl derivative. (177°).

Octyl alcohol $CMe_3.CH_2.CMe_2(OH)$. *Isodibutol.* [c. – 20°.] (147°). S.G. $\frac{0}{}$ ·842. Formed from 'di-isobutylene' hydroiodide and Ag_2O (Butlerow, *A.* 189, 53). Yields $CMe_3.CO_2H$ and acetone on oxidation.

Sec-**Octyl alcohol.** (182°–186°). Obtained from *n*-octane by chlorination and conversion of the mixed octyl chlorides into acetates (Schorlemmer). Yields propionic and valeric acids on oxidation.

Acetyl derivative. (200°).

OCTYL ALLOPHANATE $C_{10}H_{20}N_2O_3$ *i.e.* $C_8H_{17}O.CO.NH.CO.NH_2$. [156°]. Formed from octyl alcohol and $Cl.CO.NH_2$ (Gattermann, *A.* 244, 40). Silky needles, v. sol. hot alcohol.

n-**OCTYLAMINE** $C_8H_{17}NH_2$. (186°) (E.); (180°) (H. a. D.). Formed, together with di- and tri-octyl-amine, by heating octyl iodide with alcoholic NH_3 at 100°, or octyl alcohol with ammoniacal $ZnCl_2$ at 280° (Renesse, *A.* 166, 85; Merz a. Gasiorowski, *B.* 17, 629). Formed also by reducing nitro-octane (Eichler, *B.* 12, 1885), and produced by decomposition of the urea $C_8H_{17}NH.CO.NH.CO.C_8H_{17}$ [100°], which is produced by the action of KOBr on ennoic amide $C_8H_{17}.CO.NH_2$ (Hofmann, *B.* 15, 773; Hoogewerff a. van Dorp, *R. T. C.* 6, 387). Oil.—B'HCl.—$B'_2H_2PtCl_6$.—Picrate [113°]. Plates (H. a. D.).

Sec-**Octylamine** $C_6H_{13}.CH(NH_2).CH_3$. *Caprylamine.* (175°) (B.); (163°) (Jahn, *M.* 3, 172). Formed, together with the di- and tri-octyl-amines, by heating iso-octyl chloride with aqueous NH_3 (Malbot, *C. R.* 105, 575; *A. Ch.* [6] 13, 507; *cf.* Squire, *C. J.* 7, 108; Cahours, *A.* 92, 399; *C. R.* 39, 254; Bouis, *A. Ch.* [3] 44, 139). Formed also by heating the alcohol with ammoniacal $ZnCl_2$ at 260° (Merz a. Gasiorowski, *B.* 17, 634).—B'HCl.—B'HI.—$B'HAuCl_4$.—$B'_2H_2PtCl_6$.—$B'HNO_3$.—$B'_2H_2SO_4$: crystalline, v. sol. water.

Di-*n*-octyl-amine $(C_8H_{17})_2NH$. [37°]. (298°). V.D. 8·27 (obs.).—B'HCl.—$B'_2H_2PtCl_6$: nearly insoluble yellow plates (M. a. G.).

Di-*iso*-octyl-amine. (260°–270°). V.D. 8·49 (obs.).—B'HCl.—$B'HAuCl_4$.—$B'_2H_2PtCl_6$.

Tri-*n*-octylamine $(C_8H_{17})_3N$. (367°). Solid, sl. sol. 90 p.c. alcohol.—$B'_2H_2PtCl_6$.

Tri-*iso*-octyl-amine $(C_8H_{17})_3N$. (c. 370°). Oil. —$B'_2H_2PtCl_6$: reddish-brown mass.

n-**OCTYL-BENZENE** $C_8H_{17}.C_6H_5$. [–7°]. (263°). S.G. $\frac{15}{15}$ ·849. Formed from bromobenzene, *n*-octyl bromide, and sodium (Schweinitz, *B.* 19, 641; Ahrens, *B.* 19, 2718).

Octyl-benzene $Pr.CH_2(CH_2)_4.C_6H_5$. (245°–255°). Formed by heating phenacyl-isoamylmalonic acid with zinc-dust (Paal a. Th. Hoffmann, *B.* 23, 1502). Oil, with blue fluorescence.

References.—Bromo-, Chloro-, and Iodo-octyl-benzene and Octyl-phenyl-amine.

n-**OCTYL-BENZENE SULPHONIC ACID** $C_8H_{17}.C_6H_4.SO_3H$. Formed by sulphonation of *n*-octyl-benzene (Schweinitz, *B.* 19, 642).—BaA'_2 aq.—PbA'_2 3aq.—AgA'aq: minute soluble prisms.

n-**OCTYL-BENZOIC ACID** $C_{15}H_{22}O_2$ *i.e.* $C_8H_{17}.C_6H_4.CO_2H$[1:4]. [139°]. Formed by saponifying its nitrile which is obtained by distilling the formyl derivative of *p*-octyl-phenylamine with zinc-dust (Beran, *B.* 18, 138). Plates or needles.—AgA'.

Nitrile $C_8H_{17}.C_6H_4.CN$. (c. 312° uncor.).

OCTYL BROMIDES. Formed from the corresponding alcohols, Br, and P (Zincke, *A.* 152, 5; Lachovitch, *A.* 220, 181).

$CH_3(CH_2)_6CH_2Br$. (199°) (Z.); (204° cor.) (Perkin). S.G. $\frac{15}{15}$ 1·1180; $\frac{25}{25}$ 1·1099.

$C_6H_{13}.CHBr.CH_3$. (188°). S.G. $\frac{22}{}$ 1·099.

OCTYL CARBAMATE $NH_2.CO_2C_8H_{17}$. [55°]. (231°). Formed from *sec*-octyl (capryl) alcohol and CNCl at 100° (Arth, *Bl.* [2] 45, 703; *A. Ch.* [6] 8, 430). Crystals, v. sol. alcohol.

n-**OCTYL CHLORIDE** $CH_3(CH_2)_6CH_2Cl$. Mol. w. 148·5. (180°) (Zincke, *A.* 152, 4); (183° cor.) (Perkin). S.G. $\frac{15}{15}$ ·8786; $\frac{25}{25}$ ·8719. M.M. 10·128 at 18°. Formed from *n*-octyl alcohol.

Sec-**Octyl chloride** $C_6H_{13}.CHCl.CH_3$. (172° cor.). S.G. $\frac{15}{15}$ ·8708; $\frac{25}{25}$ ·8639. M.M. 10·248 at 18° (Perkin). Formed from *sec*-octyl alcohol and HCl (Bouis, *A.* 92, 398; Malbot, *Bl.* [3] 3, 68). Obtained also, together with the preceding isomeride, by chlorinating *n*-octane (Schorlemmer, *A.* 152, 152).

Octyl chloride $\text{Pr}.CH_2.CH_2.CHMe.CH_2Cl$. A mixture of this chloride with $\text{Pr}.CH_2.CHCl.\text{Pr}$ is formed by chlorinating $\text{Pr}CH_2.CH_2\text{Pr}$ (Williams, *C. J.* 35, 127; *cf.* Schorlemmer, *A.* 144, 190).

Octyl chloride $CMe_3.CH_2.CClMe_2$. (145°–150°). S.G. $\frac{0}{}$ ·890. Formed from 'diisobutylene' and HCl at 100° (Butlerow, *A.* 189, 51).

Octyl chloride CEt_2PrCl. (155°). (Butlerow, *Bl.* 5, 24).

n-**OCTYLENE** C_8H_{16}. *Octene.* (123°). S.G. $\frac{17}{}$ ·722. Formed from *n*-octyl alcohol, I, and P (Möslinger, *A.* 185, 52).

Octylene C_8H_{16}. (123°) at 750 mm. S.G. $\frac{9·9}{4}$ ·7294 (S.); $\frac{20}{4}$ ·7197 (Brühl, *A.* 235, 11). C.E. (9·9–123·4) ·00138. μ_D 1·413. S.V. 177·2 (Schiff, *A.* 220, 90). Formed by heating *sec*-octyl alcohol with H_2SO_4 or fused $ZnCl_2$ (Bouis, *A.* 92, 396). Formed also, together with octyl bromide, by the action of P and Br on *sec*-octyl alcohol (Lachovitch, *A.* 220, 185). It is also a product of the action of NH_3Aq on *sec*-octyl iodide at 150° (Malbot, *A. Ch.* [6] 13, 514). Oil, with unpleasant odour. Not affected by cold alcoholic KOH. Is perhaps identical with the preceding octylene.

Octylene $CMe_2:CH.CMe_3$. *Diisobutylene.* (103° i.V.) (B.); (112°) (Malbot, *A. Ch.* [6] 19, 370; *C. R.* 108, 957). S.G. $\frac{0}{}$ ·734. H.C. 1,252,500. H.F. 51,500. Formed by polymerisation of isobutylene by heating with H_2SO_4 (1 pt.) and water (1 pt.) at 100° (Butlerow, *B.* 8, 1683; 9, 1687; *A.* 180, 245; 189, 44; *J. R.* 1882, 190; Konovaloff, *Bl.* [2] 34, 334). Yields acetone, $CMe_3.CO_2H$, and oxy-octoic acid on oxidation.

Octylene CMePr:CHEt. (120·4° cor.). S.G. $\frac{20}{0}$ ·7314. Formed in the action of MeI and Zn on di-propyl ketone (Sokoloff, *J. pr.* [2] 39, 444).

Octylene CEtPr:CHMe or CEt_2:CHEt. (119°). S.G. $\frac{20}{0}$ ·7365. A product of the action of EtI and zinc on ethyl propyl ketone (Sokoloff, *J. pr.* [2] 39, 440). Oil. Yields acetic, propionic, and butyric acids on oxidation.

Octylene PrCH:CHPr. (116°–120°). Formed from PrCH(OH).CH(OH)Pr and HI at 140°, followed by alcoholic potash (Fossek, *M.* 4, 673).

Octylenes of undetermined composition have been prepared by Schorlemmer (*A.* 125, 113), Cahours (*J.* 1850, 402; 1863, 529); Renard (*Bl.* [2] 39, 541), Wurtz (*A.* 128, 230), Cloëz (*B.* 7, 823), Williams (*B.* 10, 908), Thorpe a. Young (*A.* 165, 14), and Fittig (*A.* 117, 77).

OCTYLENE BROMIDE *v.* DI-BROMO-OCTANE.

OCTYLENE GLYCOL *v.* DI-OXY-OCTANE.

OCTYLENE OXIDE $C_8H_{16}O$. (145°). S.G. $\frac{15}{}$ ·831. Formed by the action of KOH at 180° on the chloro-octyl alcohol formed by union of octylene with HOCl (Clermont, *C. R.* 68, 1323).

n-**OCTYL IODIDE** $C_8H_{17}I$. (220°) (Möslinger, *B.* 9, 998); (225·5°) (Dobriner, *A.* 243, 29). S.G. $\frac{0}{0}$ 1·3533 (D.); $\frac{15}{15}$ 1·3407; $\frac{25}{25}$ 1·3316 (Perkin). C.E. (0°–10°) ·00089 (D.). M.M. 16·197 at 20·7°. S.V. 222·6. Formed from the alcohol and HI.

Sec-**Octyl iodide** C_6H_{13}.CHMeI. (211°). S.G. $\frac{16}{}$ 1·31 (*B.*); $\frac{0}{}$ 1·355 (Krafft, *B.* 19, 2222). Formed from the alcohol (Bouis, *A. Ch.* [3] 44, 131; Squire, *C. J.* 7, 108).

Octyl iodide $C_8H_{17}I$. (120° *in vacuo*). S.G. $\frac{21}{}$ 1·314. Formed from octylene and HI (De Clermont, *Bl.* [2] 12, 212).

DI-OCTYL-MALONIC ACID $C_{19}H_{36}O_4$ *i.e.* $(C_8H_{17})_2C(CO_2H)_2$. [75°]. Crystals, insol. water (Conrad a. Bischoff, *B.* 13, 597; *A.* 204, 163).

Ethyl ether Et_2A''. (338°). S.G. $\frac{18}{15}$ ·896.

OCTYL NITRITE C_8H_{17}.O.NO. (176°). S.G. $\frac{17}{}$ ·862. Formed from octyl alcohol and HNO_2 (Eichler, *B.* 12, 1887).

Sec-**Octyl nitrite** C_6H_{13}.CHMe.O.NO. (165°). S.G. $\frac{0}{}$ ·881. Formed by the action of glyceryl trinitrite on *sec*-octyl alcohol (Bertoni, *G.* 16, 520). Oil, v. sol. ether.

OCTYL OXIDE $(C_8H_{17})_2O$. (292°). S.G. $\frac{0}{0}$ ·8204. C.E. (0° 10°) ·00088. S.V. 403·6. Formed from $C_8H_{17}ONa$ and $C_8H_{17}I$ (Möslinger, *A.* 185, 56; Dobriner, *A.* 243, 10).

o-**OCTYL-PHENYL-AMINE** $C_8H_{17}.C_6H_4.NH_2$. —$B'HCl$.—$B'_2H_2SnCl_4$ (Ahrens, *B.* 19, 2725).

p-**Octyl-phenyl-amine** [20°]. (310° cor.). Formed by heating octyl alcohol with aniline and $ZnCl_2$ at 280° (Beran, *B.* 18, 132).—$B'HCl$.—$B'_2H_2SO_4$.—$B'_2H_2C_2O_4$: white plates.

Formyl derivative [56°]. Plates.

Acetyl derivative $C_{14}H_{21}$.NHAc. [93°].

Benzoyl derivative. [117°]. Plates. The corresponding derivative of *sec*-octyl-phenyl-amine melts at 109°.

n-**OCTYL-PHOSPHINE** $C_8H_{17}PH_2$. (c. 186°). S.G. $\frac{17}{}$ ·821. Formed by heating octyl iodide with PH_4I and ZnO (Möslinger, *A.* 185, 65).—B'HI: crystalline.

OCTYL SULPHATES.

n-**Octyl-sulphuric acid** $C_8H_{17}O.SO_3H$ (Möslinger, *A.* 185, 62). Forms a sparingly soluble Ba salt, and an easily soluble K salt.

Sec-**Octyl-sulphuric acid** $C_8H_{17}O.SO_3H$ (Bouis, *C. R.* 33, 144; 38, 935).—BaA'_2 3aq.—KA' aq: pearly crystals.

n-**OCTYL SULPHIDE** $(C_8H_{17})_2S$. (above 310°). S.G. $\frac{17}{}$ ·842. From the chloride and K_2S (Möslinger, *A.* 185, 59).

Sec-**OCTYL SULPHOCYANIDE** $C_9H_{17}NS$ *i.e.* C_6H_{13}.CHMe.S.Cy. (142°). From the iodide and potassium sulphocyanide (Jahn, *B.* 8, 805).

OCTYL-THIENYL METHYL KETONE $C_4H_2S(C_8H_{17}).CO.CH_3$. (c. 352°). Formed, together with oily $C_4HS(C_8H_{17})(CO.CH_3)_2$ (which yields an oxim [58°]), by the action of AcCl on octyl-thiophene in presence of $AlCl_3$ (Schweinitz, *B.* 19, 646). Oil, volatile with steam.

n-**OCTYL-THIOCARBIMIDE** C_8H_{17}.N:CS. (232°). Formed from *n*-octylamine (Jahn, *B.* 8, 804; *M.* 3, 173).

(α)-**OCTYL-THIOPHENE** $C_8H_{17}.C_4H_3S$. (258°). S.G. $\frac{20·5}{20·5}$ ·8118. Formed from octyl

bromide, (a)-iodo-thiophene and Na in ether (Schweinitz, *B.* 19, 644). Oil.

References.—Bromo- and Iodo- octyl-thiophene.

OCTYL-THIOPHENE DICARBOXYLIC ACID $C_8H_{17}.C_4HS(CO_2H)_2$. [185°]. Formed by oxidising $C_4HS(C_8H_{17})(CO.CH_3)_2$ with alkaline $KMnO_4$ (Schweinitz, *B.* 19, 646). Needles.—BaA″ $1\frac{1}{2}$aq.—CuA″ $2\frac{1}{2}$aq.—Ag_2A″ 3aq: yellow pp.

Sec-**OCTYL-THIO-UREA** $C_8H_{17}NH.CS.NH_2$. [114°]. Formed from *sec*-octyl-thio-carbimide and NH_3 (Jahn, *B.* 8, 804; *M.* 3, 173). Plates.

OCTYL-TOLYL-AMINE $C_6H_3Me(C_8H_{17})NH_2$. (325°). Formed by heating o-toluidine with octyl alcohol and $ZnCl_2$ at 280° (Beran, *B.* 18, 145). Oil.—B′HCl.—$B'_2H_2SO_4$.—$B'_2H_2C_2O_4$.

Acetyl derivative. [81°]. Needles.

Benzoyl derivative. [117°]. Plates.

OCTYL-UREA. *Ennoyl derivative* $C_8H_{17}.NH.CO.NH.CO.C_8H_{17}$. [97°]. From ennoic amide, Br, and NaOHAq (Hofmann, *B.* 15, 760).

ŒNANTH-DIACETONAMINE *v.* Acetonamine.

ŒNANTHIC ACID *v.* Heptoic acid.

ŒNANTHOL *v.* Heptoic aldehyde.

ŒNANTHYLAMINE *v.* Heptylamine.

ŒNANTHYLIC ACID *v.* Heptoic acid.

ŒNANTHYLIDENE *v.* Heptinene.

ŒNOGLUCIN $C_6H_6O_3$. [208·5°]. A substance resembling phloroglucin prepared from œnolin, the red colouring matter of wine, by potash-fusion (Gautier, *Bl.* [2] 33, 583). Tables (containing 2aq), m. sol. water. Gives no colour with $FeCl_3$.

ŒNOLIN $C_{21}H_{20}O_{10}$? A colouring matter ppd. by adding lead subacetate to red wine (Glénard, *C. R.* 47, 268; Gautier, *Bl.* [2] 32, 103) or by adding lime (Varenne, *Bl.* [2] 29, 109). Its composition is variable.

OIAZTHIOLES. Derivatives of $\left\langle{N:CH \atop N:CH}\right\rangle S$.

OILS. Liquids nearly or quite insol. water. In a more restricted sense, the term oil is applied to neutral liquids derived from plants or animals. Oils are said to be 'fixed' when they cannot be distilled either alone or with steam without undergoing decomposition; oils that can be so distilled being termed volatile or essential oils. Most of the fixed oils are glycerides of stearic, palmitic, and oleïc acids (*v.* Glycerin). Fatty oils that absorb oxygen from the air and thus become slowly converted into varnishes are termed drying oils, *e.g.* linseed, hazel-nut, hemp, and poppy oils. Drying oils contain glycerides of linoleïc and similar unsaturated acids (*v.* Linoleïc acid and Fat). Essential oils consist either wholly of hydrocarbons or of mixtures of hydrocarbons with compounds of carbon, hydrogen, and oxygen. These oxygenated compounds may be compound ethers (oil of chamomile), phenols (oil of thyme; oil of caraway), ketones (oil of rue), aldehydes (oil of cinnamon), or acids (oil of valerian). Many essential oils deposit a solid (stearoptene) on cooling strongly, leaving a liquid portion (elæoptene). Most of the essential oils contain terpenes or at any rate hydrocarbons of the formula $(C_5H_8)_n$ (*v.* Terpenes). The individual oils are described in their alphabetical places. See also Fat.

OLEANDRINE. A poisonous alkaloid [70°–75°], in the leaves of the oleander (Lukomski, *J.* 1861, 546; Betelli, *J.* 1875, 783). Minute crystals (by sublimation).

OLEFINES. Hydrocarbons, C_nH_{2n}, homologous with ethylene, so called from their property of combining with chlorine and bromine, even in the dark, forming oily dichlorides and dibromides (*v.* vol. ii. p. 716).

OLEIC ACID $C_{18}H_{34}O_2$. Mol. w. 282. [8°] (Schön, *A.* 244, 262); [14°] (Gottlieb). (223° at 10 mm.); (286° at 100 mm.) (Krafft a. Noerdlinger, *B.* 22, 819). S.G. $\frac{19}{}$ ·808. Occurs as glyceryl ether (trioleïn, vol. ii. p. 622) in most fixed oils and fats (Chevreul, *Recherches sur les corps gras*, p. 205; Varrentrapp, *A.* 35, 196; Laurent, *A. Ch.* [2] 65, 149; Gottlieb, *A.* 57, 40; Heintz, *P.* 83, 555; 89, 583; 90, 143; Berthelot, *A. Ch.* [3] 41, 243). Prepared by saponifying olive or almond oil with potash, decomposing the soap with tartaric acid, heating the separated fatty acids with PbO, extracting lead oleate with ether, shaking the extract with HClAq, decanting and evaporating the ethereal solution.

Properties.—White needles or (above 14°) oil. Insol. water, v. sol. alcohol, miscible with ether. May be distilled by superheated steam at 250°. Neutral to litmus, but when impure it absorbs oxygen, becoming acid and rancid. Gives a crimson colour (Pettenkofer's reaction) when heated with sugar or furfuraldehyde and H_2SO_4 (Mylius, *H.* 11, 492).

Reactions.—1. Yields, on distillation, sebacic, acetic, and hexoic acids, CO_2, CH_4, C_2H_4, and CO (Engler, *B.* 22, 593).—2. *Potash-fusion* gives acetate, palmitate, and hydrogen.—3. *Nitrous acid* converts it into the isomeric elaïdic acid, which is solid.—4. *Nitric acid* oxidises it to acetic, propionic, butyric, valeric, hexoic, heptoic, octoic, ennoic, decoic, suberic, pimelic, adipic. and azelaic acids.—5. *Glycerin* yields on heating mono- and tri-oleïn.—6. *Bromine* combines, forming di-bromo-stearic acid (Overbeck, *J. pr.* 97, 159).—7. HIAq and red P at 205° in sealed tubes yield stearic acid (Goldschmiedt, *Sitz. W.* 72, 366; Muter, *An.* 2, 63).—8. Alkaline $KMnO_4$ gives azelaic acid and di-oxy-stearic acids [137°] (A. Saytzeff, *J. pr.* [2] 31, 541; *Bl.* [2] 45, 255). 9. *Iodine* (1 p.c.) in sealed tubes at 270° forms stearic acid (Wilde a. Reychler, *Bl.* [3] 1, 295). 10. Conc. H_2SO_4, followed by water, yields oxy-stearic acid [79°], oxy-stearic lactone [48°], and oily $C_{16}H_{33}.CH(O.SO_3H).CO_2H$ (Sabanéeff, *Bl.* [2] 46, 819; Geitel, *J. pr.* [2] 37, 74).

Salts.—KA′. S. 25 in the cold. Deliquescent. Its solution deposits a gelatinous acid salt when greatly diluted.—NaA′. S. 10 at 12°. S. (alcohol of S.G. ·82) 5 at 13°. S. (boiling ether) 1.—LiA′.—CaA'_2: granular pp.—SrA'_2.—BaA'_2: crystalline.—$BaH_2A'_4$: flocculent (Gössmann, *A.* 86, 322).—MgA'_2.—PbA'_2. [c. 80°]. White powder, sol. boiling ether, turpentine oil, and ligroïn.—$Pb_2A'_2O$. [100°].—$Pb_3A'_2O_2$ (Schön). —MnA'_2: sl. sol. alcohol, v. sol. ether.—FeA'_2: insol. alcohol, v. sol. ether.—AlA'_3: sl. sol. ether. —$Hg_2A'_2$: grey flocks, insol. water, sol. alcohol and ether.—ZnA'_2.—CuA'_2.—AgA′.

Methyl ether MeA′. S.G. $\frac{18}{}$ ·88. Oil.

Ethyl ether EtA′. (307°) at 307 mm. S.G. $\frac{15}{15}$ ·875; $\frac{25}{25}$ ·870. M.M. 21·9 at 15° (Perkin).

Glyceryl derivatives *v.* vol. ii. p. 622.

Amide $C_{18}H_{33}O(NH_2)$. [78°] (R.); [75°]

(C.). Formed by the action of alcoholic ammonia on oil of almonds or oil of hazel-nuts (Rowney, *C. J.* 7, 200; Carlet, *Bl.* 1859, 73).

Elaïdic acid. [47°]. A polymeride of oleic acid produced by the action of nitrous acid on oleic acid. It may also be got by saponifying its glyceryl derivative, elaïdin, which is formed when olive oil is solidified by nitrous acid gas or by mercurous nitrate (Boudet, *A. Ch.* [2] 50, 391; Laurent, *A. Ch.* [2] 65, 149; Meyer, *A.* 35, 174; Gottlieb, *A.* 57, 54). Laminæ (from alcohol), m. sol. ether. May be distilled. Acid to litmus. On fusion with potash it yields acetate and palmitate. Alkaline $KMnO_4$ forms di-oxy-stearic acid. Combines with bromine forming di-bromo-stearic acid [27°] (Burg, *Bl.* [2] 3, 191).

Salts.—NaA′: plates.—$NaHA'_2$.—AgA′.

Methyl ether MeA′. S.G. $\frac{18}{}$ ·872. Oil.

Ethyl ether EtA′. S.G. $\frac{18}{}$ ·869.

Glyceryl ether $C_3H_5A'_3$. *Elaïdin.* [32°]. Nodules, almost insol. alcohol.

Amide. [94°]. Formed from elaïdin and alcoholic NH_3. Needles.

Iso-oleic acid $C_{18}H_{34}O_2$. [45°]. Formed by the action of alcoholic potash at 120° on iodostearic acid obtained from oleic acid and HI (Michael a. Saytzeff, *J. pr.* [2] 35, 386; 37, 277; Benedikt, *M.* 9, 520). Got also by distilling, at 100 mm. pressure, oxy-stearic acid (*v.* OLEIC ACID, *Reaction* 10). Trimetric plates (from ether), insol. water, v. e. sol. alcohol, m. sol. ether.

Reactions.—1. Yields acetate and palmitate by potash-fusion.—2. $KMnO_4$ forms di-oxy-stearic acid [78°].—3. *Bromine* forms a liquid dibromide.—4. HI yields an oily iodostearic acid.

Salts.—NaA′.—ZnA'_2.

OLEÏN *v.* GLYCERIN, *Oleyl derivative.*

OLIBANUM. *Incense.* A gum resin exuding from *Boswellia papyrifera.* It contains 7 p.c. essential oil, 72 p.c. of resin soluble in alcohol, and 20 p.c. of gum (arabin) (Stenhouse, *A.* 35, 306; Kurbatoff, *Z.* [2] 7, 201; *A.* 173, 1; *cf.* Braconnot, *A. Ch.* [2] 58, 60). The essential oil contains a terpene, olibene $C_{10}H_{16}$ (157°), S.G. $\frac{12}{}$ ·863, and an oxidised substance. Olibene forms a hydrochloride $C_{10}H_{16}HCl$ [127°].

OLIVE OIL. S.G. $\frac{20}{4}$ ·913 (Long, *Am.* 10, 392). An oil expressed from olives (*Olea europæa*). It contains the glyceryl ethers of oleic and palmitic acids. The glycerides of unsaturated acids are present in greater quantity (87 p.c.) than those of saturated fatty acids (13 p.c.) (Hazura a. Grüssner, *M.* 10, 248).

OLIVIL $C_{14}H_{18}O_5$. [120°]. A neutral substance occurring, together with resin and a little benzoic acid, in the gum of the olive-tree. The resin is removed by ether, and the residue crystallised from alcohol (Pelletier, *A. Ch.* [2] 3, 105; 51, 196; Sobrero, *A.* 54, 67; Amato, *G.* 8, 83). Anhydrous crystals (from alcohol) or prisms containing Aq (from water). Reduces silver salts. Alkaline $KMnO_4$ yields vanillin. Conc. HIAq yields MeI and EtI.

OMICHOLIN $C_{21}H_{30}NO_5$? A red resin obtained, together with the similar omicholic acid from urine (Thudichum, *C. R.* 106, 1803).

OMPHALOCARPIN. A neutral substance in the fruit of *Omphalocarpum Procera* (Naylor, *Ph.* [3] 12, 478). Needles (from alcohol).

ONOCERIN $C_{12}H_{20}O$. Occurs, together with ononin, in the root of *Ononis spinosa* (Hlasiwetz, *J. pr.* 65, 142). Hair-like crystals (from alcohol). Chlorine forms resinous $C_{12}H_{18}Cl_2O$.

ONONIN $C_{30}H_{34}O_{13}$. [235°]. A glucoside occurring in the root of the spinous rest-harrow (*Ononis spinosa*) (Reinsch, *Rep. Pharm.* [2] 26, 12; Hlasiwetz, *Sitz. W.* 15, 142). Tasteless needles (from alcohol), sl. sol. boiling water, nearly insol. ether. Its alcoholic solution is ppd. by lead subacetate.

Reactions.—1. Boiling *baryta-water* splits it up into formic acid and crystalline onospin $C_{29}H_{31}O_{12}$ [162°].—2. Dilute H_2SO_4 yields glucose and formonetin $C_{24}H_{20}O_6$, which is further split up by baryta-water into formic acid and ononetin $C_{23}H_{22}O_6$ [120°]. Formonetin and ononetin crystallise from alcohol. Ononetin and onospin are coloured red by $FeCl_3$.

OPHIOXYLIN $C_{16}H_{12}O_6$? [72°]. S. ·15 at 100°; S. (alcohol) 33 at 78°. Occurs in the root of *Ophioxylon serpentinum* (Bettink, *R. T. C.* 8, 319). Dimetric needles. Conc. H_2SO_4 colours it blood-red and, on warming, indigo-blue. Its alkaline solution is violet.

OPIANIC ACID $C_{10}H_{10}O_5$ *i.e.* $C_6H_2(OMe)_2(CHO).CO_2H$. Mol. w. 210. [146°]. An acid obtained by the oxidation of narcotine (*q. v.*) (Liebig a. Wöhler, *A.* 44, 126; 50, 1; Blyth, *A.* 50, 29; Anderson, *Tr. E.* 20 [2] 347; Matthiessen a. Foster, *C. J.* 16, 345; 21, 357). It is also formed by the action of $KMnO_4$ and dilute HNO_3 on hydrastin (Freund a. Will, *B.* 19, 2799). Purified by passing a rapid current of nitrous acid gas (which does not affect it) through its boiling aqueous solution (Prinz, *J. pr.* [2] 24, 355). It may also be purified by etherification, the ether being subsequently decomposed by boiling with water (Liebermann a. Kleemann, *B.* 20, 881).

Properties.—Needles or prisms, v. sol. alcohol, ether, and hot water. Tastes bitter.

Reactions.—1. Readily oxidised to hemipic acid.—2. Reduced by sodium-amalgam to meconin.—3. Boiling conc. KOHAq yields hemipic acid and meconin.—4. Conc. HClAq at 100° yields MeCl and $C_6H_2(OMe)(OH)(CHO)CO_2H$ HIAq acts in like manner. Dilute HClAq at 170° forms isovanillin $C_6H_3(OMe)(OH)CHO$ and protocatechuic aldehyde.—5. HNO_3 forms nitro-opianic acid, nitro-hemipic acid, and a compound $C_{20}H_{20}N_2O_{12}$.—6. PCl_5 yields a chloride reduced by zinc and HCl to meconin.—7. Heating with malonic acid, HOAc, and NaOAc forms $C_6H_2(OMe)_2{<}\begin{matrix}CO\text{———}O\\CH(CH_2.CO_2H)\end{matrix}{>}$ (Liebermann, *B.* 19, 2284).—8. H_2SO_4 (30 pts.) at 180° forms rufiopin, a red colouring matter (Anderson, *C. J.* 9, 277; Liebermann a. Chojnacki, *B.* 4, 194).—9. Distillation with *soda-lime* yields methyl-vanillin. 10. *Tolylene-o-diamine* forms a crystalline compound [243°] (Bistrzycki, *B.* 21, 2523).—11. *Benzidine* yields $C_{32}H_{28}N_2O_8$ [above 320°].—12. *Urea* forms $C_{11}H_{12}N_2O_5$ [259°].—13. *Hydrazobenzene* produces $C_6H_2(OMe)_2{<}\begin{matrix}CO\text{———}O\\CH(NPh.NHPh)\end{matrix}{>}$ [188°]. 14. An alcoholic solution of *hydroxylamine hydrochloride* forms, on boiling, hemipimide, but in the cold it yields the isomeric oxim-anhydride $C_6H_2(OMe)_2{<}\begin{matrix}CO.O\\CH:N\end{matrix}$ [115°] (Liebermann, *B.* 19,

2923). This body suddenly changes, at its melting-point, to hemipimide, with great rise of temperature.—15. *Aniline* in HOAc forms, on boiling, $C_6H_2(OMe)_2(CO_2H)CH:NPh$ [187°].—16. *Ammonia* forms opiammon $C_{20}H_{19}NO_8$, a yellowish powder, decomposed by water at 150° into NH_3 and opianic acid.—17. Aqueous *sulphurous acid* forms crystalline $C_{10}H_{10}O_5H_2SO_3$, whence the salts BaA'_2 3aq and PbA'_2 6aq may be obtained.—18. H_2S forms yellow amorphous $C_{10}H_{10}SO_4$.—19. *Phenol* and H_2SO_4 in the cold form amorphous opiaurin $C_{20}H_{18}O_6$, which forms a purple solution with potash.—20. *Phenylhydrazine acetate* forms $C_{16}H_{14}N_2O_3$ crystallising in needles [175°] (Liebermann, *B.* 19, 763).—21. *Salicylic acid* and $ZnCl_2$ form $C_{14}H_{10}O_3$ [140°], whence $C_{14}H_9AcO_3$ [152°] (Michael, *Am.* 5, 95).

Salts.—KA' $2\frac{1}{2}$aq (Wegscheider, *M.* 3, 348).—KA' aq: triclinic plates.—BaA'_2 2aq: efflorescent prisms.—PbA'_2 2aq: sparingly soluble crystals. [150°].—PbA'_2; tufts of silky prisms.—AgA'.

Methyl ether MeA'. [85°] (W.); [102°] (L.). Formed from the silver salt and MeI, or by boiling the acid with MeOH. Monoclinic.

Ethyl ether EtA'. [92°].

Propyl ether PrA'. [103°].

Acetyl derivative $C_{10}H_9AcO_5$. [121°].

Propionyl derivative. [111°]. Needles.

Anhydride $\{C_6H_2(OMe)_2(CHO).CO\}_2O$. *Triopianide.* [234°]. Formed by heating the acid for two hours in a current of dry air. Needles (from acetone).

Oxim $C_6H_2(OMe)_2(CO_2H).CH:NOH$. [83°]. Formed from the acid (1 mol.), dilute KOH (4 mols.), and hydroxylamine hydrochloride ($1\frac{1}{2}$ mols.) in the cold (Perkin, jun., *C. J.* 57, 1071). Long slender needles, v. sol. alcohol. At 130° it suddenly becomes solid owing to the formation of hemipimide.

Di-phenyl-hydrazide $C_6H_2(OMe)_2(CO_2H).CH:N.NPh_2$. [172°]. CaA'_2 8aq.

Chloro-opianic acid $C_6HCl(OMe)_2(CHO).CO_2H$. [211°]. Needles (Prinz, *J. pr.* [2] 24, 366).

Bromo-opianic acid. [192°]. (P.); [204°] (Wegscheider, *M.* 4, 267). Needles.—BaA'_2 aq.

Nitro-opianic acid $C_6H(NO_2)(OMe)_2(CHO).CO_2H$. [166°]. Formed by nitration of opianic acid (Prinz). Yellow prisms (from water). With acetone and dilute NaOHAq it yields the tetra-methyl derivative of tetra-oxy-indigo dicarboxylic acid (Liebermann, *B.* 19, 352). Aniline in HOAc reacts, forming $C_6H(NO_2)(OMe)_2(CO_2H).CH:NPh$ [184°].—KA' 3aq: prisms.—BaA'_2 3aq: yellow needles.

Ethyl ether EtA'. [96°].

Acetyl derivative $C_{10}H_8AcNO_7$. Crystals.

Phenyl-hydrazide $C_6H(OMe)_2(NO_2)(CO_2H).CH:N_2HPh$. [184°]. Red needles (Liebermann, *B.* 19, 764). By boiling with HOAc it is converted into 'nitro-opianyl-phenyl-hydrazine' $C_{16}H_{13}N_3O_5$ [173°].

Di-phenyl-hydrazide $C_{22}H_{19}N_3O_6$. [217°]. Prisms, sl. sol. ether (Bistrzycki, *B.* 21, 2520).

Nitroso-opianic acid? $C_6H(OMe)_2(NO)(CHO).CO_2H$ [6:5:3:4:1]. [176°]. Formed by reducing nitro-opianic acid with NaOMe (Kleemann, *B.* 20, 875). Long yellowish-green needles.—AgA': felted needles.

Amido-opianic acid $C_6H(NH_2)(OMe)_2(CHO).CO_2H$. Formed by reduction of nitroso-opianic acid (K.).—HA'HCl.

Acetyl derivative $C_{24}H_{24}N_2O_{11}$. [233°].

Phenyl-hydrazide $C_6H(NH_2)(OMe)_2\!<\!\begin{smallmatrix}CH:N\\CO.NPh\end{smallmatrix}$. [143°]. Needles (Liebermann, *B.* 19, 2276).

Noropianic acid $C_6H_2(OH)_2(CHO)CO_2H$. [171° cor.]. Formed by heating opianic acid with HIAq. Crystals (containing $1\frac{1}{2}$aq).

Methyl derivative $C_6H_2(OMe)(OH)(CHO).CO_2H$. [154°] (P.); [142°] (Wegscheider, *M.* 3, 790). Formed by heating opianic acid with HClAq at 100°. Prisms (containing *x*aq). Chlorine forms the chloro- derivative $C_9H_7ClO_5$ [206°]. On nitration it yields $C_6H(NO_2)(OMe)(OH)(CHO).CO_2H$ [203°], which crystallises in needles (containing aq), and yields an oxim decomposing at 252°, and converted by HOAc into the anhydride $C_9H_6N_2O_6$ [252°]; the nitro- acid also yields a phenyl-hydrazide [179°] converted by HOAc into an anhydride [191°] (Elbel, *B.* 19, 2306).—KA' 2aq.—$BaC_9H_6O_5$ aq.

Iso-opianic acid *v. Methyl derivative* of ALDEHYDO-VANILLIC ACID.

Iso-noropianic acid $C_6H_2(OH)_2(CHO).CO_2H$ [4:3:5:1]. [above 240°]. Formed by heating aldehydo-vanillic acid with HClAq at 175° (Tiemann a. Mendelsohn, *B.* 10, 400). Needles.

Pseudopianic acid $C_6H_2(OMe)_2(CHO)CO_2H$ [1:2:3:4]. [122°]. A product of the action of boiling dilute H_2SO_4 on berberol (Perkin, jun., *C. J.*, 57, 1065). Slender needles (from hot water). When warmed with phenol and H_2SO_4 it gives a green colour, changing to violet-brown.—KA'.—AgA': needles.

Oxim $C_{10}H_{10}O_4(NOH)$. [124°]. Needles.

OPIANYL-ACETIC ACID $C_{12}H_{14}O_7$ *i.e.* $C_6H_2(OMe)_2(CO_2H).CH(OH).CH_2.CO_2H$. Formed, as barium salt, by boiling meconin-acetic acid (p. 198) with baryta water (Liebermann a. Kleemann, *B.* 19, 2292). The acid when liberated from its salts at once loses H_2O and is reconverted into its lactone: meconin-acetic acid.—A'Ag: crystalline pp.—A'_2BaAq: prisms.

OPINIC ACID $C_9H_8O_5$. [148°]. Formed by the action of HI on hemipic acid (Liechti, *Z.* [2] 6, 196; *A. Suppl.* 7, 151; Beckett a. Wright, *J.* 1876, 809). Prisms (containing 2aq). Coloured violet by $FeCl_3$.

OPIONIN. [227°]. A substance present in small quantity in Smyrna opium (Hesse, *A.* 228, 299). Small needles, v. sol. alcohol, ether, and alkalis, v. sl. sol. water. Neutral to litmus. When fused with potash it yields opionic acid [126°].

OPIUM. The dried juice obtained from the unripe capsules of *Papaver somniferum.* It contains morphine, codeïne, narcotine, narceïne, thebaïne, papaverine, meconic acid, and meconin. The quantity of morphine varies from 3 to 15 p.c. Hesse (*A.* 153, 47; *Suppl.* 8, 290) obtained also codamine, lanthopine, laudanine, meconidine, cryptopine, protopine, laudanosine, and hydrocotarnine. Kauder describes tritopine (*Ar. Ph.* 228, 419). The three alkaloids morphine, codeïne, and thebaïne are strong bases, while papaverine, narcotine, and narceïne are feeble bases. The various constituents of opium are described in their alphabetical position.

OPOPANAX. The dried juice obtained from the roots of the *Pastinaca Opopanax*. It contains 33 p.c. of gum, 2·8 p.c. of malic acid, and 42 p.c. of a resin which yields protocatechuic acid on fusion with potash (Pelletier; Hlasiwetz a. Barth, *J.* 1866, 630; Hirschsohn, *C. C.* 1877, 182).

ORANGE PEEL OIL. S.G. $\frac{20}{20}$ ·8435. The essential oil of orange peel consists mainly of a terpene (174°), but contains also an aldehyde $C_{10}H_{16}O$ (224°–228°) (Wright, *C. J.* 18, 1186; 20, 552; Semmler, *B.* 24, 202). It contains no cymene (Hartley, *C. J.* 37, 677). Tanret (*Bl.* [2] 46, 501) got from orange peel resinous 'aurantiamaric acid' $C_{10}H_{12}O_4$, $[\alpha]_D = -28°$, and uncrystallisable 'aurantiamarine' $C_{22}H_{26}O_{12}$? $[\alpha]_D = -60°$, a very bitter substance.

ORCEÏN $C_{28}H_{24}N_2O_7$. A colouring matter obtained from orcin by the action of aqueous ammonia and air. Purified by exhausting with ether, and crystallising from dilute alcohol (Zulkowsky a. Peters, *M.* 11, 227; *cf.* Robiquet, *A. Ch.* [2] 42, 245; 58, 320; Dumas, *A.* 27, 145; Laurent a. Gerhardt, *A. Ch.* [3] 24, 315; Liebermann, *B.* 7, 247; 8, 1649). Micro-crystalline mass, with metallic lustre; insol. water, ether, and CS_2. Its solutions are crimson, but are turned bluish-violet by ammonia or potash.

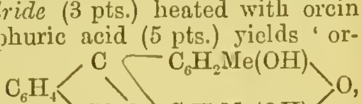
ORCENE DIALDEHYDE. This name is given by Tiemann and Helkenberg (*B.* 12, 1003) to two isomerides $C_6HMe(OH)_2(CHO)_2$ (α) [118°] and (β) [168°] formed, together with orcyl aldehyde $C_8H_8O_3$, by the action of chloroform and KOH upon orcin. The (α)- isomeride forms a di-anilide $C_6HMe(OH)_2(CH:NPh)_2$ [281°].

ORCIN $C_7H_8O_2$ *i.e.* $C_6H_3Me(OH)_2$ [1:3:5]. *Di-oxy-toluene. Methyl-resorcin.* Mol. w. 124. [108°] (Nevile a. Winther, *C. J.* 41, 417); [57°] (when containing aq). (c. 288). H.F.p. 109,276 (Stohmann, *J. pr.* [2] 34, 315). Obtained by boiling orsellic acid with water or by action of alkalis on lecanoric, erythric, and evernic acids and picroerythrin, and also by dry distillation of the same bodies (Robiquet, *A. Ch.* [2] 42, 245; 58, 320; Liebig a. Will, *A.* 27, 147; Dumas, *A.* 27, 140; Schunck, *A.* 41, 159; 54, 269; Stenhouse, *Tr.* 1848, 85; *A.* 68, 93, 99; *Pr.* 12, 263; *C. J.* 16, 327; 20, 223; De Luynes, *A.* 128, 330; 130, 31; Lamparter, *A.* 134, 256). Formed also by potash-fusion from aloes (Hlasiwetz a. Barth, *A.* 134, 287); *p*-chloro-toluene sulphonic acid (Vogt a. Henniger, *C. R.* 74, 1107); toluene *m*-disulphonic acid; *s*-bromo-cresol; *s*-di-bromo-toluene; and *s*-bromo-toluene sulphonic acid (Nevile a. Winther, *C. J.* 41, 417). Formed also from nitro-*m*-cresol by reduction and application of the diazo-reaction.

Synthesis. — Acetone - di - carboxylic ether $OC(CH_2.CO_2Et)_2$ when treated with sodium condenses to di-oxy-phenyl-acetic-di-carboxylic ether $C_6H(OH)_2(CO_2Et)_2.CH_2.CO_2Et$, the latter by the energetic action of alkalis is converted into di-oxy-phenyl-acetic acid $C_6H_3(OH)_2.CH_2.CO_2H$, whose silver-salt on dry distillation yields orcinol (Cornelius a. Pechmann, *B.* 19, 1446).

Properties.—Monoclinic prisms (containing aq), v. sol. water, alcohol, and ether. Sweet taste. Turns red in air. Its aqueous solution gives a white pp. with lead subacetate and a dark red pp. with $FeCl_3$. It reduces ammoniacal $AgNO_3$. Dry bromine forms tri-bromo-orcin. Bromine water yields penta-bromo-orcin (Stenhouse a. Groves, *C. J.* 37, 403). Its solution is not rendered acid by borax. Nitrous acid gives an orange-pink colour in dilute solutions (Lindo, *C. N.* 58, 1, 15). It forms a deliquescent compound with picric acid.

Reactions.—1. *Air* and *ammonia* yield orceïn together with yellow $C_{21}H_{19}NO_5$ soluble in ether and an amorphous body, resembling litmus, insoluble in ether and alcohol (Zulkowsky a. Peters, *M.* 11, 227). Dry ammonia forms colourless crystals of $C_7H_8O_2NH_3$. — 2. *Ammonium carbonate* yields 'para-orsellic' acid $C_6H_8O_4$ aq [151°] (Senhofer a. Brünner, *C. J.* 40, 265).—3. KOH and CO_2 form pseudo-orsellic acid (Schwarz, *B.* 13, 1643).—4. Heating with HOAc (1½ pts.) and $ZnCl_2$ (2 pts.) forms crystalline $C_{27}H_{24}O_2$ as well as 'orcaceteïn' $C_{18}H_{16}O_4$, a yellow powder (Rasinski, *J. pr.* [2] 26, 56). On boiling orcin (9 g.) with HOAc (13·5 g.) and phosphorus oxychloride (18 g.) there is formed $C_6H_2Me(OH)_2.CO.CH_3$ [146°] crystallising in needles.—5. Orcin (3 pts.) heated with *aceto-acetic ether* (2 pts.) and a little H_2SO_4 at 100° forms insoluble $C_{17}H_{16}O_5$ [249°] which yields $C_{17}H_{15}AcO_5$ [200°] and $C_{17}H_{13}Br_3O_5$ crystallising in plates.—6. HNO_3 saturated with HNO_2 acting upon an ethereal solution of orcin forms a scarlet dye 'azo-orcin' $C_{14}H_{11}NO_3$ which forms an alkaline solution with orange-red fluorescence (Krämer, *B.* 17, 1882).—7. H_2SO_4 saturated with nitrous acid forms a dye $C_{21}H_{21}NO_6$ which yields alkaline solutions with red fluorescence and $C_{21}H_{21}NO_7$ which does not yield fluorescent solutions (K; Brunner, *B.* 21, 251).—8. A mixture of HNO_3 and HBr yields $C_{21}H_{20}BrNO_6$ and $C_{48}H_{27}Me_8BrN_2O_{13}$; the alkaline solutions of these bodies exhibit brown and red fluorescence respectively (Brunner, *B.* 21, 2484).—9. A mixture of HNO_3 (10 c.c. of S.G. 1·39) and HCl (30 c.c. of S.G. 1·2) on the water-bath yields $C_{21}H_{20}ClNO_6$, a greenish mass which yields $C_{21}H_{16}Ac_4ClNO_6$.—10. *Chloral hydrate* and water on boiling form crystalline $C_{23}H_{24}O_8$ whence $C_{23}H_{19}Ac_5O_8$ [185°] (Michael a. Ryder, *Am.* 9, 135).—11. Fusion with NaOH yields resorcin, tetra-oxy-di-phenyl-methane, and finally phloroglucin (Barth, *M.* 3, 645).—12. *Benzoic aldehyde* and a little HClAq give a white resin $C_{22}H_{24}O_4$ (M. a. R.).—13. *Chloroform* and dilute potash form, on boiling, two isomeric 'orcene dialdehydes' $C_6HMe(OH)_2(CHO)_2$ and 'orcyl aldehyde' $C_6H_2Me(OH)_2CHO$ [177°] (Tiemann, *B.* 12, 999). Another product of the action of potash and chloroform on orcin is homofluoresceïn (vol. ii. p. 558) which is probably orcin-aurin $C_{22}H_{18}O_5$, a body which is formed by heating orcin with formic acid and $ZnCl_2$ at 100° (Nencki, *J. pr.* [2] 25, 277; Grimaux, *Bl.* [3] 3, 850).—14. *Phthalic anhydride* (3 pts.) heated with orcin (5 pts.) and sulphuric acid (5 pts.) yields 'orcin-phthaleïn'



which crystallises from acetone in colourless needles, dissolving in alkalis with red colour, and yielding the acetyl derivatives $C_{22}H_{15}AcO_5$ [150°] and $C_{22}H_{14}Ac_2O_5$ [220°]. Orcin-phthaleïn is reduced by zinc-dust and NaOHAq to orcin-phthalin $C_{22}H_{20}O_5$ which yields $C_{22}H_{18}Ac_2O_5$ [211°] (E. Fischer, *A.* 183, 72).—15. Concentrated sulphuric

acid at 70° produces orcin disulphonic acid $C_6HMe(OH)_2(SO_3H)_2$ which yields the crystalline salts $Pb_2C_7H_4S_2O_8$ 6½aq and $Pb_3(C_7H_5S_2O_8)_2$ 8aq (Hesse, *A.* 117, 324).—16. Fuming HNO_3 acting on orcin dissolved in ether forms orcirufin $C_{14}H_{11}NO_3$ crystallising in needles [225°] which are blue by reflected light and form a crimson solution in alkalis exhibiting yellow fluorescence. Orcirufin yields an acetyl derivative [204°] and an ethyl ether [269°] (Nietzki a. Maeckler, *B.* 23, 720).—17. *Aldehyde* dissolved in alcohol forms on addition of a few drops of HClAq, a compound $C_{18}H_{20}O_4$ crystallising in tables (Michael a. Comey, *Am.* 5, 349).—18. *Chloro-acetic acid* and caustic soda forms $C_6H_3Me(OCH_2.CO_2H)_2$ [217°] crystallising in needles. This acid forms the salts Na_2A''3aq, K_2A''3aq, and CaA''2aq; the ether Et_2A''[107°]; and two nitro- derivatives one of which melts at 140° (Saarbach, *J. pr.* [2] 21, 162).—19. *Di-chloro-quinonimide* in alcoholic solution forms brown needles of 'orcirufamine' $C_{13}H_{10}N_2O_2$, which dissolves in acids with reddish-violet colour and orange fluorescence. It dyes silk, and yields a crystalline mono-acetyl derivative (N. a. M.).

Acetyl derivative $C_6H_3Me(OAc)_2$. [25°]. Needles, nearly insol. water.

Benzoyl derivative $C_6H_3Me(OBz)_2$. [88°]. Needles (Rasinski, *J. pr.* [2] 26, 65).

Orthocarbonyl derivative $(C_6H_3MeO_2)_2C$. [195°]. Formed by distilling $C_6H_3Me(O.CO_2Et)_2$, which is produced by the action of $ClCO_2Et$ on sodium-orcin (Wallach, *A.* 226, 86; Bender, *B.* 13, 700).

Methyl ether $C_6H_3Me(OMe)(OH)$. (c. 273°). Liquid, sl. sol. water (Tiemann a. Streng, *B.* 14, 2001).

Di-methyl ether $C_6H_3Me(OMe)_2$. (244°). V.D. 76·2 (H = 1) (obs.). Mobile liquid.

Di-ethyl ether $C_6H_3Me(OEt)_2$. [16·5°]. (252° cor.) Needles. Yields $C_6HBr_2Me(OEt)_2$ [144°] (Herzig a. Zeisel, *M.* 11, 315; *cf.* De Luynes a. Lionet, *C. R.* 65, 213).

Nitroso- derivative $C_7H_7(NO)O_2$. [157°]. Yellow needles, detonating at its melting-point (Nietzki a. Maeckler, *B.* 23, 723).

References. — Tri-amido-, Amido-di-imido-, Di-bromo-nitro-, Tri-chloro-, and Iodo-orcin.

***m*-Orcin**; **Iso-orsin**; **Cresorcin**; and **Lutorcin** *v.* Di-oxy-toluene.

β-orcin *v.* Betorcin.

ORCYL ALDEHYDE *v.* Di-oxy-toluic aldehyde.

OREOSELIN $C_{14}H_{12}O_4$. *Oreoselone.* [170°]. Formed by the action of alcoholic potash or acids on peucedanin (Wagner, *J. pr.* 62, 275; Hlasiwetz, *A.* 174, 70; Heut, *A.* 176, 73). Needles (from alcohol), v. sl. sol. water. Its solution in H_2SO_4 exhibits bluish-green fluorescence. Potash-fusion yields resorcin and acetic acid. It yields an acetyl derivative [123°] and an isovaleryl derivative [97°].

OREOSELONE $C_{14}H_{10}O_3$. [190°]. Formed by passing HCl over dry athamantin (Schnedermann a. Winckler, *A.* 51, 320). Needles (from alcohol), insol. water.

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ORNITHINE $C_5H_{12}N_2O_2$. Obtained, together with benzoic acid, by boiling ornithuric acid with hydrochloric acid (Jaffé, *B.* 10, 1925).—$B'_3H_2Cl_2$.—$B'HCl$.—$B'_32H_2C_2O_4$.—$B'HNO_3$.

Benzoyl derivative $C_5H_{11}BzN_2O_2$. [225°-230°].

ORNITHURIC ACID $C_{19}H_{20}N_2O_4$. [182°]. Excreted by birds after a dose of benzoic acid (Jaffé, *B.* 10, 1925; 11, 406). Needles, v. sl. sol. hot water.—CaA'_2.—BaA'_2: powder, v. e. sol. water.

ORSEILLE *v.* Archil.

ORSELLIC ACID *v.* Di-oxy-toluic acid and Lecanoric acid.

OSAZONES *v.* Hydrazones.

OSMATES *v.* Osmium, *Salts of oxyacids of*, p. 646.

OSMIAMIC ACID *v.* Osmium, *Nitrogen-containing acid of*, p. 644.

OSMIRIDIUM *v.* Iridium, *Alloys of*, p. 47.

OSMIUM. Os. At. w. 190·3. Mol. w. unknown. Infusible at highest temperature attained by O-H flame. S.G. 22·477 at 17·5° (Deville a. Debray, *P. M.* [4] 50, 651). S.H. 19° to 98° ·03113 (Regnault, *P. M.* [4] 23, 103). C.E. ·00000657 (Fizeau, *C. R.* 68, 1125).

Occurrence.—As metal, alloyed with Ir, Pt, Rh, Ru, and Pd. The residues obtained by heating various Pt ores with *aqua regia* contain from 17 to 50 p.c. Os (*v.* Deville a. Debray, *A. Ch.* [3] 56, 431; Berzelius, *P.* 13, 435, 527; 15, 208). In 1804 Tennant showed that the metallic residue remaining after treating Pt ore with *aqua regia* contained two new metals (*T.* 1804. 411); to one of these metals he gave the name *iridium*, because of the colours of its oxides (ἶρις = rainbow), and to the other, the name osmium, because of the peculiar smell of its volatile oxide (ὀσμή = smell).

Formation.—1. By ppg. K_2OsO_4Aq by NH_4Cl, and heating the pp. in H.—2. By heating $(NH_4)_2OsCl_5$ or $(NH_4)_2OsCl_6$.—3. By strongly heating any of the sulphides of Os in absence of air.—4. By warming K perosmate in HClAq, with a formate; or by digesting the same salt with Hg, and heating the Os-Hg amalgam thus obtained.—5. By passing vapour of OsO_4 mixed with H or CO through a red-hot tube.—6. By passing OsO_4 vapour along with N through a hot tube lined with C (obtained by previously passing C_6H_6 vapour through the tube).

Preparation.—When Pt ores are treated with *aqua regia*, osm-iridium remains, partly as lustrous tablets, and partly as a black powder. Sand and gangue are removed by fusing the osm-iridium with Na_2CO_3, boiling with water, then with HClAq, and again with water. Os is obtained from this residue by various methods, which are based on the ready oxidation of Os to OsO_4 and the volatility of this compound. The lustrous tablets of osm-iridium yield much more Os than the black powder. OsO_4 may be obtained by the following methods.—1. The osm-iridium is heated to redness in a tube of porcelain, or Pt, while a current of air or O (previously passed through H_2SO_4) is sucked through the tube; the exit end of the tube is connected with a dry flask, or a series of dry Woulf's bottles, kept at a low temperature; the connecting tubes must be wide, else they may get choked with crystals of OsO_4; a vessel containing KOHAq is placed between the receiver and the aspirator, to absorb the last traces of OsO_4

(Fremy, *J. pr.* 63, 342).—2. The osm-iridium is very well mixed with an equal weight of dry NaCl, and the mixture is heated to low redness in a rapid stream of moist Cl, in a glass or porcelain tube; the apparatus is connected with a wide-necked tubulated receiver, from which a tube passes into KOHAq. or NH_3Aq. $OsCl_4$ is formed, and decomposed by the H_2O present to OsO_4, HCl, and Os which again combines with Cl to form $OsCl_4$, which $OsCl_4$ is again decomposed by H_2O, and so on (Wöhler, *P.* 31, 161; 104, 368; 107, 357). Schneider (*A. Suppl.* 5, 261) places the osm-iridium in a large Hessian crucible, the lid of which is cemented on by $CaSO_4$ and carries a porcelain tube passing into a receiver.—3. The osm-iridium may be treated with molten KOH and $KClO_3$ (Fritzsche, *J. pr.* 37, 483); or with KOH and KNO_3 (Claus, *C. C.* 1862. 129; Gibbs, *A.* 120, 108); or with BaO_2 and $Ba(NO_3)_2$ (Deville a. Debray, *A. Ch.* [3] 56, 431); in each case the K perosmate obtained is distilled with *aqua regia* and OsO_4 is obtained. The preparation of OsO_4 from osm-iridium is easily accomplished; but the process is extremely unpleasant, and also very dangerous, inasmuch as the vapour of OsO_4 rapidly attacks the eyes and lungs.

Os is obtained from OsO_4 by reducing the vapour by H or CO, or by C (Deville a. Debray, *l.c.*; *cf. Formation*, Nos. 5 and 6), or a solution of OsO_4 in KOHAq may be reduced by warming with alcohol, the violet-red crystalline pp. of K_2OsO_4 may be dissolved in water, ppd. by NH_4Cl, and the pp. reduced to Os by heating in H (Fremy, *l.c.*). Or the OsO_4 may be dissolved in NH_3Aq, warmed for some hours till blackish-brown (N is evolved, and an ammoniacal solution of Os_2O_3 remains), and evaporated until a brown pp. of impure Os_2O_3 forms; the pp. may then be washed, dissolved in HClAq, NH_4Cl added, the solution evaporated to dryness, and the residue heated in a retort as long as HCl is evolved and NH_4Cl sublimes. Os remains as a compact porous mass (Berzelius).

Os may be obtained in crystals by dissolving the metal in Sn, by heating to redness in a carbon crucible with 8 parts Sn, and allowing the mass to cool (Deville a. Debray, *C. R.* 82, 1076). The crystals are purified by dissolving out Sn, and heating the residue in a stream of HCl. Os is also obtained in crystals by passing the vapour of OsO_4, mixed with N, through a hot porcelain-tube lined with C. The lining of C is obtained by passing C_6H_6 vapour through the tube at a temperature high enough to decompose the C_6H_6. By alloying Os with Zn, and treating the alloy with HClAq, Os is obtained as a black powder which is easily ignited (D. a. D., *A. Ch.* [3] 56, 399).

Properties and Reactions.—As obtained by reducing its compounds at high temperatures, Os is a lustrous, blue-white metal, resembling Pt or Sn. Prepared by reduction at lower temperatures, Os is a greyish-black powder, without metallic lustre. From solution in Sn, Os separates in hard, bluish crystals, probably belonging to the regular system; S.G. 22·477. Deville a. Debray heated Os to the temperature at which Rh melts (c. 2000°) without fusing it. The Os was placed in a carbon-crucible placed in a cylinder of lime, resting on a block of lime, and surrounded by three other similar blocks; a powerful O-H flame was caused to play over, and around, the lime cylinder (*A. Ch.* [3] 56, 385; 61, 5).

Os is easily oxidised to OsO_4. The finely divided metal obtained at low temperatures smells of OsO_4 at the ordinary temperature; when heated in air, it burns and is completely volatilised. A compact mass of Os ignites when strongly heated in air, but ceases to burn when the source of heat is removed; Os prepared at very high temperatures may be heated to c. 225° without change. Finely divided Os, which has not been strongly heated, is oxidised to OsO_4 by heating with conc. HNO_3 or *aqua regia*; if the metal has been exposed to a very high temperature, it cannot be oxidised in the wet way. Os is oxidised, to K_2OsO_4, by molten KOH; the oxidation is hastened by addition of KNO_3 or $KClO_3$. Heated in Cl, $OsCl_4$ is produced. Os forms a phosphide when heated in P vapour. The spectrum of Os has been examined by Huggins (*T.* 154, 139), and Thalén (*v. B. A.* 1884. 431).

The atomic weight of Os has been determined (1) by heating in O and weighing the OsO_4 produced (Berzelius, *P.* 13, 546; Fremy, *A. Ch.* [3] 12, 514); (2) by reducing K_2OsCl_6 in H, washing out KCl, and weighing Os (Berzelius, *P.* 13, 530; Seubert, *B.* 21, 1839; *A.* 261, 257); (3) by determining S.H. of Os (Regnault, *P. M.* [4] 23, 103). The older values were too high. Seubert's analyses of K_2OsCl_6 and $(NH_4)_2OsCl_6$, conducted in 1888, gave the mean value 191·12, but this number was regarded by S. as rather too high; in 1891 S. re-determined the at. w. very carefully and obtained the value 190·3.

Os is distinctly metallic in its physical characters, but some of its chemical properties are those of a non-metal, *e.g.* acidic character of OsO_4 and existence of salts the negative radicle of which is OsO_3. Os belongs to the group of Pt metals, to which group Cu, Ag, and Au are more or less closely related (*v.* COPPER GROUP OF ELEMENTS, ii. 250; and NOBLE METALS, this vol. p. 628). Os is more closely related to Ru than to the other Pt metals; the analogy is shown in the existence of volatile oxides MO_4 capable of existing as gases, in the salts K_2MO_4, and probably KMO_4, and in other respects. The existence of K_2OsO_4, the fact that this salt is oxidised probably to $KOsO_4$ which salt is reduced to K_2OsO_4 by KOHAq, and also the existence of H_4OsCy_6, and salts of this acid, emphasise the analogies between Os on the one hand, and Mn and Fe on the other hand.

Detection and Estimation.—Compounds of Os heated with a little Na_2CO_3 on Pt foil give the peculiar, chlorine-like, odour of OsO_4; at the same time the non-luminous flame becomes luminous from separation of Os. Salts of OsO are easily oxidised; *e.g.* solution of $OsCl_2$, which is deep-blue, becomes violet in air, and then dark red ($OsCl_3$), and finally yellow ($OsCl_4$). Salts of Os_2O_3, *e.g.* K_3OsCl_6, give a brown-red pp. ($Os_2O_3.xH_2O$) with KOHAq, a grey-brown pp. sol. in NH_3Aq, with $AgNO_3Aq$. and a blue colour (reduction to $OsCl_2$) on warming with tannic acid. Salts of OsO_2, *e.g.* K_2OsCl_6, give no pp. with KOHAq in the cold, but on warming the liquid goes blue, and then black OsO_2xH_2O

suddenly separates. Borax produces no change at ordinary temperatures, but a black pp. forms on warming; this distinguishes OsO_2 salts from salts of IrO_2, which become blue on heating with borax, and after a little give a blue pp. Tannic acid does not react in the cold; on warming, the liquid becomes blue. Alkali salts of OsO_3 form violet solutions in water; HNO_3 oxidises to salts of OsO_4; NH_3Aq followed by NH_4ClAq ppts. yellow $OsO_2(NH_3.NH_3Cl)_2$, which gives Os on heating. OsO_4 or OsO_4Aq, is recognised by its smell; addition of KOHAq to dilute solutions of OsO_4 removes the smell. A delicate test for Os consists in fusing with KOH and a little KNO_3, dissolving K_2OsO_4 formed in water, adding NH_4Cl, washing the yellow pp. of $OsO_2(NH_3.NH_3Cl)_2$ with very dilute HClAq, dissolving it in slightly warm water, and adding K_4FeCy_6Aq, when a splendid violet colour is produced (Gibbs, *Am.* 3, 233). Os is usually estimated as the metal. Os is separated from other metals by dissolving in *aqua regia*, adding HNO_3, and distilling. The OsO_4 may be led into excess of NH_3Aq; the solution is saturated with H_2S and boiled, the pp. of OsS_2 is collected, washed, dried, and placed in a small carbon-crucible which is placed inside a Hessian crucible, the space between being filled with sand, and heated for some hours to c. 220°–250°; compact Os is thus obtained.

References.—Tennant, *T.* 1804 411: Berzelius, *P.* 13, 435, 527; 15, 208: Wöhler, *P.* 31, 161: Claus a. Jacobi, *J. pr.* 85, 142; 90, 65; *A.* 63, 355: Deville a. Debray, *A. Ch.* [3] 56, 393: Fremy, *A. Ch.* [3] 12, 522; 44, 391: Fritzsche a. Struve, *J. pr.* 41, 97.

Osmium, acids of. No oxyacid of Os has been isolated, but salts of the hypothetical acids H_2OsO_4 and $HOsO_4$ are known (*v. Osmium, salts of oxyacids of*, p. 646). A peculiar acid, $H_2N_2Os_2O_5$, generally known as *Osmiamic acid*, exists (*v. Osmium, nitrogen-containing acid of*, p. 644). *Osmocyanhydric acid*, H_4OsCy_6, and salts of this acid have been obtained (*v.* Cyanides, vol. ii. p. 343). Salts of the hypothetical acids H_2OsCl_6 and H_4OsCl_6 are known (*v. Osmium, chlorides of*; p. 644).

Osmium, alloys of. Alloys with *copper* and *gold* were described by Tennant (*T.* 1804. 411) as very ductile, insoluble in *aqua regia*. An amalgam with *mercury* is obtained by the reaction of Hg with OsO_4Aq (*v.* Claus, *J. pr.* 90, 65). The alloy with *iridium* occurs native; composition varies between c. Os_4Ir and $OsIr_3$; this alloy usually contains Ru, Rh, and Au, besides Os and Ir (*v.* Iridium, *Alloys of*, this vol. p. 47). Alloys of Os and Ir were obtained by Deville by melting Os and Ir with Cu_2S, and treating the fused mass with HClAq and then with HNO_3Aq (*M. S.* 1882. 1228).

Osmium, ammonio-salts of, or Osm-ammonium salts (*Ammoniacal osmium bases*). Not many of these compounds have been prepared. Those which are known seem best looked on as two or more NH_4 groups with H replaced by the radicle OsO or OsO_2. The constitutional formulæ and the nomenclature of the osm-ammonium salts are not settled; in this article compounds supposed to contain the radicle OsO are called *Osmosyl-ammonium compounds*, and those supposed to contain the radicle OsO_2 are called *Osmyl-ammonium compounds* (after the analogy of NO and NO_2 compounds).

Osmosyl-diammonium hydroxide $OsO(NH_3.OH)_2$ (*Ammoniated oxyosmous hydroxide. Oxyosmiumammonium hydroxide*). Simplest empirical formula = $OsO_2.2NH_3.H_2O$. Obtained by dissolving OsO_4 in excess of conc. NH_3Aq, and warming the red solution in a closed flask to 40°–60° until a black pp. begins to form when the flask is opened (Claus a. Jacobi, *J. pr.* 79, 28). N escapes during the process (?$3OsO_4 + 10NH_3 = 3OsO(NH_3.OH)_2 + 2N_2 + 3H_2O$). Forms a brown-black powder; decomposed by heat to Os with evolution of N and H_2O; insol. water, sol. acids, and reppd. by KOHAq or NH_3Aq. Amorphous basic salts (not fully examined) are obtained by evaporating the acid solutions; these salts are decomposed by water to neutral and more basic salts (Claus a. Jacobi, *J. pr.* 90, 65; *cf.* Berzelius, *P.* 13, 435, 527). The base dissolves in KOHAq; on boiling, NH_3 is evolved and a pp., $OsO_2.xH_2O$ containing NH_3, separates.

Osmyl-tetrammonium hydroxide $OsO_2(NH_3.NH_3.OH)_2Aq$ (*Ammoniated oxyosmic hydroxide. Osmidiammonium hydroxide. Oxyosmiumdiammonium hydroxide. Osmyl-ditetramine hydroxide*). Simplest empirical formula = $OsO_3.4NH_3.H_2OAq$. Known only in solution. A solution of this base is obtained by decomposing the chloride by Ag_2O and H_2O, or the sulphate by BaOAq (*v. infra*), and filtering; the solution is yellow, has an alkaline reaction, and is easily decomposed with formation of OsO_4, NH_3, and a black pp. (Claus, *J. pr.* 79, 28).

Osmyl-tetrammonium chloride $OsO_2(NH_3.NH_3Cl)_2$ (*Oxyosmiumdiammonium chloride*). The formula is sometimes written $OsO_2Cl_2.4NH_3$, and the salt is called *ammoniated osmium oxychloride*; the formula is also written $OsO_2.4NH_3.Cl_2$, and the salt is called *osmyl-ditetramine chloride* (Gibbs, *Am.* 3, 233); Fremy (*A. Ch.* [3] 12, 522) wrote the formula $OsO_2(NH_2)_2.2NH_4Cl$, calling the salt *osmiamide-ammonium chloride*; Claus and Jacobi (*J. pr.* 79, 28; 85, 142; 90, 65) gave the formula $Os(NH_3)_4Cl_2.2H_2O$, and the name *osmio-diammonio-chloride*. The investigations of Gibbs (*Am.* 3, 233) confirmed the empirical formula $OsO_2Cl_2.4NH_3$. Obtained as a yellow crystalline pp. by adding NH_4Cl to K_2OsO_4Aq (Fremy, *A. Ch.* [3] 12, 522) (?$K_2OsO_4Aq + 4NH_4Cl = OsO_2(NH_3.NH_3Cl)_2 + 2KClAq + 2H_2O$). Slightly sol. cold water, more sol. hot water, insol. NH_4ClAq. May be crystallised from water containing HCl; ppd. from solution by conc. HClAq. Aqueous solution quickly decomposes, giving off OsO_4; on evaporation a brown solid is obtained, which behaves like $OsO(NH_3.OH)_2$; the solution gives a fine violet colour with K_4FeCy_6Aq (Gibbs, *l.c.*). The compound is decomposed by heat, giving a residue of Os.

The *chloroplatinate* is obtained, as orange-yellow crystals, slightly sol. cold water, by boiling $OsO_2(NH_3.NH_3Cl)_2$ with $PtCl_4Aq$ (Gibbs, *l.c.*).

Osmyl tetrammonium sulphate, nitrate, &c. The *sulphate* is obtained by pouring K_2OsO_4Aq into conc. cold $(NH_4)_2SO_4Aq$; small orange-yellow crystals, easily sol. hot water (Gibbs, *l.c.*). The *nitrate* is obtained by a similar reaction, and the *oxalate* also; using cold conc. NH_4NO_3Aq

and $(NH_4)_2C_2O_4Aq$ instead of $(NH_4)_2SO_4Aq$ (Gibbs, *l.c.*).

Osmium, chlorides of. Two chlorides of Os have been prepared, $OsCl_2$ and $OsCl_4$; $OsCl_3$ is known in solution; no chloride has yet been gasified; these are the only haloid compounds of Os known at present, except $OsCy_2$ be classed as a haloid compound. $OsCl_3$ and $OsCl_4$ combine with alkali chlorides to form $OsCl_3.3MCl$ and $OsCl_4.2MCl$ respectively; $OsCl_2$ also probably forms double salts, but they have not been isolated satisfactorily. $OsCy_2$ forms an acid, H_4OsCy_6, from which various salts (osmocyanides) are obtained. $OsCl_2$ and $OsCl_4$ are formed by direct union of Cl with Os.

Osmous chloride $OsCl_2$ (*Osmium dichloride. Osmosochloride*). Obtained by heating finely divided Os in a long tube in a stream of dry Cl. Two sublimates are obtained; the less volatile (green) is $OsCl_2$, the more volatile (red) is $OsCl_4$. As thus prepared $OsCl_2$ forms dark-green deliquescent needles, which probably contain H_2O; by heating again in perfectly dry Cl, $OsCl_2$ is obtained free from moisture as a nearly black sublimate (Claus a. Jacobi, *J. pr.* 90, 65). An indigo-blue solution of $OsCl_2$ may be prepared by dissolving $OsO.xH_2O$ in HClAq; the solution soon becomes violet, then dark red, and then yellow from formation of $OsCl_3$ and $OsCl_4$; the yellow solution again becomes blue by the action of reducers (C. a. J., *l.c.*). $OsCl_2$ dissolves in water, forming a green liquid, which is decolourised and decomposed on dilution with formation of Os, OsO_4Aq, and HClAq. Solutions of $OsCl_2$ in alkali chloride solutions are not decomposed by dilution; double salts are probably present (C. a. J.). Berzelius said that double salts of $OsCl_2$ are formed by the action of alcohol on the salts M_3OsCl_6 and M_4OsCl_6 (*P.* 13, 435, 527). $OsCl_2$ is sol. alcohol and ether. The aqueous solution conducts electricity, but the alcoholic and ethereal solutions do not (*v.* Hampe, *Z.* 11, 1549; 12, 23).

Osmoso-osmic chloride $OsCl_3$ (*Osmium trichloride. Osmochloride. Osmium sesquichloride*). This chloride is only known in solution, and in combination with alkali chlorides. The brown to purple solution obtained by the action of air on $OsO.xH_2O$ in HClAq probably contains $OsCl_3$ (C. a. J.). By treating a solution of OsO_4 in HClAq with Hg, and evaporating *in vacuo* over conc. H_2SO_4, Berzelius (*P.* 13, 435, 527) obtained a purple, varnish-like substance, which perhaps was $OsCl_3$.

Double Salts.—*Ammonium-osmium trichloride* (*Ammonium chlorosmite*) $2(OsCl_3.2NH_4Cl).3H_2O$. Reddish-brown crystals; obtained by passing H_2S into OsO_4 in much HClAq till the solution is red, adding NH_4Cl, and evaporating (Claus, *J. pr.* 79, 28). The salt dissolves in water with a dark-purple colour, which is unchanged by addition of alkali, but reduction begins on warming. On heating, Os and NH_4Cl are formed (Berzelius, *l.c.*).

Potassium-osmium trichloride (*Potassium chlorosmite*) $2(OsCl_3.3KCl).6H_2O$. Formed by strongly heating in Cl a mixture of equal parts KCl and powdered Os, dissolving in water, crystallising out K_2OsCl_6, and evaporating the mother-liquor; also by dissolving KOH in conc. OsO_4Aq, adding NH_3Aq, and when the solution is yellow and before K_2OsO_4 separates, saturating with HClAq and evaporating to dryness on a water-bath, when the salt is obtained on the bottom of the basin, while KCl and NH_4Cl are deposited on the upper parts. Forms dark brownish-red crystals; easily sol. water, with deep cherry-red colour; easily sol. alcohol, insol. ether. The salt loses $3H_2O$ in air, and the rest at 150°–180°. The aqueous solution easily decomposes with separation of $Os_xO_yCl_z$.

Osmio chloride $OsCl_4$ (*Osmium tetrachloride. Osmichloride*). Obtained, as a dark-red powder, by heating finely-powdered Os in dry Cl; $OsCl_2$ is formed at the same time. $OsCl_4$ is the more volatile of the two chlorides. In presence of moisture, becomes cinnabar-red, and then forms yellow needles (? $OsCl_4.xH_2O$). Dissolves in a little water to form a yellow solution, which is decomposed and decolourised on dilution (Berzelius, *l.c.*). $OsCl_4$ is a non-conductor of electricity (Hampe, *Z.* 11, 1549; 12, 23). $OsO_2.2H_2O$ dissolves in conc. HClAq, forming a dark greenish-brown solution, which probably contains $OsCl_4$.

Double salts.—*Potassium-osmium tetrachloride* (*Potassium chlorosmate*) K_2OsCl_6 ($=OsCl_4.2KCl$). Obtained by heating an intimate mixture of equal parts KCl and finely-powdered Os in dry Cl to low redness, removing excess of KCl by a little water, dissolving the residue in hot water, and allowing to crystallise (Berzelius, *l.c.*). Claus a. Jacobi (*l.c.*) obtained the salt by adding KCl to OsO_4 in HClAq, then adding alcohol and evaporating. Dark-brown lustrous octahedra; cinnabar-red when powdered. Sol. water, forming a yellow solution, from which alcohol ppts. the salt, incompletely, as a red crystalline powder. Not decomposed at low redness, but at a higher temperature Os and KCl are formed. OsO_4 is produced by distilling HNO_3 over K_2OsCl_6 (Berzelius, *l.c.*). Is not acted on by SO_2Aq at ordinary temperatures (K_2IrCl_6 is reduced). KOHAq does not decompose a cold solution of K_2OsCl_6, but on warming the solution becomes blue, and then suddenly ppts. black $OsO_2.2H_2O$ (Claus, *l.c.*; other reactions of K_2OsCl_6Aq are given).

Ammonium chlorosmate, silver chlorosmate, and *sodium chlorosmate* are described by Claus a. Jacobi (*J. pr.* 79, 28; 85, 142; 90, 65; *A.* 63, 355).

Supposed compound of Osmium hexachloride. Berzelius (*P.* 13, 435, 527; 15, 208) obtained a brown salt, which he supposed to be a compound of NH_4Cl and $OsCl_6$, by saturating OsO_4 with NH_3Aq, after a time adding excess of HClAq, digesting for some days with Hg, filtering, and evaporating. According to Claus (*l.c.*), the salt is $2(OsCl_3.2NH_4Cl).3H_2O$ (*v. supra*; *Ammonium-osmium trichloride*).

Osmium, cyanide of, $OsCy_2$; and *osmocyanhydric acid* and its salts, H_4OsCy_6; *v.* Cyanides, vol. ii. p. 343.

Osmium, hydrated oxides or hydroxides of, *v. Osmium, oxides and hydrated oxides of,* p. 645.

Osmium, nitride of. The brass-yellow substance, obtained by passing H over the pp. produced by adding HNO_3 to K_2OsO_4Aq, is probably a nitride of Os (Claus, *P.* 65, 202).

Osmium, nitrogen-containing acid of, *and*

its salts. $H_2N_2Os_2O_6Aq$ or ? $H_2N_2Os_2O_5Aq$. This acid is generally known as *osmiamic acid.* An aqueons solution of this acid is obtained by decomposing the Ba salt by the equivalent quantity of H_2SO_4Aq, or by treating the moist Ag salt with HClAq, and filtering. The clear yellow solution remains unchanged for some days if dilute; but if it be concentrated, OsO_4 and a black pp. containing Os are formed, and gas is evolved. The aqueous solution of the acid evolves CO_2 from carbonates, and decomposes KCl; Zn dissolves in it, with evolution of gas and partial decomposition of the acid. The solution is decomposed by acids on warming, with production of OsO_4 (Fritzsche a. Struve, *J. pr.* 41, 97). F. a. S. gave the formula $H_2N_2Os_2O_5$; this was upheld by Claus (*J. pr.* 90, 65). Gerhardt (*J. Ph.* [3] 12, 304) gave the formula $H_2N_2Os_2O_6$. The K salt is obtained by the action of NH_3Aq on OsO_4 in excess of KOHAq; the reaction is expressed thus by F. a. S.: $2OsO_4 + 2NH_3 + Aq = H_2N_2Os_2O_5Aq + O + 2H_2O$; Claus gives the equation $6OsO_4 + 8NH_3 + Aq = 3H_2Os_2N_2O_5Aq + N_2 + 9H_2O$. According to F. a. S. no gas is evolved during the reaction. If this is correct neither of the equations can express the change which occurs. The salts of osmiamic acid explode when heated; some explode when struck.

Potassium osmiamate $K_2N_2Os_2O_6$ or ? $K_2N_2Os_2O_5$. Prepared by dissolving solid OsO_4 in conc. KOHAq, to which conc. NH_3Aq has been added. The solution is clear yellow, and deposits yellow crystals of the salt. Claus a. Jacobi (*l.c.*) dissolve KOH in very dilute OsO_4Aq, add ½ vol. NH_3Aq, and evaporate rapidly until the salt begins to crystallise out, after which crystallisation is allowed to proceed. Citron yellow, tetragonal crystals. Sol. warm water. also in alcohol, sl. sol. cold water, insol. ether. Explodes at c. 180°. Decomposed by conc. HClAq, with evolution of Cl and formation of two kinds of red crystals (*v.* F. a. S., *l.c.*).

Silver osmiamate $Ag_2N_2Os_2O_6$ or ? $Ag_2N_2Os_2O_5$. A citron-yellow crystalline powder; sl. sol. water or dilute HNO_3Aq; sol. NH_3Aq, forming therewith a crystalline compound; blackens in light; explodes at 80°, also when struck by a hammer. Prepared by dissolving OsO_4 in an ammoniacal solution of a salt of Ag, and adding excess of HNO_3Aq; or by adding excess of HNO_3Aq, followed by solution of a salt of Ag, to OsO_4 dissolved in NH_3Aq.

Ammonium, barium, mercurous, sodium, and *ammoniated zinc, osmiamates* have been prepared (F. a. S., *l.c.*).

Osmium, oxides and hydrated oxides of. Four oxides of Os are known; OsO, Os_2O_3, OsO_2, and OsO_4. Salts in which OsO_3 acts as the negative radicle have been prepared (*v. infra, Osmium, salts of oxyacids of*). A hydrate of OsO has been obtained, but not pure; it rapidly absorbs O; the hydrate $OsO_3.3H_2O$ is known, as are also the hydrates $OsO_2.H_2O$ and $OsO_2.2H_2O$. No oxy-salts have been obtained directly from the oxides of Os; a few oxy-salts corresponding with OsO are known. OsO_4 acts as a weak acidic anhydride; this oxide is easily reduced to OsO_2, or to Os. OsO_4 is the only oxide prepared by the direct union of Os with O. Chlorides corresponding with OsO and OsO_2 have been obtained, and the chloride $OsCl_3$ which corresponds with Os_2O_3 probably exists in solution (*v. Osmium, chlorides of*, p. 644).

Osmous oxide OsO (*Osmium monoxide*). A greyish-black solid, insol. acids; obtained by heating in a stream of CO_2 a mixture of Na_2CO_3 and $OsSO_3$ or $OsSO_3.2K_2SO_3.2KHSO_3.4H_2O$, and washing the residue with water (Claus a. Jacobi, *J.pr.* 85, 142; 90, 65). The salt $OsSO_3$ is formed by evaporating OsO_4Aq with excess of SO_2; the salt $OsSO_3.2K_2SO_3.2KHSO_3.4H_2O$ is formed by heating K_2OsCl_6Aq with K_2SO_3, and washing with water the powder which separates. *Hydrated osmous oxide*, $OsO.xH_2O$, was obtained by C. a. J. by the action of warm, very conc. KOHAq on $OsSO_3$, in absence of air; it forms a blue-black pp. which very rapidly absorbs O from the air. Berzelius obtained a greenish-black pp. by boiling $OsCl_2$ in KClAq with KOHAq; this pp. was supposed to be $OsO.xH_2O$, but C. a. J. say it cannot be washed free from alkali. A few salts are known corresponding with OsO, *e.g.* $OsSO_3$, but none is obtained directly from the oxide.

Osmo-osmio oxide Os_2O_3 (*Osmium sesquioxide*). A black powder; insol. acids. Obtained by gently heating, in a stream of CO_2, a mixture of $K_3OsCl_6.3H_2O$ and Na_2CO_3, and washing with water (C. a. J., *l.c.*). Deville a. Debray (*C. R.* 82, 1076) say that this oxide is often formed, as copper-red crusts, in the preparation of Os, by passing OsO_4 vapour mixed with N through a hot tube lined with C, the lining of C being formed by passing C_6H_6 vapour through the tube heated to redness. Berzelius supposed that a compound of Os_2O_3 with NH_3 was formed by the action of NH_3Aq on OsO_4Aq; but the pp. thus formed was shown by C. a. J. to be $OsO(NH_3.OH)_2$ (*v. Osmosyl-diammonium hydroxide*, p. 643). No oxy- salts are known corresponding with Os_2O_3; a solution of $OsCl_3$ has been prepared.

Hydrated osmo - osmic oxide $Os_2O_3.3H_2O$; a brown-red pp., somewhat sol. cold KOHAq, sol. acids even after drying; obtained by adding KOHAq to K_2OsCl_6Aq (C. a. J., *l.c.*).

Osmic oxide OsO_2 (*Osmium dioxide*). Obtained by Berzelius (*P.* 13, 435, 527; 15, 208) by heating a mixture of K_2OsCl_6 and Na_2CO_3 in CO_2, washing the residue with water, and then with HClAq; as thus prepared OsO_2 forms a greyish-black powder. Claus a. Jacobi (*l.c.*) obtained OsO_2 in the form of a copper-red, metal-like solid, by strongly heating $OsO_2.2H_2O$ in a covered crucible (OsO_4, H, and H_2O are also formed). $OsO_2.2H_2O$ is obtained by the action of acids on K_2OsO_4Aq. OsO_2 may be heated to redness in absence of air (Berzelius); but Claus says that OsO_4 and Os are formed. Heated in air, or acted on by HNO_3 and HClAq, OsO_4 is produced. Reduced by H at ordinary temperatures. Detonates when heated with combustible bodies. A sulphate corresponding with OsO_2 is said to be prepared by the action of cold HNO_3Aq on OsS_2, but little is known of its properties. The corresponding chloride, $OsCl_4$, is known.

Hydrated osmic oxide $OsO_2.2H_2O$; a black pp. obtained by adding very dilute H_2SO_4Aq to K_2OsO_4Aq, OsO_4 being formed at the same time (C. a. J., *l.c.*). The moist hydrate dissolves in HClAq, HNO_3Aq, or H_2SO_4Aq; oxidation begins

very quickly, with change of colour from purple to yellow-brown, green, and brownish-yellow on heating. From the solution in HClAq, Zn ppts. Os (Wöhler, *A.* 140, 256). By heating $OsO_2.2H_2O$ to 200° in dry N, Fremy obtained the hydrate $OsO_2.H_2O$ (*A. Ch.* [3] 12, 515).

Osmium tetroxide OsO_4 (*Perosmic anhydride.* Often called *perosmic acid*, and formerly generally known as *osmic acid*). Mol. w. 254·84. V.D. 128·5 at c. 280° (Deville a. Debray, *C. R.* 82, 1076).

Formation.—1. By heating Os in air or O.—2. By heating Os, or any of the lower oxides, with HNO_3 or *aqua regia.*—3. By the action of dilute acids on K_2OsO_4Aq; $OsO_2.2H_2O$ being formed at the same time.—4. According to Claus (*J. pr.* 79, 28) by the action of Os on steam; H being evolved.

Preparation.—1. Finely powdered Os is gently warmed in a stream of dry O; the Os is placed in one bulb of a two-bulbed tube, and the OsO_4 condenses in the second bulb.—2. Three parts osm-iridium are fused with 1 part KNO_3, the cold mass is dissolved in water, the solution is neutralised by H_2SO_4Aq, and OsO_4 is distilled off into a cold receiver.

Properties.—Long, colourless, translucent, monoclinic, needles (Mallet, *Am. S.* [2] 29, 49). Melts considerably under 100°, and boils a few degrees above its melting-point. OsO_4 is very volatile; the vapour smells abominably, and is extremely poisonous, attacking the eyes and lungs; Deville nearly lost his eyesight while working with OsO_4 (*v.* D. a. D., *A. Ch.* [3] 56, 400). Claus says the best antidote is H_2S gas. The V.D. was determined by D. a. D. at 246°–285°; it agrees with the formula OsO_4. OsO_4 may be vapourised in H; if the mixed vapours are passed through a hot tube, Os is deposited. OsO_4 is slowly dissolved by water, the solution does not react acid; sol. alcohol or ether, solutions are reduced with ppn. of Os.

Reactions.—1. Reduced to Os by heating with *hydrogen*; also by heating in a *gas-flame*; an aqueous solution of OsO_4 is readily reduced by most *metals*; the solution is also reduced by *phosphorus*, *ferrous sulphate*, *stannous chloride*, *sulphurous acid* (a blue liquid is produced by SO_2Aq, perhaps containing an oxide which has not been isolated), and by many *carbon compounds* (*e.g.* $H.CO_2H$, tannin, sugar, alcohol, &c.) (*v.* Tennant, *T.* 1804. 411; Berzelius, *P.* 13, 435, 327; 15, 208; Döbereiner a. Weiss, *A.* 14, 17, 251; Butlerow, *A.* 84, 278; Claus a. Jacobi, *J. pr.* 90, 65).—2. A large excess of *ammonia solution* evolves N, and ppts. $OsO(NH_3.OH)_2$ (*v. Osmosyl-diammonium hydroxide*, p. 643).—3. OsO_4 dissolves in *potash*, forming a red-yellow liquid which probably contains K perosmate (*q. v.* under *Osmium, salts of oxyacids of, infra*).—4. *Hydrogen sulphide* ppts. an oxysulphide (*q. v.*) from OsO_4Aq; on saturating OsO_4Aq with H_2S, and adding an acid, OsS_4 is ppd. (*v. Osmium, sulphides of*, p. 647).—5. *Hydrochloric acid* does not react with OsO_4; but on addition of KOHAq, K_2OsCl_6 is produced. OsO_4 is a very weak acidic anhydride: an aqueous solution does not affect the colour of litmus, nor does it decompose carbonates; KOHAq probably forms K perosmate.

Osmium, oxyacids of. No oxyacid of Os has been isolated; salts of the hypothetical H_2OsO_4 (osmates) are known, and some of the reactions of OsO_4 indicate the existence of unstable salts derived from the oxide OsO_4 (*v. infra, Osmium, salts of oxyacids of*).

Osmium, oxychloride of. The black pp. obtained by boiling dilute K_2OsCl_6Aq is probably an oxychloride (Claus a. Jacobi, *J. pr.* 90, 65).

Osmium, oxysulphides of. The pp. obtained by passing H_2S into OsO_4Aq is said by von Meyer to have the composition $Os_3O_5S_7.3H_2O$, and to be changed to $2OsO_3S.3H_2O$ by the action of air (*J. pr.* [2] 16, 77). Dried at 180°–200°, OsO_3S is obtained (von M., *l.c.*).

Osmium, phosphide of. A phosphide of Os is said to be formed by heating Os in P vapour; it appears black if prepared at a moderate temperature, but white and metal-like if produced by heating strongly; it burns in air to OsO_4 and osmous phosphate (Berzelius, *P.* 13, 435, 527; 15, 208).

Osmium, salts of. Very few salts have been obtained by replacing the H of oxyacids by Os. Osmium sulphite, $OsSO_3$, is formed by evaporating OsO_4Aq with SO_2Aq; a complex salt $OsSO_3.2K_2SO_3.2KHSO_3.4H_2O$ is obtained by heating K_2OsCl_6 with K_2SO_3Aq; osmous phosphate and sulphate are also said to exist, but they have not been analysed (Berzelius). An osmic sulphate is stated to be produced by the action of cold HNO_3Aq on OsS_2 (Berzelius). No salt of Os has been formed by the direct reaction of Os or any of its oxides with an oxyacid (*v.* Sulphites, Sulphates).

Osmium, salts of oxyacids of. Some salts of the hypothetical *osmic acid*, H_2OsO_4, have been isolated; and there are indications of the existence of alkali *perosmates*, *i.e.* salts derivable from OsO_4.

Osmates $M^I_2OsO_4$ (formerly called *Osmites*). Neither the acid H_2OsO_4, nor the anhydride OsO_3, has been isolated (*cf.* Mallet, *Am. S.* [2] 29, 49). Alkali osmates are obtained by the reducing action of alcohol on OsO_4 in KOHAq; a Ba salt is formed by the prolonged reaction of warm BaOAq on OsO_4 in a closed vessel; osmates of Ca, Pb, and Sr are obtained as insoluble pps. from the alkali salts.

Potassium osmate $K_2OsO_4.2H_2O$. A violet-coloured, crystalline pp. of this composition is formed by adding alcohol to OsO_4 dissolved in KOHAq; the solution is red, then becomes colourless, and deposits the salt. Fremy obtained the salt in large octahedra by adding KNO_2Aq to OsO_4 in large excess of KOHAq (*J. pr.* 33, 411). According to Claus (*J. pr.* 34, 173, 424) $K_2OsO_4.2H_2O$ is obtained by warming OsO_4 in an excess of KOHAq; this reaction is similar to the reduction of $KMnO_4Aq$ to K_2MnO_4Aq by KOH. Violet-red octahedra. Sol. water, insol. alcohol or ether; slightly sol. conc. salt solutions (Gibbs, *Am. S.* [2] 31, 70). An aqueous solution decomposes rapidly on warming to K perosmate and $OsO_2.xH_2O$. H_2SO_4Aq forms OsO_4 from K_2OsO_4Aq, and separates $OsO_2.xH_2O$ (Claus a. Jacobi, *l.c.*). HNO_3Aq produces a similar change (Fremy, *l.c.*). SO_2Aq produces a blue solution. NH_4ClAq forms $OsO_2(NH_3.NH_2Cl)_2$, and $(NH_4)_2SO_4Aq$ produces $OsO_2(NH_3.NH_3)_2SO_4$ (*v. Osmyl-tetrammonium*

chloride and *sulphate*, p. 643). NH_3Aq is said to form $OsO_2(NH_2)_2$ (Fremy, *l.c.*).

Barium osmate $BaOsO_4.H_2O$ (Claus, *J. pr.* 34, 173, 224); *Calcium, lead, sodium,* and *strontium osmates* have been obtained (Fremy, *J. pr.* 33, 411).

PEROSMATES (formerly called *osmates*). These salts have not been prepared pure. Fremy (*J. pr.* 33, 409) says a perosmate of K is formed by dissolving OsO_4 in large excess of KOHAq, and the salt is decomposed on dilution; the solution in excess of KOHAq is colourless, but absorbs O and becomes brown; on boiling, K_2OsO_4 is formed, and an oxide of Os containing more O than OsO_4 is volatilised. On the other hand, Claus (*J. pr.* 85, 142; 90, 65) says that the greater part of the OsO_4 can be distilled off from a solution of this oxide in excess of KOHAq, but that some decomposes to K_2OsO_4Aq and O. Claus also says that OsO_4 distils off, at 60°, when Cl is passed into $OsO_2.xH_2O$ suspended in a large excess of KOHAq. From a conc. solution of OsO_4 in KOHAq, HNO_3Aq ppts. OsO_4 mixed with $OsO_2.xH_2O$, according to Wöhler (*A.* 140, 256). Wöhler (*l.c.*) melted Os with KOH and KNO_3, and obtained a black solid which formed a deep-red solution in water. This solution was supposed by Wöhler to contain K perosmate; only a very little OsO_4 was obtained by distilling, and the residual liquid deposited K_2OsO_4 on cooling. The mother-liquor from the K_2OsO_4 was yellow; on treatment with CO_2 it became colourless, and then violet, and deposited OsO_4 and a greyish-violet pp.

Osmium, sulphides of. A sulphide of Os is formed by heating Os with S (Berzelius, *P.* 13, 435, 527; 15, 208).

OSMIC SULPHIDE OsS_2 (*Osmium disulphide*). A dark brownish-yellow solid; slightly soluble in water. Produced, according to Fremy (*J. pr.* 33, 409), by passing H_2S into K_2OsO_4Aq; according to Claus (*J. pr.* 79, 28), also by passing H_2S into K_2OsCl_6Aq.

OSMIUM TETRASULPHIDE $OsS_4.xH_2O$. Obtained by saturating OsO_4 in HClAq with H_2S; on attempting to dry the pp. it is partly oxidised; above 100°, the pp. burns to OsO_4 and SO_2; easily oxidised by HNO_3Aq; heated in absence of air, $OsS_2.OsS_3$ is said to be produced (Berzelius; Claus). The pp. obtained by passing H_2S into OsO_4Aq is an *oxysulphide* (*q.v.*).

M. M. P. M.

OSMOCYANIDES and *Osmocyanhydric acid* v. CYANIDES, vol. ii. p. 343.

OSMOSE. When two liquids are separated by the intervention of a porous diaphragm, a flow of liquid takes place from one side of the septum to the other, or sometimes an unequal flow of the two liquids in opposite directions, so that the quantity of liquid increases on one side of the septum and diminishes on the other. This phenomenon was originally designated by the correlative terms Endosmose and Exosmose, but it is better expressed by the shorter word Osmose (from ὠσμός, impulsion), which includes the two former. For the application of osmotic methods to chemical questions *v.* MOLECULAR WEIGHTS, this vol. p. 417; also PHYSICAL METHODS; section, *Electrical methods*.

OSOTRIAZOLE $C_2H_3N_3$ *i.e.* $NH{<}^{N:CH}_{N:CH}$ [22·5°]. (204°) at 715 mm. Formed by heating its carboxylic acid. Sol. water and alcohol, insol. ligroïn (Pechmann, *A.* 262, 320).—B'HCl. —B'HgCl: glittering needles.

Benzoyl derivative $NBz{<}^{N:CH}_{N:CH}$. [100°].

OSOTRIAZOLE CARBOXYLIC ACID $NH{<}^{N:CH}_{N:C.CO_2H}$. [211°]. Formed by the action of $KMnO_4$ on amido-phenyl-osotriazole carboxylic acid, which is got by reducing the nitro- acid formed by nitrating the acid produced by the action of soda on the phenyl-hydrazide of di-nitroso-acetone (Pechmann, *A.* 262, 315). Crystalline powder, v. sol. boiling water.—CaA'_2 2aq.

OSOTRIAZONES and **OSOTETRAZONES** *v.* HYDRAZONES.

OSSEÏN *v.* PROTEÏDS, *Appendix C.*

OSTRUTHIN $C_{14}H_{17}O_2$ (Gorup-Besanez, *A.* 183, 321); $C_{18}H_{20}O_3$ (Jassoy, *C. C.* 1890 [i] 766). [115°]. Occurs in the roots of *Imperatoria Ostruthium.* Triclinic crystals, v. sl. sol. boiling water, v. sol. alcohol and ether. Its alcoholic solution exhibits blue fluorescence. Forms a crystalline compound with dry HCl.

Acetyl derivative [78°]. Plates.

OTOBITE $C_{24}H_{26}O_5$. [133°]. Occurs in the fruit of *Myristica otoba* (Uricoechea, *A.* 91, 370). Pearly prisms (from ether), insol. water.

OUABAIN $C_{30}H_{46}O_{12}$. [c. 185°]. S.·65 at 11°; S. (alcohol) 3·75 at 11°. $[\alpha]_D = -33°$. A poisonous glucoside present in Ouabaio root, used as arrow-poison, and in the seeds of the glabrous *Strophantus* of Gabon (Arnaud, *C. R.* 106, 1011; 107, 348, 1162; *Bl.* [3] 1, 10). Rectangular plates (containing 7aq) v. sl. sol. water. Its solution is ppd. by tannin. It yields a sugar and a resin on boiling with acids.—BaA'_2: deliquescent pp.

OXALACETIC ACID $C_4H_4O_5$. *Oxaloxyl-acetic acid.*

Oxim $CO_2H.C(NOH).CH_2.CO_2H$. [125°]. Formed by the action of alcoholic NaOH on the ether $CO_2Et.C(NOH).CH_2.CO_2H$ [107°], which is obtained by the action of water on the dihydride of di-nitroso-di-oxy-terephthalic ether (Cramer, *B.* 24, 1204). An isomeric oxim $CO_2Et.C(NOH).CH_2.CO_2H$ [54°] is formed from oxalacetic acid and hydroxylamine. It yields $CO_2H.C(NOH)CH_2CO_2H$ [88°], whence AcCl forms an anhydride $C_4H_3O_4$ [105°] yielding $C_4H_2AcO_4$ [105°].

Phenylhydrazide of the *methyl ether* $CO_2Me.CH_2.C(N_2HPh).CO_2Me$. [118°]. Mol. w. 257 (obs.); (calc. 250). Formed from di-methyl acetylene dicarboxylate and phenyl-hydrazine (Buchner, *B.* 22, 2930). Plates. Yields oxy-phenyl-pyrazole carboxylic acid on saponification.

Mono-ethyl ether $CO_2Et.CH_2.CO.CO_2H$. [97°]. Obtained from the di-ethyl ether and cold dilute KOH (Wislicenus, *B.* 19, 3226; *A.* 246, 323). Needles, v. sol. water. Its aqueous solution is coloured deep red by $FeCl_3$.

Anilide of the ethyl ether $CO_2Et.CO.CH_2.CO.NHPh$. [88°]. Formed from oxalic ether, acetanilide, and NaOEt (Wislicenus a. Sattler, *B.* 24, 1250). Needles, v. sol. alcohol.

p-Toluide of the ethyl ether. [135°].

Ethyl anilide of the ethyl ether $CO_2Et.CO.CH_2.CO.NEtPh$. [69°]. Formed from

NaOEt, oxalic ether, and NEtAcPh (Wislicenus a. Sattler, *B.* 24, 1254).—$Cu(C_{14}H_{16}NO_4)_2$. [139°].

Di-ethyl ether $CO_2Et.CH_2.CO.CO_2Et$. 132° at 24 mm.). S.G. $\frac{23\cdot5}{4}$ 1·159. Formed by the action of sodium on an ethereal solution of oxalic and acetic ethers (Wislicenus, *B.* 19, 3225; 20, 3392; *A.* 246, 315). Oil. $FeCl_3$ colours its alcoholic solution red.

Reactions.—1. Decomposed by dilute acids into acetic and oxalic acids.—2. Dilute (10 p.c.) H_2SO_4 yields pyruvic acid.—3. *Sodium* forms the compound $CO_2Et.CHNa.CO.CO_2Et$, which reacts with alkyl iodides, forming alkyl-oxal-acetic ethers $CO_2Et.CHX.CO.CO_2Et$. The copper compound $Cu(C_8H_{11}O_5)_2$ crystallises from alcohol in green needles [163°].—4. *Phenyl-hydrazine* reacts forming a phenyl-hydrazide $CO_2Et.CH_2.C(N_2HPh)CO_2Et$ [78°], crystallising in plates, and forming $CO_2Et.C\genfrac{<}{}{0pt}{}{CH_2.CO}{N\ \ .NPh}>$ [182°] on heating.—5. *Aniline* at 0° forms $CO_2Et.CH_2.C(NPh).CO_2Et$ (c. 200° at 10 mm.), which gives no colour with alcoholic $FeCl_3$. The condensation-products include $C_{14}H_{15}NO_3$ [108°] and $C_{12}H_{11}NO_3$ [213°] (Wislicenus a. Spiro, *B.* 22, 3349).—6. Aqueous KOAc yields $CO_2Et.CH:C(CO_2H).CH(CO_2Et).CO.CO_2Et$, which forms the crystalline salts BaA'_2 2aq and PbA'_2 (Claisen a. Hori, *B.* 24, 124).—7. Its oxim is reduced by sodium-amalgam to mono-ethyl aspartates $CO_2H.CH(NH_2).CH_2.CO_2Et$ [201°] and $CO_2H.CH_2.CH(NH_2).CO_2Et$ [165°] (Piutti, *C. C.* 1888, 68, 1459).—8. *Benzamidine hydrochloride* and dilute (10 p.c.) aqueous caustic soda yields $CO_2Et.CO.CH_2.CO.NH.CPh:NH$ [180°] (Pinner, *B.* 22, 1628, 2615).

Reference.—AMIDO-OXALOXYL-ACETIC ACID.

OXALAMIDO-BENZOIC ACID *v.* CARBOXY-PHENYL-OXAMIC ACID.

OXALANTIN $C_6H_6N_4O_6$. Formed by reducing alloxanic acid with zinc and HClAq (Limpricht, *A.* 111, 133; *cf.* Schlieper, *A.* 56, 2). Small crystals, sl. sol. water. Decomposed by alkalis into NH_3 and oxaluric acid.

OXALBUTYRIC ETHER $CO_2Et.CO.CHEt.CO_2Et$. (138° at 20 mm.). Formed from oxalic ether, butyric ether, and NaOEt (Arnold, *A.* 246, 337). Oil. Gives a red colour with $FeCl_3$.

OXALETHYLAMYLINE *v.* ETHYL-BUTYL-GLYOXALINE.

OXAL-ETHYL-ETHYLINE *v.* METHYL-ETHYL-GLYOXALINE.

OXALETHYLINE *v.* METHYL-ETHYL-GLY-OXALINE.

OXALETHYLŒNANTHYLINE *v.* ETHYL-HEXYL-GLYOXALINE.

OXAL ETHYL PROPYLINE *v.* DI-ETHYL-GLYOXALINE.

OXALIC ACID $H_2C_2O_4$ 2aq, *i.e.* $CO_2H.CO_2H$ 2aq or $C(OH)_3.C(OH)_3$.[187°] (when anhydrous) (Staub a. Smith, *B.* 17, 1742 *note*). S.G. (hydrated) $\frac{18\cdot5}{4}$ 1·653 (Clarke, *Am.* 2, 174). S. (of $H_6C_2O_6$) 9·5 at 14·5° (Nichols, *C. N.* 22, 14); (of $H_2C_2O_4$) 5·3 at 10°, 10·2 at 20°; 120 at 90° (Alluard, *C. R.* 59, 500); 5·5 at 10°; 8·8 at 20°; 63·8 at 70°. S. (alcohol) 23·5 at 15° (Burgoin, *Bl.* [2] 29, 243). S. (ether) 1·27 at 15° (Miczynski, *M.* 7, 257). R_∞ 36·74 (in a 7·41 p.c. aqueous solution) (Kanonnikoff, *J. pr.* [2] 31, 347). H.C.v. 61,100; H.C.p. 60,200. H.F. 196,800 (Stohmann, *J. pr.* [2] 40, 204); 198,000 (von Rechenberg). S.H. (0°-50°) ·3359 (Hess, *A. Ch.* [2] 35, 410).

Heat of neutralisation 28,100.

Occurrence.—As acid potassium salt in sorrel (*Oxalis acetosella* and *Rumex acetosa*) (Savary, A.D. 1773; Wiegler, A.D. 1779); as sodium salt in *Salsola* and *Salicornia*; as calcium salt in the root, bark, and leaves of many plants, (often found as crystals, *raphides*), in urine, urinary calculi, and in the Malpighian vessels of the caterpillar of *Sphinx Convolvuli.* Calcium oxalate is found also in many lichens, and as the mineral Whewellite. Ferrous oxalate occurs in lignite beds; and ammonium oxalate in guano. Free oxalic acid occurs in some fungi (*e.g. Fistulina hepatica* (Hamlet a. Plowright, *C. N.* 36, 93).

Formation.—1. By the oxidising action of fused potash or of nitric acid on alcohol, glycol, sugars, starch, cellulose, citric, tartaric, myristic, and other fatty acids. Also by oxidising acetic acid and phenol with alkaline $KMnO_4$ (Japp, *C. J. Proc.* 4, 91).—2. Ammonium oxalate is among the products of the decomposition of cyanogen by water.—3. By heating sodium or potassium formate above 400° (Merz a. Weith, *B.* 15, 1507). 4. By the action of NaOEt on di-bromo-acetic ether.—5. By passing CO_2 over a mixture of sodium and sand at about 360° (Drechsel, *Z.* [2] 4, 120).—6. By heating C_2Cl_6 with dry KOH for some days at 220° (Geuther, *A.* 111, 174). C_2Cl_4 with dry KOH at 200° forms oxalate and hydrogen.—7. By the spontaneous decomposition of $CH_3.CH(ONO_2).CO_2H$ (Henry, *B.* 12, 1837).—8. By the action of damp oxygen upon $CCl_2:CCl(OMe)$ (Henry).—9. A product in the preparation of picric acid from phenol (Perkin, *C. J. Proc.* 4, 91).—10. By oxidising chloranilic acid (Groves, *C. J. Proc.* 4, 91).—11. A by-product in the preparation of nitrous ether (Frickhinger, *Ar. Ph.* [3] 24, 1065).

Preparation.—By heating sawdust with a mixture of NaOH and KOH at 240°-250°; the yield being less when NaOH is used alone (Thorn, *D. P. J.* 210, 24). The product is boiled with water, and the filtrate evaporated. Sodium oxalate separates in granules, which are then boiled with milk of lime. The calcium salt is then decomposed by H_2SO_4. Oxalic acid may be freed from the last trace of alkaline oxalates by crystallisation from boiling dilute (10 p.c.) HClAq. Octahedral crystals of anhydrous oxalic acid $H_2C_2O_4$ may be obtained by allowing a solution of oxalic acid (1 pt.) in warm H_2SO_4 (12 pts.) to stand for some days. These crystals take up water (2aq) from the air, and fall to powder (Villiers, *C. R.* 90, 821; *cf.* Riechardt, *J.* 1864, 371). According to Lescœur (*C. R.* 104, 1799) dried oxalic acid takes up $2\frac{2}{5}$aq from the air.

Estimation.—By precipitation as calcium oxalate, followed by conversion into $CaCO_3$ or CaO; or by titration with $KMnO_4$ or baryta-water.

Properties.—Large monoclinic crystals (containing 2aq), v. sol. water and alcohol. Gives off its water of crystallisation at 100°, and, in a few weeks, over H_2SO_4 (Erdmann, *J. pr.* 85, 213). Partially sublimes at 150°, but is partly split up into water, CO, and CO_2. Its aqueous solution decomposes slowly in light, but the decomposition of dilute solutions may be prevented by

heating for half an hour at 70° Neubauer (*Fr.* 9, 392). When a gas is passed through a strong solution of oxalic acid at 100° CO_2 is given off (Carles, *C. R.* 71, 226). A 5 p.c. solution containing 1 p.c. of uranium nitrate is rapidly decomposed by sunlight into CO_2, formic acid, and CO (Seekamp, *A.* 122, 113). Ammonium oxalate is also decomposed by sunlight, but the oxalates of K, Li, and Na are but slightly affected (Downes a. Blunt, *Pr.* 29, 219). Ferric chloride is reduced by oxalic acid in sunlight, and also by heating above 50° (Lemoine, *Bl.* [2] 46, 289). Oxalic acid reduces Au and Pt from their salts. Oxalic acid expels HCl when heated with dry NaCl. $CaCl_2$ ppts. solutions of alkaline oxalates, the ppd. CaC_2O_4 being insol. acetic acid and ammonia, but sol. HClAq, and immediately reppd. by ammonia.

Reactions.—1. Heated with *glycerin* (1 pt.) it yields CO_2 and formic acid, but when a small quantity of glycerin ($\frac{1}{4}$ pt.) is used, decomposition takes place at a higher temperature, allyl alcohol being formed from the glycerin. Oxalic acid also yields formic acid when distilled with glycol, mannite, dulcite, erythrite, and quercite, but not with sugars (Lorin, *C. R.* 77, 129, 363; 84, 1136).—2. On heating with conc. H_2SO_4 or with P_2O_5 it is resolved into water, CO, and CO_2.—3. PCl_5 yields CO, CO_2, HCl, and $POCl_3$. PCl_3 acts in like manner.—4. Boiling nitric acid slowly oxidises it to CO_2.—5. PbO_2 and MnO_2 rapidly oxidise it in aqueous solution, yielding CO_2 and the corresponding oxalate. Dried oxalic acid is oxidised by rubbing with PbO_2, great rise of temperature occurring.—6. MnO_2 and dilute H_2SO_4 completely oxidise it to CO_2. $KMnO_4$ and CrO_3 also oxidise it.—7. *Chlorine-water* and HClO yield HCl and CO_2.—8. *Potash-fusion* yields hydrogen and a carbonate.—9. Liberates Cl, Br, and I when its saturated solution is boiled with $KClO_3$, $KBrO_3$, and KIO_3 respectively (Guyard, *Bl.* [2] 31, 299).—10. The *copper-zinc couple* forms small quantities of glycollic acid (Balbiano a. Alessi, *G.* 12, 190; *cf.* Plimpton, *B.* 11, 516).—11. $SbCl_5$ in chloroform forms crystals of $Sb_2Cl_8C_2O_4$ [149°], which are decomposed by water with formation of oxalic acid (Anschütz a. Evans, *A.* 239, 285).—12. Primary *alcohols* heated with dry oxalic acid yield a mixture of mono- and di-alkyl oxalates; on distillation the mono-alkyl oxalates split up into CO_2 and alkyl formates. Secondary *alcohols* give but little alkyl oxalate, while tertiary *alcohols* are wholly split up by oxalic acid into water and hydrocarbons (Cahours a. Demarçay, *C. R.* 83, 668; 86, 991).—13. *Electrolysis* of potassium oxalate yields CO_2 at the positive pole (Burgoin, *A. Ch.* [4] 14, 157).—14. A solution of *molybdic acid* in oxalic acid yields, on addition of HNO_3 and evaporating, monoclinic crystals of $H_2C_2O_4MoO_3$ aq; $a:b:c = {\cdot}947:1:1{\cdot}073$; $\beta = 93°\ 52'$. This 'oxalomolybdic acid' yields the salts $Ag_2C_2O_4MoO_3$, $BaC_2O_4MoO_3$, and $Na_2C_2O_4MoO_3$ 5aq (Péchard, *C. R.* 108, 1053).—15. *Ammoniacal cupricoxide* at 150° yields $(NH_4)_2CO_3$ and Cu_2O (Cazeneuve, *Bl.* [2] 32, 277).

Salts (Souchay a. Lenssen, *A.* 99, 31; 100, 308; 102, 35, 41; 103, 308; 105, 245).—K_2A''aq: monoclinic crystals; $a:b:c = {\cdot}675:1:1{\cdot}157$; $\beta = 69{\cdot}5°$ (De la Provostaye, *A. Ch.* [3] 4, 454). S. 33 at 16° (Nichols).—K_2A''3aq.—KHA''. *Salt of sorrel.* Monoclinic crystals (Marignac, *J.* 1855, 462).—KHA''aq.—$KHA''\frac{1}{2}$aq: trimetric crystals; $a:b:c = {\cdot}459:1:6{\cdot}196$. S. 3·8 at 8°.—$KHA''\frac{1}{4}$aq: trimetric crystals (Rammelsberg, *P.* 93, 24).—$KH_3A''_2$2aq. Triclinic prisms: $a:b:c = 2{\cdot}100:3{\cdot}256:1$; $\alpha = 96°12'$; $\beta = 79°\ 29'$; $\gamma = 97°\ 5'$ (Wollaston, *Tr.* 1808, 99; Anderson, *C. J.* 1, 231; De la Provostaye). S. 1·8 at 13° (N.).—Na_2A''. S. 3 at 15°. Neutral in reaction.—$NaHA''$aq: monoclinic crystals which redden litmus. S. 1·7 at 15°.—Li_2A''. S. 8 at 19·5°.—$LiHA''$aq. S. 8 at 17°.—$(NH_4)_2A''$aq. S. 4·2 at 15° (N.); 2·2 at 0° (Engel, *C. R.* 102, 365). Hemihedral efflorescent trimetric prisms; $a:b:c = {\cdot}776:1:{\cdot}733$ (Anschütz, *B.* 18, 1394). Ppd. by adding NH_4Cl or NH_4OAc to its solution (Heintz, *J. pr.* 87, 309).—$(NH_4)_2A''$ 2aq. Occurs in guano (Tanner, *C. N.* 32, 162).—$(NH_4)HA''$aq: trimetric prisms; $a:b:c = {\cdot}453:1:{\cdot}559$.—$(NH_4)H_3A''_2$2aq: triclinic prisms, isomorphous with $KH_3A''_2$2aq. S. 3·25 at 0° (Engel).—$(NH_4)HSO_4H_2C_2O_4$: monoclinic crystals.—Rb_2A''aq (Piccard, *J. pr.* 86, 449).—$RbHC_2O_4$.—$RbH_3A''_2$3aq (Stolba, *C. C.* 1878, 331).—CaA''aq. Crystalline powder, formed by ppg. hot solutions (Schmid, *A.* 97, 225).—CaA''3aq: occurs, mixed with CaA''aq in the pp. formed from cold solutions.—$(CaA'')_2CaCl_2$24aq.—$CaA''CaCl_2$7aq (Fritzsche, *P.* 28, 121).—SrA''aq. S. 5 at 100°.—SrA''3aq (Wicke, *A.* 90, 101).—$SrH_2A''_2$2aq.—$SrA''SrCl_2$6aq.—$(SrA'')_3SrCl_2$16aq (Rainey, *Pr.* 14, 144).—BaC_2O_4 aq. S. ·04.—$BaH_2A''_2$2aq. S. ·3 at 15° (Clapton, *C. J.* 5, 223).—$Be(NH_4)_2A''_2$ (Sénarmont, *J.* 1857, 295; Shadwell, *J.* 1881, 681).—$BeK_2A''_2$.—$Be_2K_2A''_2(OH)_2$2aq (Philipp, *B.* 16, 752).—MgA'' 2aq. S. ·07 at 16°; ·08 at 100°.—$Mg(NH_4)_{12}A''_7$9aq.—$Mg_5(NH_4)_{26}A''_{18}$24aq.—$Mg(NH_4)_{10}A''_6$8aq.—$Mg(NH_4)_{14}A''_8$8aq.—$Mg_3(NH_4)_2A''_4$2aq (Brandes, *Schw. J.* 27, 18).—$MgK_2A''_2$6aq.—ZnA'' 2aq.—$Zn(NH_4)_4A''_3$3aq (Kayser, *P.* 60, 140).—$ZnK_2A''_2$4aq.—CdA'' 3aq. S. ·008 in the cold; ·009 at 100°.—$CdA''(NH_3)_2$aq.—$Cd(NH_4)_{12}A''_7$9aq.—$Cd(NH_4)_{16}A''_9$11aq.—$Cd(NH_4)_8A''_5$8aq.—$CdK_2A''_2$2aq.—$CdNa_2A''_2$2aq.—$Al_2A''(OH)_4$ (Mathieu-Plessy, *C. R.* 97, 1033).—$Al_2Na_4A''_4(OH)_2$9aq (Lenssen, *J. pr.* 86, 314).—$Al_2(NH_4)_2A''_3(OH)_2$5aq.—$Al_2(NH_4)_6A''_4(OH)_4$3aq.—$Al_2Na_4A''_4(OH)_2$6aq.—$Al_2Na_6A''_5(OH)_2$5aq.—$Al_2K_2A''_3(OH)_2$2aq.—$Al_2K_4A''_4(OH)_2$2aq.—$Al_2MgA''_3(OH)_2$5aq.—$Al_2Ba_3A''_5(OH)_2$8aq (Collin, *B.* 3, 315).—$Ce_2A''_3$9aq (Jolin, *Bl.* [2] 21, 540).—$La_2A''_3$9aq (Clève, *Bl.* [2] 21, 202).—Tl_2A' (Crookes, *C. J.* 17, 150; Kuhlmann, *C. R.* 55, 607).—$TlHA''$aq.—$Sm_2A''_3$10aq.—$SmKA''_2$$2\frac{1}{2}$aq (Clève, *Bl.* [2] 43, 171).—FeA'' $1\frac{1}{2}$aq. *Humboldtine.*—FeA'' 2aq: yellow crystals. S. ·022 in the cold; ·026 at 100°.—$K_2FeA''_2$2aq: golden needles, sol. water.—$K_2FeA''_2$aq.—$(NH_4)_2FeA''_2$3aq.—$Fe(NH_4)_3A''_3$3aq: greenish crystals. S. 48 at 17°.—$Fe(NH_4)_3A''_3$4aq.—$FeNa_3A''_3$$4\frac{1}{2}$aq.—$FeK_3A''_3$3aq. S. 7 at 17°.—$KFeA''_2$$2\frac{1}{2}$aq. S. 92 at 21°.—$Ba_3Fe_2A''_6$7aq.—$K_6Cr_2A''_6$6aq. Deep-blue monoclinic prisms; obtained by reducing $K_2Cr_2O_7$ with oxalic acid (Gregory; Rammelsberg, *P.* 93, 24; Werner, *C. J.* 53, 404, 602; *C. J. Proc.* 3. 142; C. A. Schunck, *C. N.* 51, 152; Hartley, *C. J. Proc.* 3, 4). S. 20 at 15°. The solution is red with green reflex, and gives no pp. with $CaCl_2$.—$K_2Cr_2A''_4$8aq; red monoclinic crystals (Croft, *P. M.* [3] 21, 197). S. 10.—$Na_6Cr_2A''_6$3aq: blue prisms.—$Na_6Cr_2A''_6$9aq.—$(NH_4)_6Cr_2A''_6$6aq: blue scales. S. 75 at 15°.—

$(NH_4)_2Cr_2A''_4$ 8aq: red crystals.—$Ag_6Cr_2A''_6$ 9aq: blue needles. S. 11 at 100°.—$Ba_3Cr_2A''_6$ 12aq: dark-violet needles.—$Ba_3Cr_2A''_6$ 8aq (Werner).—$Ba_3Cr_2A''_6$ 18aq.—$Ba_3Cr_2A''_6$ 6aq (Clarke, *B.* 14, 1640).—$Ca_3Cr_2A''_6$ 18aq.—$Ca_3Cr_2A''_6$ 36aq (Reece, *C. R.* 21, 1116).—$Cr_2Cl_2A''_2 10NH_3$ (Jörgensen, *J. pr.* [2] 20, 143; 30, 28).—$Cr_2A''_3(NH_3)_{12}$ 4aq.—$KCaCrA''_3$ 4aq. Pleochroic; red, blue, and green (Hartley, *Pr.* 21, 499).—$K_2Ca_2Cr_2A''_6$ 6aq (Werner): blue prisms.—$KBaCrA''_3$ 3aq.—$Sr_3Cr_2A''_6$ 18aq.—$KSrCrA''_3$ 6aq.—$Pb_3Cr_2A''_6$ 15aq.—UrA'' 6aq.—$Ur(NH_4)_4A''_4$.—UrO_2A'' 3aq.—$UrO_2(NH_4)_2A''_2$ 4aq.—$(UrO_2)K_2A''_2$ 3aq.—MnA'' 2½aq. S. ·05 in the cold; ·08 at 100°.—MnA'' 2aq. Decomposes at 150° into CO_2, CO, and MnO (Castelaz, *Bl.* [2] 50, 645).—MnA'' 3aq. S.G. (of MnA'') $\frac{21\cdot4}{4}$ 2·444 (Clarke, *Am.* 2, 174).—$K_6Mn_2A''_6$ 6aq: black monoclinic prisms (Kehrmann, *B.* 20, 1594).—$Mn(NH_4)_2A''_2$ 2aq.—$Mn(NH_4)_4A''_3$ 4aq.—$Mn(NH_4)_{10}A''_6$ 8aq.—$Mn(NH_4)_{14}A''_8$ 8aq.—$MnA''NH_3$ 6aq.—$MnK_2A''_2$ 2aq.—CoA'' 2aq.—$Co_3A''(OH)_4$.—$CoK_2A''_2$ 6aq.—$CoA''Cl\ 5NH_3$ (Krok, *J. pr.* [2] 18, 239).—$CoA''Br\ 5NH_3$.—$Co(OH)A''(NH_4)_2SO_4 3NH_3$.—$Co_2A''(NO_2)5NH_3$.—$CoA''(NO_3)$ 5aq.—$CoNiA''_2(NH_3)_4$ 4½aq (Rautenberg, *A.* 113, 360).—NiA'' 2aq.—$NiA''(NH_3)$ 3aq (Winkelblech, *A.* 13, 278).—$K_2NiA''_2$ 6aq.—CuA'' ½aq.—$Cu(NH_4)_2A''_2$ 2aq.—$CuA''(NH_3)_2$aq.—$CuA''NH_3$.—$CuLi_2A''_2$ 2aq (Troost, *A. Ch.* [3] 51, 103).—$CuK_2A''_2$ 2aq.—$CuK_2A''_2$ 4aq.—$CuNa_2A''_2$ 2aq.—PbA'' (Pelouze, *A. Ch.* [2] 79, 104; [3] 4, 104).—$Pb_3A''O_2$.—$Pb_2A''(NO_3)_2$ 2aq: pearly plates (Johnston, *P. M.* [3] 13, 25; Dujardin, *J. pr.* 15, 308).—$Pb_6A''(NO_3)_6O_2$ 3aq.—$PbK_2A''_2$ 2½aq (Reis, *B.* 14, 1174).—Hg_2A'': white pp., insol. water.—Hg_2A''aq.—HgA''.—$Hg(NH_4)_2A''_2$ 2aq.—$HgK_2A''_2$ 2aq.—$Bi_2A''_3$ 7½aq.—$Bi_2A''_2(OH)_2$ ½aq.—$Bi(NH_4)_{15}A''_9$ 12aq.—$BiK_7A''_5$ 12aq.—$BiK_{11}A''_7$ 12aq.—$BiKA''_2$aq.—$Sb_2A''_2O$aq.—$Sb_2K_2A''_4$aq.—$Sb_2K_6A''_6$ 3aq.—$SbK_3A''_3$ 2aq (Kay, *C. N.* 57, 193).—$SbK_3A''_3$ 4aq (Wagner, *Chem. Zeit.* 12, 1726): crystallises also with 1½aq, 4½aq, and 6aq.—$Sb_2K_2H_2A''_5$ 3aq. $Sb_2Na_6A''_6$ 9aq (Svenssen).—$SbNa_5A''_4$ 10aq.—$Sb(NH_4)_3A''_3$ 2aq.—$Sb(NH_4)A''_2$ 5aq (Svenssen, *B.* 3, 314).—$Sb_4(NH_4)_6A''_9$ 16aq.—$SbH(NH_4)_4A''_4$ 7aq.—$AsK_3A''_3$ 3aq.—$Pd(NH_4)_2A''_2$ 2aq (Kane).—$Pd(NH_4)_2A''_2$ 8aq.—$PtNa_2A''_2$ 4aq.—$PtCl_2A''4NH_3$.—$PtK_2A''_2$ 2aq (Clève, *Bl.* [2] 45, 191).—$Pt(NH_4)_2A''_2$ 2aq.—$PtAg_2A''_2$ 2aq.—$PtCaA''_2$ 6½aq.—$PtCaA''_2$ 4½aq.—$PtCaA''_2$ 8aq.—$PtSrA''_2$: crystallises with 3½aq, 6½aq, and 3aq.—$PtBaA''_2$ 3aq.—$PtBaA''_2$ 2aq.—$PtMgA''_2$ 6aq.—$PtFeA''_2$ 6aq.—$PtMnA''_2$ 7aq.—$PtNiA''_2$ 7aq.—$PtZnA''_2$ 7aq.—$PtCoA''_2$ 8aq.—$PtCdA''_2$: crystallises with 5aq, 4½aq, and 4aq.—$PtCuA''_2$ 6aq.—$PtHg_2A''_2$ 1½aq.—$PtHg_2A''_2$ 2aq.—$PtPbA''_2$ 3aq.—$PtA''2NH_3$.—$PtA''(NH_3)_2$ aq.—$PtA''(NH_3)_3$ 1½aq.—SnA''.—$Sn(NH_4)_2A''_2$ aq.—$SnK_2A''_2$aq.—$Sn_6A''O_{10}$ 6aq.—$Ti_{13}A''_2O_{24}$ 12aq.—Ag_2A'': white pp.—$Ag_2A''4NH_3$.

Mono-methyl ether $MeHA''$. (109° at 12 mm.). Solid (Anschütz a. Schönfeld, *B.* 19, 1442; *A.* 254, 8).—$KMeA''$ (Salomon, *B.* 8, 1509).

Di-methyl ether Me_2A''. Mol. w. 118. [54°]. (164°) (Dumas a. Péligot, *A. Ch.* [2] 58, 44; Wöhler, *A.* 81, 376; Erlenmeyer, *N. Rep. Pharm.* 23, 624; Purdie, *C. J.* 51, 629). S.V. 116·7. H.F. 180,900 (Stohmann, *J. pr.* [2] 40, 353. Monoclinic tables, sol. water, alcohol, and ether. Its aqueous solution slowly decomposes into oxalic acid and MeOH.

Tetra-methyl ether $CO_2Me.C(OMe)_3$. (76° at 12 mm.). S.G. $\frac{20}{4}$ 1·1312. Formed from $CO_2Me.CCl_2(OMe)$ and NaOMe (Anschütz, *A.* 254, 31). Converted by PCl_5 into $Me_2C_2O_4$.

Mono-ethyl ether $EtHA''$. *Ethyloxalic acid.* (117° at 15 mm.). S.G. $\frac{20}{4}$ 1·2175. Formed from $Et_2C_2O_4$ (1 mol.) and KOH (1 mol) in alcohol (Mitscherlich, *P.* 33, 332). Formed also by heating anhydrous oxalic acid (1 pt.) with absolute alcohol (1 pt.) at 135°, decanting from unused oxalic acid, and distilling *in vacuo* (Anschütz, *B.* 16, 2413; *A.* 254, 9). Liquid. When distilled under atmospheric pressure it yields formic acid and $Et_2C_2O_4$.—$KEtA''$: scales, decomposed by heat into CO and $KEtCO_3$ (Eltekoff, *B.* 6, 1259).

Di-ethyl ether Et_2A''. *Oxalic ether.* (186° cor.). S.G. $\frac{20}{4}$ 1·0793. μ 1·4156; R_∞ 54 (Brühl). S.V. 166·2 (Brühl, *A.* 203, 27); $\frac{15}{15}$ 1·0856; $\frac{25}{25}$ 1·0761 (Perkin, *C. J.* 45, 508). M.M. 6·654 at 12·8°. S.H. ·45 (R. Schiff, *G.* 17, 286). Formed by distilling dehydrated oxalic acid (11 pts.) with absolute alcohol (14 pts.) (Bergmann, *Opuscula*, i. 256; Löwig, *J. pr.* 83, 129), or by heating KHC_2O_4 (1 pt.) with alcohol (1 pt.) and H_2SO_4 (2 pts.) (Dumas a. Boullay, *J. Ph.* 14, 113).

Preparation.—Equal weights of dry oxalic acid and alcohol (97 p.c.) are boiled for 4 hours and distilled; as soon as the thermometer reaches 110° a quantity of alcohol equal to the weight of the distillate is added, and the mixture boiled again for 4 hours; the mixture is then distilled; 825 g. oxalic acid give 750 g. (or 56 p.c.) oxalic ether and 110 g. formic ether (Schatzky, *J. pr.* [2] 34, 500).

Properties.—Colourless oil with slight odour, v. sol. alcohol. Decomposed by water, especially on heating. Alcoholic potash yields a pp. of $KEtC_2O_4$. With $SnCl_2$ it forms crystalline $Et_2C_2O_4SnCl_4$, decomposed by water (Lewy, *C. R.* 21, 371). $TiCl_4$ yields $Et_2C_2O_4TiCl_4$ and $Et_2C_2O_4 2TiCl_4$ (Demarçay, *C. R.* 70, 1414).

Reactions.—1. Gaseous NH_3 yields $CO_2Et.CONH_2$.—2. Aqueous NH_3 forms oxamide. 3. *Ethylamine* yields $C_2O_2(NHEt)_2$; *diethylamine* forms $CO_2Et.CONEt_2$; while *triethylamine* has no action (Hofmann). Alanine forms two compounds $C_{12}H_{20}N_2O_6$ [127°] and [154°].—4. *Sodium* and *potassium* decompose it, yielding CO and Et_2CO_3. NaOEt acts in the same way (Geuther, *Z.* [2] 4, 656).—5. *Sodium-amalgam* yields des-oxalic ether $C_6H_4Et_3O_8$, and, when alcohol is present, tartaric and glycollic acids.—6. $ZnEt_2$, followed by water, yields $CO_2Et.CEt_2(OH)$ (Frankland, *Pr.* 12, 396). Other zinc-alkyls act in the same way (Frankland a. Duppa, *Pr.* 13, 140; 14, 17, 79, 83, 191).—7. Acted on by Zn and a mixture of EtI and allyl iodide a mixture of $HO.CEt_2.CO_2Et$ and $HO.C(C_3H_5)_2.CO_2Et$ is formed, and not $HO.CEt(C_3H_5).CO_2Et$ (Barataeff, *J. pr.* [2] 35, 7). 8. *Resorcin* (1 mol.) and NaOEt (2 mols.) in alcohol slowly form $C_{11}H_{10}O_6$, which crystallises from alcohol in pale-yellow prisms [c. 256°], and yields the acetyl derivative $C_{11}H_7Ac_3O_6$ [127°] (Michael, *J. pr.* [2] 35, 510).—9. *Phenylhydrazine* forms $C_2O_2(N_2H_2Ph)_2$ [278°] and $N_2H_2Ph.CO.CO_2Et$ [119°] (E. Fischer, *A.* 190,

131; Bulow, *A.* 236, 197). In presence of alcoholic NaOEt the product is $N_2H_2Ph.CO.CO_2H$ [170°] (Michael, *J. pr.* [2] 35, 458).—10. *Acetone* in presence of NaOEt (1 pt.) in alcohol (60 pts.) forms $CH_3.CO.CH_2.CO.CO_2Et$ [18°] (214°). This body is converted by baryta-water into oxytoluic acid, an intermediate body being $CH_2Ac.C(OH)(CO_2H).CHAc.CO.CO_2Et$ [90°]. Acetone (2 mols.) and NaOEt (2 mols.) in ether yield $CH_3.CO.CH_2.CO.CO.CH_2.CO.CH_3$ [121°] crystallising in white prisms (Claisen a. Stylos, *B.* 20, 2188; 21, 1141; 22, 3271; 24, 116). A mixture of acetone, NaOAc, KOAc, and Ac_2O yield a coloured product $C_6H_6O_3$. Another product of the action of alcoholic NaOEt on acetone and oxalic ether is $CO(CH_2.CO.CO_2Et)_2$ [104°], which yields chelidonic acid on warming with mineral acids. On adding sodium to a mixture of oxalic ether and EtOAc dissolved in Et_2O, oxalacetic ether is formed.—11. *Succinic ether* and NaOEt yield oxalosuccinic ether $CO_2Et.CH(CO.CO_2Et).CH_2.CO_2Et$ and a compound $C_{16}H_{22}O_{10}$ [90°] (Wislicenus, *B.* 22, 889).—12. Alcoholic *acetophenone* and NaOEt form benzoyl-pyruvic acid $C_6H_5.CO.CH_2.CO.CO_2H$ [158°]. Acetophenone and NaOEt in ether yield $BzCH_2.CO.CO.CH_2Bz$ [180°] (Claisen, *B.* 21, 1131).—13. *Chloro-acetic ether* and *zinc* yield 'ketipic' ether $CO_2Et.CH_2.CO.CO.CH_2.CO_2Et$ [77°] (Fittig a. Daimler, *B.* 20, 202).—14. Heating with *oxalic*, *formic*, or *acetic acids* at 140° yields formic ether, CO_2, and CO. Benzoic acid has no action even at 240° (Lorin, *Bl.* [2] 49, 344).—15. *Benzyl cyanide* and NaOEt yield $CN.CHPh.CO.CO_2Et$ [130°] whence boiling dilute H_2SO_4 forms phenyl-pyruvic acid [155°] (Erlenmeyer, *B.* 22, 1483).—16. A solution of *urea* in alcoholic NaOEt gives a pp. of sodium parabanate $\begin{matrix}CO.NNa\\CO.NH\end{matrix}\!\!>\!CO$ (Michael, *J. pr.* [2] 35, 457).—17. *Phthalide* and NaOEt in ether yield $C_6H_4\begin{cases}CH.CO.CO_2Et\\CO.O\end{cases}$ [121°], whence phenylhydrazine forms $C_{18}H_{16}N_2O_4$ [159°] (Wislicenus, *A.* 246, 342).—18. *Chlorine* in sunlight forms $(C_2Cl_5)_2C_2O_4$ [144°], whence potash yields $CCl_3.CO_2K$ (Malaguti, *A. Ch.* [2] 74, 299).

Tetra-ethyl ether $CO_2Et.C(OEt)_3$. (98° at 12 mm.). S.G. $\frac{20}{4}$ 1·0020. Formed from $CO_2Et.CCl_2(OEt)$ and NaOEt (Anschütz, *A.* 254, 32). Converted by PCl_5 into $Et_2C_2O_4$.

Methyl ethyl ether $CO_2Me.CO_2Et$. (174°). S.G. $\frac{0}{0}$ 1·1557. S.V. 139·1 (Wiens, *A.* 253, 297). Formed by distilling $KEtC_2O_4$ with $KEtSO_4$ (Chancel, *Compt. Chim.* 1850, 373, 403), and by the action of MeOH on $COCl.CO_2Et$ or of EtOH on $COCl.CO_2Me$ (Paul, *C. J. Proc.* 2, 168). Converted by repeated distillation into a mixture of $Me_2C_2O_4$ and $Et_2C_2O_4$.

Di-methyl di-ethyl ether $CO_2Me.C(OMe)(OEt)_2$. (92° at 13 mm.). Formed from $CO_2Me.CCl_2(OMe)$ and NaOEt at 100° (Anschütz, *A.* 254, 35).

Di-methyl di-ethyl ether $CO_2Et.C(OEt)(OMe)_2$. (96° at 12 mm.). Formed from $CO_2Et.CCl_2(OEt)$ and NaOMe at 100°.

n-Propyl-ether PrHA″. (119° at 13 mm.). S.G. $\frac{20}{4}$ 1·1578. Liquid (Anschütz a. Schönfeld, *B.* 19, 1442; *A.* 254, 6).

Di-n-propyl ether Pr_2A'' (213·5°). S.G. $\frac{0}{0}$ 1·0384. S.V. 215·4 (W.; *cf.* Cahours, *C. R.* 77, 749). S.H. ·451.

Tetra-n-propyl ether $CO_2Pr.C(OPr)_3$. (257°). S.G. $\frac{20}{4}$ ·9566. Formed from $CO_2Pr.CCl_2(OPr)$ and NaOPr (A.).

Iso-propyl ether $CO_2Pr.CO_2H$. (111° at 13 mm.). S.G. $\frac{20}{4}$ 1·1657. Decomposes on boiling into $Pr_2C_2O_4$, isopropyl formate, CO_2, CO, and water (Anschütz, *A.* 254, 6).—$CO_2Pr.CO_2K$.

Di-isobutyl ether $(C_4H_9)_2A''$. (225°). S.G. $\frac{14}{}$ 1·002. S.H. ·457. Yields $K(C_4H_9)C_2O_4$ (Cahours, *C. R.* 77, 1403).

Tetra-isobutyl-ether $(C_4H_9O)_3C.CO_2C_4H_9$. (146° at 10 mm.). S.G. ·921. Formed from $C_4H_9O.CCl_2.CO_2C_4H_9$ and $NaOC_4H_9$ (Anschütz, *A.* 254, 33).

Di-n-butyl ether $(C_4H_9)_2A''$. (243°). S.G. $\frac{0}{0}$ 1·0099. S.V. 258·4 (Wiens).

Isoamyl ether $(C_5H_{11})HA''$. Oil, smelling of bugs (Balard, *A. Ch.* [3] 12, 309).—CaA'_2 2aq.—AgA′: pearly scales.

Di-isoamyl ether $(C_5H_{11})_2C_2O_4$. (265°). S.G. $\frac{11}{}$ ·968 (Delffs, *J.* 1854, 26). S.H. ·464 (Schiff). Oil, smelling of bugs (Balard).

Tetra-amyl ether $(C_5H_{11}O)_3C.CO_2C_5H_{11}$. (190° at 14 mm.). S.G. $\frac{20}{4}$ ·9141 (A.).

Ethyl heptyl ether $CO_2Et.CO_2C_7H_{15}$. (263·7°). S.G. $\frac{0}{0}$ ·9954. S.V. 284·9 (Wiens).

Propyl heptyl ether $Pr(C_7H_{15})A''$. (284°). S.G. $\frac{0}{0}$ ·9814. S.V. 315·7.

Propyl octyl ether $Pr(C_8H_{17})A''$. (291°). S.G. $\frac{0}{0}$ ·9725. S.V. 340·4 (Wiens).

Allyl ether $(C_3H_5)_2A''$. (215·5° i.V.) (Kekulé, *B.* 6, 387). S.G. $\frac{15}{}$ 1·055. Formed from $Ag_2C_2O_4$ and allyl iodide (Hofmann a. Cahours, *A.* 102, 288).

Di-phenyl ether $Ph_2C_2O_4$. [130°]. Formed by heating phenol (1 pt.) with dry oxalic acid (1 pt.) and $POCl_3$ (1 pt.) at 115° (Nencki, *J. pr.* [2] 25, 283). Prisms (from alcohol), sl. sol. ether.

Di-phenyl ortho-oxalate $(PhO)_2C_2(OH)_4$. [127°]. A by-product in the manufacture of aurin. Formed by distilling phenol with dry oxalic acid, or by dissolving oxalic acid and excess of phenol in HOAc (Claparède a. Smith, *C. J.* 43, 358; Staub a. Smith, *B.* 17, 1740). Thin white plates, distilling with decomposition at 150°–180°. Sol. water, but almost at once split up into phenol and oxalic acid. Alcohol yields phenol and oxalic ether. On heating with H_2SO_4 it yields aurin.

Di-(α)-naphthyl ortho-oxalate $(C_{10}H_7O)_2C_2(OH)_4$. [163°]. Formed by heating (α)-naphthol with dry oxalic acid and HOAc (S. a. S.). Crystalline powder.

Di-(β)-naphthyl ortho-oxalate $(C_{10}H_7O)_2C_2(OH)_4$. [167°]. White crystalline powder (from HOAc); partly decomposed on distillation (Staub a. Watson Smith, *C. J.* 45, 303).

Penta-chloro-ethyl ether $CO_2H.CO_2C_2Cl_5$. Formed from $CO(NH_2).CO_2C_2Cl_5$ and NH_3Aq (Malaguti, *A. Ch.* [2] 74, 308). Colourless deliquescent needles.—NH_4A'.

Chloride of the methyl ether $CO_2Me.COCl$. (120°). S.G. $\frac{20}{4}$ 1·3316. Formed by heating $CO_2Me.CCl_2(OMe)$ for 40 hours at 215° (Anschütz, *A.* 254, 26). Liquid.

Chloride of the ethyl ether $CO_2Et.COCl$. *Chloroxalic ether. Chloro-glyoxylic ether* (*q.v.*). (136°). S.G. $\frac{20}{4}$ 1·2223. PCl_5 acting upon oxalic

ether first forms $CCl_2(OEt).CO_2Et$, which may be distilled under 15 mm. pressure; when distilled under atmospheric pressure it is split up into EtCl and $COCl.CO_2Et$ (Anschütz, *B.* 19, 2158; *A.* 254, 27). Formed also from oxalic ether and $POCl_3$ (Henry, *B.* 4, 598; 5, 949). Decomposed by water. Alcoholic NH_3 yields ethyl oxamate. Aniline forms $CO(NPhH).CO_2Et$. Mercaptan forms $CO_2Et.CO.SEt$ (Morley a. Saint, *C. J.* 43, 400). $ZnEt_2$ followed by water forms $CEt_2(OH).CO_2Et$. Carbamic ether yields $CO_2Et.NH.CO.CO_2Et$ [45°] (Salomon, *J. pr.* [2] 9, 290). $CO(NH_2)CO_2Et$ at 130° yields $NH(CO.CO_2Et)_2$ [67°].

Chloride of the propyl ether $COCl.CO_2Pr$. (154°). S.G. $\frac{20}{4}$ 1·1670. Formed by treating $Pr_2C_2O_4$ with PCl_5 and heating the resulting $CO_2Pr.CCl_2(OPr)$ at 190° (Anschütz).

Chloride of the isobutyl ether $COCl.CO_2C_4H_9$. (165°). S.G. $\frac{20}{4}$ 1·1153. Formed in like manner.

Chloride of the isoamyl ether $COCl.CO_2C_5H_{11}$. (185°). S.G. $\frac{20}{4}$ 1·0931 (A.).

Oxamic acid $CO(NH_2).CO_2H$. Mol. w. 89. [210°]. S. 1·4 at 14°. Formed by heating $CO_2(NH_4).CO_2H$ or by boiling oxamide with aqueous NH_3 (Balard, *A. Ch.* [3] 4, 93; Toussaint, *A.* 120, 237). The NH_4 salt is also formed by passing NH_3 into a cold alcoholic solution of oxalic ether (De Coppet, *A.* 137, 105. Excreted when animals are fed with oxamic ether. Prepared by heating an aqueous solution of $CO(NH_2).CO_2Et$ to boiling, adding ammonia gradually till the liquid is alkaline (Oelkers, *B.* 22, 1566). Prepared also by heating ammonium oxalate with NH_4NO_3 for four hours at 175° (Mathieu-Plessy, *C. R.* 109, 653). Crystalline powder, sl. sol. alcohol. Converted by boiling water into $(NH_4)HC_2O_4$.—NH_4A'.—$NH_4A'1\frac{1}{2}$ aq.—$NaA'\frac{1}{2}$aq.—KA' aq (Engström, *J.* 1856, 453).—MgA'_2 3aq.—CaA'_2 4aq. S. (of CaA'_2) ·16 at 13°; 4 at 100°.—BaA'_2 3aq.—PbA'_2 aq.—$Pb(OH)A'$.—FeA'_2 aq.—NiA'_2 aq.—CuA'_2 aq (Bacaloglio, *J. pr.* 81, 369).—AgA': needles.

Methyl ether MeA'. Cubes.

Ethyl ether $CO(NH_2).CO_2Et$. *Oxamethane.* [115°]. Formed from oxalic ether and dry or alcoholic NH_3. Plates (from alcohol). With $COCl.CO_2Et$ it forms $(CO_2Et.CO)_2NH$ [67]. With cyanic acid vapour at 130° it yields $C_{15}H_{21}N_6O_{12}$ [155°–160°] (Grimaux, *Bl.* [2] 21, 154), crystallising from water in needles. Chloral forms $CCl_3.CH(OH).NH.C_2O_3Et$ [121°] (Moschcles, *B.* 24, 1804).

Penta-chloro-ethyl ether C_2Cl_5A'. [134°]. Formed from $(C_2Cl_5)_2C_2O_4$ and NH_3 (Malaguti).

Isobutyl ether C_4H_9A'. [90°]. Prisms (Cahours, *C. R.* 77, 1403; Wallach, *B.* 13, 507).

Isoamyl ether $C_5H_{11}A'$. [93°].

Phenyl ether $CO(NH_2).CO_2Ph$. [132°]. Formed from $CO_2Et.CCl_2(NH_2)$ and phenol.

Acetyl derivative of the ethyl ether $CO(NHAc).CO_2Et$. [54°]. Needles.

Oxamide $CO(NH_2).CO(NH_2)$. S. ·037 at 7·3° (Henry, *C. R.* 100, 943). H.F. 169,000 (Berthelot). Formed from oxalic ether and NH_3Aq (Bauhof, A.D. 1817). Formed also by heating ammonium oxalate (Dumas, *A. Ch.* [2] 44, 129; 54, 240) and by the slow decomposition of cyanogen by water containing aldehyde (Liebig, *A.* 113, 246), or by conc. HClAq (Schmidt a. Glutz, *B.* 1, 66). It also occurs among the products of oxidation of HCy, cyanides, and ferrocyanides (Playfair; Attfield, *C. J.* 16, 94).

Properties.—White powder, sl. sol. hot water, insol. alcohol. Cupric acetate forms the salt $Cu(C_2H_3N_2O_2)_2$ aq.

Reactions.—1. By passing through a *red-hot tube* it is decomposed into CO, ammonium carbonate, HCy, and urea.—2. P_2O_5 yields, on heating, cyanogen, CO_2, and CO.—3. Boiling *dilute acids* yield oxalic acid.—4. Boiling *aqueous alkalis* also saponify it. *Magnesia* acts in the same way (Berthelot, *Bl.* [2] 47, 840).—5. *Water* at 224° forms ammonium oxalate.—6. Heating with HgO yields urea, CO_2, and Hg (Williamson). Boiling with water and HgO forms a compound $(C_2H_4N_2O_2)_2HgO$ (Dessaignes, *A.* 82, 233).—7. Ac_2O has no action at 160°. Bz_2O at 200° forms benzamide.—8. Conc. HNO_3 decomposes it in the cold.

Oxalimide $\begin{matrix}CO\\CO\end{matrix}\!\!>\!NH$. Formed from oxamic acid, PCl_5, and $POCl_3$ at 80°–90° (Ost a. Meute, *B.* 19, 3228). Monoclinic prisms, v. sl. sol. cold water, sol. NH_3Aq. Boiling water produces oxamide and oxalic acid.—C_2O_2NHgCl: crystalline powder, insol. water.

Methyl-oxamic acid $CO(NHMe).CO_2H$. [146°] (Hantzsch, *B.* 17, 2919). Formed by heating methylamine acid oxalate (Wurtz, *A. Ch.* [3] 30, 443), and, as a subsidiary product, by oxidising caffeïne with CrO_3 (Maly a. Hinteregger, *M.* 2, 128). Crystals (from hot water or by sublimation). — KA'. — CaA'_2.—CaA'_2 3aq. —BaA'_2 aq: monoclinic crystals; $a:b:c = 1·018:1:1·306$; $\beta = 87° 13'$.

Methyl ether MeA'. [85°]. Formed from $Me_2C_2O_4$ (76 g.) and methylamine (20 g.) in MeOH (30 g.) (Franchimont a. Klobbie, *R. T. C.* 8, 305).

Ethyl ether EtA'. (243°). Oil.

Methyl-oxamide $CO(NH_2).CO(NHMe)$. [229°]. Formed from oxamic ether and $NMeH_2$ (Wallach a. West, *B.* 9, 262). Minute needles.

Di-methyl-oxamide $C_2O_2(NHMe)_2$. [217°] (Mylius, *B.* 17, 291). Needles. Conc. HNO_3 yields $C_2O_2(NMe.NO_2)_2$ [124°] (Franchimont, *R. T. C.* 2, 94; 4, 193). PCl_5 yields $C_4H_5ClN_2$.

Di-methyl-oxamic acid $CO(NMe_2).CO_2H$.—CaA'_2: crystalline (Duvillier, *A. Ch.* [5] 23, 315).

Ethyl ether EtA'. (c. 244°). Not attacked by HNO_3 (S.G. 1·5) (Franchimont a. Klobbie, *R. T. C.* 8, 304).

Ethyl-oxamic acid $CO(NHEt).CO_2H$. [120°]. Tables.—CaA'_2 2aq. Prisms (Heintz, *A.* 127, 43).—CaA'_2 4aq. S. 3·17 at 17·5°.—BaA'_2 aq.

Ethyl ether EtA'. (245°). Oil (Wallach, *A.* 184, 59). Decomposed by water.

Ethyl-oxamide $CO(NH_2).CO(NHEt)$. [203°]. Needles (W.)

s-**Di-ethyl-oxamide** $CO(NHEt).CO(NHEt)$. [179°] (Schiff, *B.* 17, 1034). Formed from oxalic ether and ethylamine (W.).

u-**Di-ethyl-oxamide** $CO(NH_2).CO(NEt_2)$. [126°]. (268° cor.). From $CO_2Et.CO(NEt_2)$ and ammonia (Wallach, *A.* 214, 263). With PCl_5 it yields 'chloroxalethyline' $C_6H_9ClN_2$.

Tri-ethyl-oxamide $CO(NHEt).CO(NEt_2)$. (258°). Formed from diethyl oxamic ether and ethylamine (W.).

Methyl-ethyl-oxamide $CO(NHMe).CO(NHEt)$. [157°]. Formed from methylamine and $CO_2Et.CONHEt$ (W.).

Di-ethyl-oxamic acid $CO(NEt_2).CO_2H$. [101°]. Prisms. PCl_5 yields $CO(NEt_2).COCl$.—CaA'_2 2aq.

Ethyl ether EtA'. (250°–254°).

Isopropyl-oxamic acid $CO(NHPr).CO_2H$.—CaA'_2 (Duvillier).

Di-propyl-oxamide $C_2O_2(NHPr)_2$. [162°]. Plates, which feel fatty (Wallach, *A.* 214, 312).

Di-isobutyl oxamide [167°]. Plates, v. sol. alcohol (Malbot, *C. R.* 104, 228).

Isoamyl-oxamide [181°]. Needles.

Di-isoamyl-oxamide [129°].

Di-amyl-oxamide $C_2O_2(NH.CH_2CMe_3)_2$. [165°]. Needles (Freund, *B.* 23, 2868).

Di-allyl-oxamide $C_2O_2(NHC_3H_5)_2$. [154°]. (274°). Br yields $C_2O_2(NHC_3H_5Br_2)_2$ (Wallach a. Strecker, *B.* 13, 513).

Ethylene-oxamide $C_2O_2N_2H_2(C_2H_4)$. Amorphous precipitate formed, together with soluble $(CO_2Et.CO)_2N_2H_2C_2H_4$ by the action of alcoholic ethylene-diamine on oxalic ether (Hofmann, *B.* 5, 247). Similar products are obtained from propylene-diamine (Strache, *B.* 21, 2360).

Ethylidene-oxamide $C_2O_2N_2H_2(CHMe)$. Formed from cyanogen and crude aldehyde (Berthelot, *A.* 128, 338).

Phenyl-oxamic acid $CO(NHPh).CO_2H$. *Oxanilic acid.* [151°]. Formed by heating dehydrated oxalic acid (20 g.) with aniline (25 g.) at 140° for an hour (Laurent, *A.* 68, 15; Claus, *Z.* [2] 4, 158; Aschan, *B.* 23, 1820). The product is crystallised from water and the acid set free by dilute H_2SO_4. Needles (containing Aq) or anhydrous scales (from ether), sl. sol. cold water, v. sol. alcohol. Yields CO, water, CO_2, and di-phenyl-oxamide on heating strongly. Yields on nitration *p*-nitro-phenyl-oxamic acid [210°] crystallising in prisms containing aq (Aschan, *B.* 18, 2936). The isomeric o-nitro-phenyl-oxamic acid [112°] is formed by heating oxalic acid with o-nitro-aniline (Hübner a. Heoff, *A.* 209, 367). *m*-Nitro-phenyl oxamic ether [150°] is formed from oxalic ether and *m*-nitro-aniline. — NH_4A'. — $(NH_4)HA'_2$. — KA'aq. — NaA' 3aq: plates, v. sl. sol. cold water.—PbA'_2.—CuA'_2 (Anschütz, *B.* 22, 736).—BaA'_2.—AgA': white tables.—$(NH_2Ph)HA'_2$: needles (from water).

Chloride $CO(NHPh).COCl$. [82°].

Methyl ether MeA'. [114°]. Formed from $Me_2C_2O_4$ and aniline (Anschütz, *A.* 254, 10). Plates (from alcohol) or needles (from ligroïn).

Ethyl ether EtA'. [67°]. Converted by AcCl into $CO(NPhAc).CO_2Et$ [67°]. PCl_5 yields $NHPh.CCl_2.CO_2Et$ [72°], which splits up on melting into HCl and $NPh{:}CCl.CO_2Et$ [91°], whence aniline forms $NHC_6H_5.CO.C(NPh)(NHPh)$ [235°].

Propyl ether PrA'. [92°]. Needles.

Isopropyl ether PrA'. [52°]. Needles.

Isobutyl ether C_4H_9A'. [85°]. Plates.

Amyl ether $C_5H_{11}A'$. [50°]. Needles.

References.—BROMO-, CARBOXY-, DI-CHLORO-, and IODO- PHENYL-OXAMIC ACID.

Phenyl-oxamide $CO(NHPh).CONH_2$. A product of the action of HClAq on cyananiline (Hofmann, *A.* 73, 181). Formed also from phenyl-oxamic ether and NH_3 (Klinger, *A.* 184, 279). Crystals (from water).

Di-phenyl-oxamide $CO(NHPh).CO(NHPh)$. *Oxanilide.* [245°] (H.); [241°] (T.); [252·5°] (Reissert, *B.* 23, 2245). (320°). Formed by heating aniline oxalate at 170° (Gerhardt, *A. Ch.* [3] 14, 120; 15, 88) and by decomposing cyananiline with HClAq (Hofmann, *A.* 65, 56; 73, 181; 74, 35). Formed also from ethyl camphor-oxalate and aniline (Tingle, *C. J.* 57, 655). Nacreous scales, insol. water, sl. sol. hot alcohol.

Reactions.—1. *Nitrous acid* passed into its solution in glacial acetic acid forms the nitrosamine $CO(NHPh).CO(NPhNO)$ [86°] and di-*p*-nitro-oxanilide (Fischer, *B.* 10, 960; Senf, *J. pr.* [2] 35, 521).—2. *Chlorine* forms tetra-chloro-di-phenyl-oxamide [c. 255°] (Dyer a. Mixter, *Am.* 8, 349).—3. *Bromine* yields $C_2O_2(NHC_6H_4Br)_2$ [above 300°] whence HNO_3 yields the nitro-compounds $C_2O_2(NH.C_6H_3Br(NO_2))_2$ [288°] and $C_2O_2(NHC_6H_2Br(NO_2)_2)_2$ [c. 287°] (Mixter a. Willcox, *Am.* 9, 362).—4. *Iodine* HNO_3 and HOAc yield $C_2O_2(NHC_6H_4I\,[1{:}4])_2$.—5. *Nitric acid* forms the compounds $C_2O_2(NH.C_6H_4(NO_2))_2$ [260°]; $C_2O_2(NH.C_6H_3(NO_2)_2)_2$ melting at [300°], and $C_2O_2(NH.C_6H_2(NO_2)_3)_2$ [300°] (Mixter a. Walther, *Am.* 9, 355; *cf.* Hübner, *A.* 209, 366). The hexa-nitro-oxanilide is converted by aqueous $KHCO_3$ into $CO(NH_2).CO.NH.C_6H_2(NO_2)_3$ [c. 260°] and picric acid. Di-o- and di-*m*-nicro-oxanilides melt above 300° and 270° respectively (H.). Di-o-nitro-oxanilide yields, on reduction by tin and HOAc, a base $C_{14}H_{10}N_4$ [above 300°] which forms the salts $B''H_2Cl_2$ 2aq and $B''H_2SO_4$ 2aq.

References.—DI-BROMO- and TETRA-CHLORO-PHENYL-OXAMIDE.

Phenyl-oxamide carboxylic acid $CO(NH_2).CO.NHC_6H_4.CO_2H$. Formed by boiling the so-called carboxamido-carbimidamido-benzoic acid $CO(NH_2).C(NH).NH.C_6H_4.CO_2H$ with water (Griess, *B.* 18, 2411). Small white plates. —$BaA'_2$5aq.—AgA'.

Di-phenyl-oxamide *m*-carboxylic acid $CO(NHPh).CO.NHC_6H_4.CO_2H$ [1:3]. *Aniloxalbenzamic acid.* [300°–305°]. Formed from carboxy-phenyl-oxamic acid (or its mono-ethyl ether) and boiling aniline (Schiff, *A.* 232, 135). Plates (from alcohol).

Anilide $NHPh.CO.CO.NH.C_6H_4.CO.NHPh$. [290°–295°]. Small needles.

Di-phenyl-oxamide-di-*m*-carboxylic acid $C_2O_2(NH.C_6H_4.CO_2H)_2$. Formed by heating $CO_2Et.CO.NH.C_6H_4.CO_2H$ (Schiff, *A.* 232, 137).

Mono-amide $C_{16}H_{11}N_2O_5(NH_2)$. Formed by heating amido-benzamide with the compound $CO_2H.CO.NH.C_6H_4.CO_2H$. Crystalline. At 200° it yields the imide $C_{16}H_{10}N_2O_4(NH)$, a powder, insol. ammonia.

Di-amide $C_2O_2(NH.C_6H_4.CO.NH_2)_2$. Formed by heating $CO_2Et.CO.NH.C_6H_4.CO.NH_2$ with amido-benzamide. Insoluble powder.

***m*-Amido-phenyl-oxamic acid** $C_6H_4(NH_2).NH.CO.CO_2H$. Formed from *m*-phenylene-diamine and oxalic acid (Klusemann, *B.* 7, 1263). Needles.—AgA'.

Di-methyl-amido-phenyl-oxamic acid *v.* p. 273.

The *anhydrides* of the *methylo-hydroxides* $C_6H_4{<}{\scriptstyle NMe_2.O \atop \scriptstyle NH.CO}{>}CO$ are formed by the action of MeI in MeOH upon the sodium amido-phenyl-oxamates, the products being decomposed by Ag_2CO_3 (Griess, *B.* 18, 2408). The *m*- compound crystallises with $3\frac{1}{2}$ aq and yields

the salts $\mathrm{B'HI}$aq and $\mathrm{B'_2H_2PtCl_6}$. The *p*-isomeride crystallises (with $2\frac{1}{2}$ aq) in needles, v. sol. hot water.

***m*-Phenylene-oxamide** $\mathrm{C_2O_2(NH)_2C_6H_4}$. Formed from *m*-phenylene-diamine and oxalic ether (K.). Amorphous.

Di-phenyl-di-ethyl oxamide $\mathrm{C_2O_2(NH.C_2H_4Ph)_2}$. [180°]. Crystals (Neubert, *B.* 19, 1826).

Di-phenyl-di-methyl oxamide $\mathrm{C_2O_2(NMePh)_2}$. (250°). Formed from methyl-aniline and oxalic ether.

o-Tolyl-oxamic acid $\mathrm{CO(NHC_7H_7).CO_2H}$. [137°]. Formed by fusing $\mathrm{KEtC_2O_4}$ with o-toluidine (Mauthner a. Suida, *M.* 7, 233; 9, 735). Needles (containing aq). Yields indole when heated with zinc-dust.—$\mathrm{CaA'_2}$.—$\mathrm{BaA'_2}$aq.—AgA'.

***p*-Tolyl-oxamic acid.** [170°]. Obtained from its ether $\mathrm{CO(NHC_7H_7)CO_2Et}$ [67°] which is formed by heating oxalic ether with *p*-toluidine.

Nitro-tolyl-oxamic acid $\mathrm{C_9H_8N_2O_5}$ *i.e.* [1:4:3] $\mathrm{C_6H_3Me(NO_2).NH.CO.CO_2H}$. Formed by heating nitro-*m*-toluidine with oxalic acid (Hinsberg, *B.* 15, 2691). Yellowish-red plates (containing aq).—NaA'aq.—$\mathrm{BaA'_2}$3aq.

Ethyl ether EtA'. [127°].

o-Tolyl oxamide $\mathrm{CO(NH_2).CO(NHC_7H_7)}$ (Bladin, *Bl.* [2] 41, 129).

Di-o-tolyl-oxamide $\mathrm{C_2O_2(NHC_7H_7)_2}$. [200°]. Formed by heating oxalic acid with o-toluidine at 220° (M. a. S.). Crystals (from benzene). Converted by treatment with fuming $\mathrm{HNO_3}$ into $\mathrm{C_2O_2(NH.C_6H_2Me(NO_2)_2}$ [2:1:3:5]$)_2$ which decomposes at about 270° (Mixter a. Kleeberg, *Am.* 11, 236). On oxidation by neutral $\mathrm{KMnO_4}$ it yields $\mathrm{C_2O_2(NH.C_6H_4.CO_2H)_2}$, which forms the salts $\mathrm{Cu_2A''O}$ and $\mathrm{Ag_2A''}$.

***p*-Tolyl-oxamide** $\mathrm{CO(NH_2).CO(NHC_7H_7)}$. [237°]. Formed from *p*-toluidine cyanide $\mathrm{(C_7H_7NH_2)Cy_2}$ and HOAc (Bladin). Needles, v. sol. alcohol.

Di-*p*-tolyl-oxamide $\mathrm{C_2O_2(NHC_7H_7)_2}$. [269°]. Crystals, v. sol. hot HOAc. Yields on nitration $\mathrm{C_2O_2(NHC_7H_6NO_2)_2}$ and $\mathrm{C_2O_2(NHC_7H_5(NO_2)_2)_2}$.

Amido-tolyl-oxamic ether $\mathrm{C_{11}H_{14}N_2O_3}$ *i.e.* $\mathrm{C_6H_3Me(NH_2).NH.CO.CO_2Et}$. *Tolylene-oxamethane.* [168°]. Formed from tolylene-*m*-diamine and oxalic ether in alcohol (Tiemann, *B.* 3, 222). Plates (from alcohol). When dilute alcohol of 90 p.c. only is used the acid $\mathrm{C_6H_3Me(NH_2).NH.CO.CO_2H}$ [224°] is formed (Schiff, *B.* 23, 1819). Phenyl thiocarbimide yields $\mathrm{C_6H_3Me(NH.CS.NHPh).NH.CO.CO_2Et}$ [155°], a crystalline compound [138°], and $\mathrm{C_6H_3Me}\Big\langle\begin{matrix}\mathrm{NH.C_2O_2}\\ \mathrm{NH.CS}\end{matrix}\Big\rangle\mathrm{NPh}$. [198°]. $\mathrm{ClCO_2Et}$ forms [1:2:4] $\mathrm{C_6H_3Me(NH.CO_2Et).NH.C_2O_3Et}$ [131°], whence alcoholic ammonia yields $\mathrm{C_6H_3Me(NH.CO_2Et).NH.C_2O_2.NH_2}$ [209°] (Schiff a. Vanni, *B.* 24, 687, 1315). The compounds [1:4:2] $\mathrm{C_6H_3Me(NH.CO_2Et).NH.C_2O_3Et}$ [128°] and [1:4:2] $\mathrm{C_6H_3Me(NH.CO_2Et).NH.C_2O_2NH_2}$ [223°] are also crystalline. The following bodies of like character are also crystalline: [1:2:4] $\mathrm{C_6H_3Me(NH.CO.NH_2)(NH.C_2O_3Et)}$ [218°], [1:2:4] $\mathrm{C_6H_3Me(NH.CO.NH_2)(NH.C_2O_2NH_2)}$ [239°], [1:2:4] $\mathrm{C_6H_3Me(NH.C_2O_3Et)(NH.C_2O_2NH_2)}$ [210°], [1:2:4] $\mathrm{C_6H_3Me(NH.C_2O_3Et)_2}$ [130°], and [1:2:4] $\mathrm{C_6H_3Me(NH.C_2O_2NH_2)_2}$ [220°]. The compounds [1:2:4] $\mathrm{C_6H_3Me(NH.CO_2Et).NH.C_2O_3H}$ [170°] and [1:2:4] $\mathrm{C_6H_3Me(NH.CONH_2).NH.C_2O_3H}$ [203°] have also been prepared.

Amide $\mathrm{C_6H_3Me(NH_2).NH.C_2O_3H}$ [1:2:4]. [223°]. From the ether and alcoholic $\mathrm{NH_3}$.

Anilide $\mathrm{C_6H_3Me(NH_2).NH.C_2O_2NPhH}$ [186°] (Schiff, *B.* 24, 871).

Xylyl-oxamic acid $\mathrm{CO(NHC_6H_3Me_2).CO_2H}$. [129°]. Formed by heating *m*-xylidine with $\mathrm{KEtC_2O_4}$ (Mauthner a. Suida, *M.* 9, 745). Needles (containing aq). On heating it yields di-xylyl-oxamide $\mathrm{C_2O_2(NHC_6H_3Me_2)_2}$ [210°].—$\mathrm{CuA'_2}$.—AgA'.

ψ-Cumyl-oxamic acid $\mathrm{CO(NHC_6H_2Me_3).CO_2H}$. [167°]. Yellow needles which on heating yield di-ψ-cumyl-oxamide $\mathrm{C_2O_2(NHC_6H_2Me_3)_2}$ [230°].—NaA'3aq.—$\mathrm{KHA'_2}$.—$\mathrm{CaA'_2}$aq.—$\mathrm{AgHA'_2}$.—AgA'

Di-propyl-di-benzyl-oxamide $\mathrm{C_2O_2(NH.CH_2C_6H_4Pr)_2}$. [182°] (Goldschmidt a. Gessner, *B.* 22, 932). Crystalline.

Tetra-phenyl-di-propyl-oxamide $\mathrm{C_2O_2(NH.CH_2.CHPh.CH_2Ph)_2}$. [116°]. Formed from $\mathrm{CH_2Ph.CHPh.CH_2NH_2}$ and oxalic ether (Freund a. Remse, *B.* 23, 2862).

(α)-Naphthyl-oxamic acid $\mathrm{CO(NHC_{10}H_7).CO_2H}$. [180°]. Formed from oxalic ether and (α)-naphthylamine (Ballo, *B.* 6, 247). Needles. — KA'. — $\mathrm{CaA'_2}$. — $\mathrm{BaA'_2}$. — $\mathrm{(C_{10}H_7NH_2)HA'}$. [154°]. Needles (from water).

Ethyl ether EtA'. [106°]. Needles.

Di-(α)-naphthyl-oxamide $\mathrm{C_2O_2(NHC_{10}H_7)_2}$. [200°]. Small scales (Zinin, *A.* 108, 228).

Benzylidene-oxamide $\mathrm{C_6H_5.CH(NH)_2C_2O_2}$. Formed from oxamic ether and benzoic aldehyde (Medicus, *A.* 157, 50). Plates (containing $\frac{1}{2}$aq).

Piperidyl-oxamic ether $\mathrm{C_5H_{10}N.CO.CO_2Et}$. (290°). Formed from piperidine and oxalic ether (Wallach a. Lehmann, *A.* 237, 245). Oil.

Oxamidine $\mathrm{C(NH)(NH_2).C(NH)NH_2}$. The hydrochloride of this base B'HCl aq is formed by the action of alcoholic $\mathrm{NH_3}$ on the hydrochloride of oximido-ethyl ether (Pinner, *B.* 16, 1656). It crystallises in plates, v. sol. water.

Oxalamidoxim $\mathrm{C(NOH)(NH_2).C(NOH)(NH_2)}$. [200°]. Formed by the action of hydroxylamine on cyananiline or on cyanogen (E. Fischer, *B.* 22, 1932; Ephraim, *B.* 22, 2305; Zinkeisen, *B.* 22, 2946; Vorlander, *B.* 24, 814). Colourless prisms, v. sol. hot water, sl. sol. alcohol. $\mathrm{ClCO_2Et}$ forms $\mathrm{C(NO.CO_2Et)NH_2.C(NO.CO_2Et)NH_2}$ [168°]. Aldehyde produces $\mathrm{CH_3CH}\Big\langle\begin{matrix}\mathrm{HN}\\ \mathrm{ON}\end{matrix}\Big\rangle\mathrm{C.C}\Big\langle\begin{matrix}\mathrm{NH}\\ \mathrm{NO}\end{matrix}\Big\rangle\mathrm{CHCH_3}$ [198°]. Succinic anhydride yields the acid $\mathrm{CO_2H.C_2H_4.C}\Big\langle\begin{matrix}\mathrm{N}\\ \mathrm{O.N}\end{matrix}\Big\rangle\mathrm{C.C}\Big\langle\begin{matrix}\mathrm{N}\\ \mathrm{N.O}\end{matrix}\Big\rangle\mathrm{C.C_2H_4.CO_2H}$ [200°]. Chloral yields $\mathrm{C_8H_6N_4O_4Cl_8}$ [197°].—B'HCl: prisms, insol. alcohol.

Di-acetyl derivative [184°]. Crystals. On heating with $\mathrm{Ac_2O}$ it yields $\mathrm{CMe}\Big\langle\begin{matrix}\mathrm{N}\\ \mathrm{O.N}\end{matrix}\Big\rangle\mathrm{C.C}\Big\langle\begin{matrix}\mathrm{N}\\ \mathrm{N.O}\end{matrix}\Big\rangle\mathrm{CMe}$. [165°].

Di-benzoyl derivative [217°]. Excess of BzCl forms $\mathrm{PhC}\Big\langle\begin{matrix}\mathrm{N}\\ \mathrm{O.N}\end{matrix}\Big\rangle\mathrm{C.C}\Big\langle\begin{matrix}\mathrm{N}\\ \mathrm{N.O}\end{matrix}\Big\rangle\mathrm{CPh}$ [246°], insol. water.

Di-ethyl ether $\mathrm{C(NOEt)(NH_2).C(NOEt)(NH_2)}$. [115°]. Formed from oxalamidoxim, EtI, and NaOEt (Zinkeisen, *B.* 22, 2950). Needles, sl. sol. hot water.

Oxaluramidoxim $\mathrm{C(NOH)(NH.CO.NH_2).C(NOH).NH.CO.NH_2}$. [192°]. Formed from oxalamidoxim and conc.

aqueous potassium cyanate (Z.). White needles, insol. cold water.

Phenyl-oxalamidoxim C(NOH)(NHPh).C(NOH)(NH_2). [c. 180°] (Z.); [148°] (Tiemann, *B.* 22, 1936). Formed from alcoholic hydroxylamine hydrochloride and solid cyananiline (Zinckeisen, *B.* 22, 2954). Plates. Ac_2O produces $C(NOH)(NHPh).C\Big\langle{}^{N}_{N.O}\Big\rangle CMe$ [172°].—B'HCl: colourless needles.

Di-benzoyl derivative [189°]. Needles.

Hydroxylamide of oxalic acid $C_2O_2(NH.OH)_2$. Formed from oxalic ether and hydroxylamine (Lossen, *A.* 150, 314). Minute prisms (from water). Explodes at 105°.—NaHA″.—KHA″.—CaA'_2. — $BaH_2A''_2$. — ZnA″. — Ag_2A''. — $NH_2(OH)H_2A''$.

Oxalyl-tetra-methyl-di-hydrazine $C_2O_2(NH.NMe_2)_2$. [220°]. Formed from di-methyl-hydrazine and oxalic ether (Renouf, *B.* 13, 2172). Plates, sol. alcohol.

Oxalyl-di-ethyl-di-hydrazine $C_2O_2(NH.NHEt)_2$. [204°]. Formed from ethyl-hydrazine and oxalic ether (Fischer, *A.* 199, 297). Needles. Gives rise to the nitrosamine $C_2O_2(N_2HPh.NO)_2$ [145°], crystallising from water in prisms.

Oxalphenylhydrazic acid $CO(N_2H_2Ph).CO_2H$. [170°]. Formed from oxalic ether, phenyl-hydrazine, and alcoholic NaOEt (Michael, *J. pr.* [2] 35, 458).—NaA′.—EtA′. [119°].

Oxalyl-di-phenyl-di-hydrazine $C_2O_2(N_2H_2Ph)_2$. [278°]. Formed from oxalic ether and phenyl-hydrazine at 110° (E. Fischer, *A.* 190, 131). Plates. With $COCl_2$ it yields $C_2O_2(N_2(CO)Ph)_2$ [above 300°].

Semi-nitrile of oxalic acid *v.* CYANOFORMIC ACID.

Semi-nitrile of ortho-oxalic acid. *Tri-ethyl ether* $C(OEt)_3CN$. (161°). S.G. $\frac{15.5}{}$ 1·003. Polymerises on standing (Bauer, *A.* 229, 178).

Tri-propyl derivative $C(OPr)_3.CN$. (216°–219°).

Nitrile of oxalic acid is CYANOGEN.

OXALIMIDO-ETHYL ETHER $C_6H_{12}N_2O_2$ *i.e.* C(NH)(OEt).C(NH)(OEt). [c. 25°]. (c. 170°). Formed from cyanogen and alcoholic HCl (Pinner a. Klein, *B.* 11, 1481). Long prisms. Benzyl-amine at 110° forms $(CH_2PhNH)_2C_2(NH)_2$ [150°] (Vorländer, *B.* 24, 806). *p*-Toluidine forms the isomeric $(C_6H_4MeNH)_2C_2(NH)_2$ [220°–230°], which is converted by hydroxylamine sulphate into $C(NOH)(NH_2).C(NOH)NHC_7H_7$ [175°], which yields a dibenzoyl derivative [194°], and by hydroxylamine hydrochloride into $C(NOH)(NH_2).C(NH)NHC_7H_7$ [148°], whence may be got $C(NOEt)NH_2.C(NH)NHC_7H_7$ [133°] and $C(NOCH_2Ph)(NH_2).C(NH)NHC_7H_7$ [165°].

OXALINES. A name given to certain alkyl-glyoxalines (Wallach, *A.* 214, 278, 325; Japp, *C. J.* 43, 197; Radziszewski, *B.* 15, 2706). They are described as alkyl-glyoxalines (*v.* also GLYOXALINES).

OXAL-METHYL-ETHYLINE *v.* DI-METHYL-GLYOXALINE.

OXALMETHYLINE is identical with METHYL-GLYOXALINE (*q. v.*).

OXAL-METHYL-PROPYLINE *v.* METHYL-ETHYL-GLYOXALINE.

OXALOXYL-AMIDO-BENZOIC ACID *v.* CYNURIC ACID and CARBOXY-PHENYL-OXAMIC ACID.

OXALPROPIONIC ETHER *v.* METHYL-OXAL ACETIC ETHER.

OXALPROPYLAMYLINE *v.* PROPYL-BUTYL-GLYOXALINE.

OXALPROPYLBUTYLINE *v.* DI-PROPYL-GLYOXALINE.

OXAL-PROPYL-ETHYLINE *v.* METHYL-PROPYL-GLYOXALINE.

OXALPROPYLINE *v.* ETHYL-PROPYL-GLYOXALINE.

OXALSUCCINIC ETHER $CO_2Et.CO.CH(CO_2Et).CH_2.CO_2Et$. (156° at 17 mm.). Formed by the action of NaOEt on an ethereal solution of oxalic and succinic ethers (W. Wislicenus, *B.* 22, 885). Oil, v. sol. alkalis. $FeCl_3$ gives a deep-red colour in alcoholic solutions. Split up, in dilute solutions, on warming into oxalic and succinic acids and alcohol. Yields a phenyl-hydrazide.

OXALURIC ACID $C_3H_4N_2O_4$ *i.e.* $NH_2.CO.NH.CO.CO_2H$. Mol. w. 132. H.F. 2,500 (Matignon, *C. R.* 113, 198). Occurs as ammonium salt in urine (Schunck, *J.* 1866, 749). Formed by heating parabanic acid with aqueous alkalis (Liebig a. Wöhler, *A.* 26, 287), and occurs among the products of the action of HCl and $KClO_3$ on guanine (Strecker, *A.* 118, 151). Its ether is produced by the action of urea on $COCl.CO_2Et$ in the cold (Henry, *B.* 4, 644). White crystalline powder, sl. sol. water. It reddens litmus. Its aqueous solution is decomposed on boiling into urea and oxalic acid. $POCl_3$ converts it into parabanic acid (Grimaux, *C. R.* 77, 1548). HNO_3 slowly decomposes it into CO_2 (54 c.c.), N_2O (38 c.c.), CO and N (15 c.c. together) (Franchimont, *R. T. C.* 6, 216).

Salts.—NH_4A': silky needles, v. sol. hot water.—KA′ aq. Trimetric crystals: $a:b:c = 1:·601:·539$.—CaA'_2 2aq. S. ·205 at 15°; 5 at 100° (P. Waage, *A.* 118, 301).—BaA'_2 2aq. S. ·158 at 9°; 1·8 at 100°.—AgA′: long silky needles.

Ethyl ether EtA′. [178°] (Salomon, *B.* 9, 374). Silky needles.

Amide $NH_2.CO.NH.CO.CO.NH_2$. [155°–160°]. Formed, together with dialuric acid, by the action of NH_3Aq and HCy on alloxan (Rösing a. Schischkoff, *A.* 106, 255; Strecker, *A.* 113, 48). Formed also by the action of alcoholic ammonia on oxaluric ether, and of dry NH_3 on parabanic acid at 130° (Roudinskōia, *Bl.* [2] 45, 250). Produced by heating urea with oxamic ether (Carstanjen, *J. pr.* [2] 9, 143). Crystalline powder, insol. cold water. Converted into ammonium oxalurate by boiling water.

Oxaluryl-hydrazine $CO(NH_2).CO.CO.N_2H_2Ph$. [215°]. Formed by heating phenyl-hydrazine parabanate (Skinner a. Ruhemann; *C. J.* 53, 550).

Dimethyl-oxaluramide $C_5H_9N_3O_3$. [225°]. Formed from di-methyl-parabanic acid and alcoholic NH_3 at 100° (Menschutkin, *A.* 178, 203). Needles.

OXALYL-DI-CHLORO-ACETIC ETHER *v.* TETRA-CHLORO-TETRA-OXY-ADIPIC ETHER.

OXALYL-DI-*p*-DIMETHYLPHENYLENE-DIAMINE *v.* TETRA-METHYL-DI-AMIDO-DI-PHENYL-OXAMIDE.

OXALYL-METHYL-THIO-UREA *v.* METHYL-THIO-PARABANIC ACID.

OXALYL-METHYL-UREA *v.* *Methyl*-PARABANIC ACID.

OXALYL-TOLYLENE-DIAMINE

$\left[\begin{smallmatrix}1 & 3\\ & 4\end{smallmatrix}\right] C_6H_3Me<\begin{smallmatrix}NH.CO\\ NH.CO\end{smallmatrix}$ or $C_6H_3Me<\begin{smallmatrix}N:C(OH)\\ N:C(OH)\end{smallmatrix}$.

Di-oxy-methyl-quinoxaline. Formed by heating the acid oxalate of tolylene-diamine to 160° (Hinsberg, *B.* 16, 1531). Converted by PCl_5 into $C_6H_3Me<\begin{smallmatrix}N:CCl\\ N:CCl\end{smallmatrix}$ [115°], crystallising in needles, insol. water.

Oxalyl-di-tolylene-tetramine $C_2O_2(NH.C_6H_3Me.NH_2\,[4:1:3])_2$. [above 300°]. Formed by reducing di-nitro-di-tolyl-oxamide (*v.* OXALIC ACID). Small needles. Above 300° it forms $C_6H_3Me<\begin{smallmatrix}N\\ NH\end{smallmatrix}>C.C<\begin{smallmatrix}N\\ NH\end{smallmatrix}>C_6H_3Me$.

Salts. — $B'_2H_2SO_4$ 5aq. — $B'H_2Cl_2$ aq. — $B'H_2PtCl_6$: yellow amorphous pp.

OXALYL-UREA *v.* PARABANIC ACID.

OXAMETHANE is the *Ethyl ether of oxamic acid v.* OXALIC ACID.

OXAMETHANE CHLORIDE *v.* DI-CHLORO-AMIDO-ACETIC ETHER.

OXAMIC ACID *v.* OXALIC ACID.

OXAMIDE *v.* OXALIC ACID.

OXAMIDINE *v.* OXALIC ACID.

ω-OXAMIDO-ACETOPHENONE-OXIM $C_6H_5.C(NOH).CH_2.NH(OH)$. [163°]. Formed by digesting a dilute alcoholic solution of ω-bromo-acetophenone with hydroxylamine hydrochloride for several hours at the boiling-point (Schramm, *B.* 16, 2183). White crystalline solid. Sol. alcohol and ether, insol. cold water and ligroïn. Dissolves in alkalis.—$C_8H_9N_2O_2Ag$.

m-**OXAMIDO-CARBIMIDO-CARBOXAMIDO-BENZOIC ACID** $(OH)NH.C(NH).CO.NH.C_6H_4.CO_2H$. Formed by the action of an aqueous solution of hydroxylamine upon cyancarboxamido-benzoic acid $NC.CO.NH.C_6H_4.CO_2H$ (vol. i. p. 157) (Griess, *B.* 18, 2416). White needles. Sl. sol. hot water.—BaA'_2 4aq.

OXANILIC ACID is *Phenyl-oxamic acid v.* OXALIC ACID.

OXANILIDE is *Di-phenyl-oxamide v.* OXALIC ACID.

OXANTHRANOL $C_{14}H_{10}O_2$ *i.e.* $C_6H_4<\begin{smallmatrix}CO\\ CH(OH)\end{smallmatrix}>C_6H_4$. *Anthrahydroquinone.* Prepared from anthraquinone (1 pt.), zinc-dust (2 pts.), and NaOH (30 pts. of 50 per cent. solution). The filtrate is ppd. by acids, but the ppd. oxanthranol must be kept in a closed bottle under carbonic acid water, as it is reoxidised by air to anthraquinone (Graebe a. Liebermann, *A.* 160, 126; 212, 65). The red solution of oxanthranol in KOHAq is attacked by alkyl iodides forming alkyl-oxanthranols. The alkyl-oxanthranols may be reduced to alkyl-anthracene di-hydrides, which may be re-oxidised to the alkyl-oxanthranols. The alkyl oxanthranols give, with PCl_5, alkyl-oxanthranyl chlorides. In these respects methyl-oxanthranol behaves differently from the others. The alkyl-oxanthranyl chlorides are converted by water back to alkyl-oxanthranols. Alkyl-oxanthranols (1 pt.) are reduced by zinc-dust (2 pts.) and ammonia (8 pts. of S.G. ·88) and water (5 pts.) to alkyl-hydro-anthranols (Liebermann, *A.* 212, 108).

Acetyl derivative $C_{14}H_9AcO_2$. Formed from oxanthranol, NaOAc and Ac_2O. Crystalline solid.

Methyl-oxanthranol $C_6H_4<\begin{smallmatrix}CO\\ CH(OMe)\end{smallmatrix}>C_6H_4$ or $C_6H_4<\begin{smallmatrix}CO\\ CMe(OH)\end{smallmatrix}>C_6H_4$. [187°]. Formed by heating a mixture of anthraquinone, NaOH, zinc-dust, water, and MeBr (Liebermann a. Landshoff, *B.* 14, 456; *A.* 212, 75). Colourless plates, sl. sol. alcohol, forming a solution with blue fluorescence. Reduced by HI and P to anthracene dihydride. Not attacked by PCl_5. An isomeride of methyl-oxanthranol [98°] is sometimes formed by the action of NaOHAq and MeI on oxanthranol (Liebermann, *B.* 21, 1175).

Ethyl-oxanthranol $C_6H_4<\begin{smallmatrix}CO\\ CH(OEt)\end{smallmatrix}>C_6H_4$. [107°]. Formed from oxanthranol, NaOHAq, and EtI at 100°. Formed also by oxidation of $C_6H_4<\begin{smallmatrix}CEt\\ C(OEt)\end{smallmatrix}>C_6H_4$ [77°] with CrO_3 in HOAc (Goldmann, *B.* 21, 2507). Needles or trimetric prisms; $a:b:c$ = ·741:1: ·495. Its alcoholic solution exhibits strong blue fluorescence. It is insol. aqueous alkalis. Reacts with hydroxylamine (E. von Meyer, *J. pr.* [2] 29, 496). HI and P reduce it to ethyl-anthracene dihydride. Conc. H_2SO_4 forms crystalline $C_{16}H_{12}O_2$. Yields a di-bromo- derivative $C_{14}H_7Br_2O(OEt)$ [123°] and a di-nitro- derivative crystallising in small needles. PCl_5 forms $C_6H_4<\begin{smallmatrix}CO\\ CEtCl\end{smallmatrix}>C_6H_4$ [89°].

Isobutyl-oxanthranol $C_6H_4<\begin{smallmatrix}CO\\ C(C_4H_9)(OH)\end{smallmatrix}>C_6H_4$. [130°]. Prisms or needles (Liebermann a. Walder, *B.* 14, 462). PCl_5 yields the chloride $C_6H_4:C_2OCl(C_4H_9):C_6H_4$ [78°], which reproduces isobutyl-oxanthranol on boiling with water.

Isoamyl-oxanthranol $C_6H_4<\begin{smallmatrix}CO\\ C(C_5H_{11})(OH)\end{smallmatrix}>C_6H_4$. [125°]. Monoclinic tables (from benzene-ligroïn). Conc. H_2SO_4 removes H_2O, forming $C_{19}H_{18}O$ [72°] which separates from alcohol as yellow needles, and forms a dibromide $C_{19}H_{18}Br_2O$ [120°]. Further action of H_2SO_4 forms a cherry-coloured liquid, whence alcohol ppts. yellow needles of $C_{19}H_{14}O$ [206°], a body which, on oxidation, yields anthraquinone carboxylic acid and a compound $C_{19}H_{12}O_4$ [157°]. The compound $C_{19}H_{14}O$ is reduced by HI in HOAc to $C_{19}H_{18}$ [93°] which crystallises from alcohol in needles, and forms on nitration a compound $C_{19}H_{16}N_2O_5$ (Liebermann, *A.* 212, 99). Phosphorus pentachloride converts isoamyl-oxanthranol into the chloride $C_6H_4<\begin{smallmatrix}CO\\ CCl(C_5H_{11})\end{smallmatrix}>C_6H_4$ [85°] which forms monoclinic crystals; $a:b:c$ = 1·266:1:2·752; β = 68° 23′. NaOAc converts the chloride into $C_{19}H_{19}AcO_2$ [73°].

Benzyl-oxanthranol $C_{21}H_{16}O_2$. [146°]. Formed by boiling anthraquinone (5 pts.), zinc-dust (5 pts.), KOH ($7\frac{1}{2}$ pts.), benzyl bromide (5 pts.), and water (100 pts.), for a long time (Levi, *B.* 18, 2153). White tables, v. sol. alcohol. Conc. H_2SO_4 at 70° forms a violet solution containing the anhydride $C_{21}H_{14}O$ which crystallises in yellow needles, oxidised by CrO_3 to anthraquinone. The anhydride yields a dibromide

$C_6H_4<\begin{smallmatrix}CO\text{———————}\\CBr(CHBrPh)\end{smallmatrix}>C_6H_4$ [148°] (Bach, *B.* 23, 1569) which on boiling with alcohol gives $C_6H_4<\begin{smallmatrix}CO\text{————}\\C(CBrPh)\end{smallmatrix}>C_6H_4$ [254°].

Acetyl derivative $C_6H_4<\begin{smallmatrix}CO\text{——————————}\\C(CH_2Ph)(OAc)\end{smallmatrix}>C_6H_4$. [281°]. Needles.

(β)-Oxanthranol $C_{14}H_{10}O_2$ *i.e.* $C_6H_4<\begin{smallmatrix}C(OH)\\|\\C(OH)\end{smallmatrix}>C_6H_4$. Obtained by careful oxidation of anthracene by adding 5·6 grms. of lead peroxide to a hot solution of 2 grms. of pure anthracene in 50 c.c. of acetic acid (Schulze, *B.* 18, 3036). Greenish-yellow needles (from alcohol). The alkaline solution is red, but quickly becomes decolourised on shaking with air from oxidation to anthraquinone. It is very oxidisable. In its properties it closely resembles oxanthranol. With ammoniacal $AgNO_3$ it gives a pp. of metallic silver. Cupric hydrate mixed with excess of NaOH is reduced to black cuprous oxide.

Di-methyl ether $C_{14}H_8(OMe)_2$ [196°].

Di-ethyl ether $C_{14}H_8(OEt)_2$; crystals.

Di-benzyl ether $C_{14}H_8(OC_7H_7)_2$ [220°]; small colourless glistening crystals.

Di-acetyl derivative $C_6H_4<\begin{smallmatrix}C(OAc)\\C(OAc)\end{smallmatrix}>C_6H_4$. [260°]. Formed from ordinary oxanthranol, Ac_2O, and NaOAc (L.). Needles (from HOAc).

Di-oxy-(β)-oxanthranol *v.* TRI-OXY-ANTHRANOL.

OXATOLUIC ACID *v.* DI-BENZYL-GLYCOLLIC ACID.

OXAZINES. Compounds derived from the hypothetical oxazine $NH<\begin{smallmatrix}CH:CH\\CH:CH\end{smallmatrix}>O$. Quinoxazine is $C_6H_4<\begin{smallmatrix}O\ .CH\\NH.CH\end{smallmatrix}$.

OXAZOLES. Compounds derived from the hypothetical oxazole $\begin{smallmatrix}CH:CH\\N\ \ :CH\end{smallmatrix}>O$ (Hantzsch, *B.* 21, 944). They are formed by the action of the halogen derivatives of ketones on acetamide and its homologues, *e.g.* $Ph.CO.CH_2Br + Me.CO.NH_2 = PhC\lessdot\begin{smallmatrix}CH.O\\N\ :CMe\end{smallmatrix} + HBr + H_2O$.

Compounds derived from $\begin{smallmatrix}CH:CH\\CH:N\end{smallmatrix}>O$ may be called is-oxazoles. Thus phenyl-isoxazole is formed by the action of AcCl on the oxim of benzoyl-acetic aldehyde (Claisen, *B.* 24, 131).

OXETHYL- *v.* OXY-ETHYL-.

OXETONES. Compounds derived from the hypothetical $CH_2<\begin{smallmatrix}CH_2\text{——}\\CH_2.O\end{smallmatrix}>C<\begin{smallmatrix}\text{——}CH_2\\O.CH_2\end{smallmatrix}>CH_2$. They are formed by treating lactones with sodium and heating the products (Fittig, *A.* 256, 57). Thus valerolactone $C_5H_8O_2$ yields $C_{10}H_{14}O_3$, which, when boiled with NaOHAq forms $C_{10}H_{15}NaO_4$, whence the acid $C_{10}H_{16}O_4$ which is split up by heat into CO_2 and di-methyl-oxetone $CH_2<\begin{smallmatrix}CH_2\text{———}\\CHMe.O\end{smallmatrix}>C<\begin{smallmatrix}\text{———}CH_2\\O.CHMe\end{smallmatrix}>CH_2$.

OXIDATION. This term was used formerly to connote chemical changes wherein oxygen was added on to an element or compound, or a compound was decomposed by the action of O with formation of oxidised products. The term was nearly synonymous with *combustion* in the earlier and more restricted meaning of that word. For an account of the phlogistic theory of combustion *v.* COMBUSTION, vol. ii. p. 241.

The term oxidation has been widened until at present it is applied to all chemical changes which result in an addition of negative radicle, simple or compound, to elements or compounds, or a decrease in the relative quantity of the positive radicle of a compound, whether this is or is not accompanied by substitution of negative radicle. Thus the following changes are classed together as oxidations:—$4Fe + 3O_2 = 2Fe_2O_3$; $2Fe + 3Cl_2 = 2FeCl_3$; $2BaO + O_2 = 2BaO_2$; $4Cu + S_2 = 2Cu_2S$; $2HgI + I_2 = 2HgI_2$; $2KNO_2 + O_2 = 2KNO_3$; $BaS + 2O_2 = BaSO_4$; $4FeSO_4 + 2H_2SO_4 + O_2 = 2Fe_2(SO_4)_3 + 2H_2O$; $2K_4FeCy_6 + Cl_2 = 2K_3FeCy_6 + 2KCl$; $2Cr_2O_3 + 4K_2O + 3O_2 = 4K_2CrO_4$; $4K_2MnO_4 + O_2 = 4KMnO_4 + 2K_2O$; $Bi_2O_3 + 4Cl + 2H_2O + 4KOH = Bi_2O_5 + 4KCl + 4H_2O$; $3C_2H_6O + 2CrO_3 = 3C_2H_4O + 3H_2O + Cr_2O_3$.

Processes of oxidation are accompanied by processes of reduction or deoxidation. The following examples make this clear (*cf.* DEOXIDATION, vol. ii. p. 377):—

Original element or compound.		Oxidiser.		Oxidised Product.		Deoxidised Product.
H_2	+	O	=	H_2O		H_2O
(The H_2O may be regarded as oxidised H, or as reduced O.)						
2Hg	+	O_3	=	Hg_2O		O_2
(The O_2 may be regarded as reduced ozone $[O_3]$).						
$SbCl_3$	+	Cl_2	=	$SbCl_5$		$SbCl_5$
(The $SbCl_5$ is oxidised $SbCl_3$, or reduced Cl_2.)						
Sn	+	$2HNO_3$	=	$SnO_2 + H_2O$	+	N_2O_3
$3H_2C_2O_4Aq$	+	$2KMnO_4Aq$	=	$6CO_2 + 3H_2O$	+	$2MnO_2 + K_2OAq$
{ PbO	+	2Cl + 2KOHAq	=	$PbO_2 + H_2O$	+	2KClAq
{ K_4FeCy_6Aq	+	Cl_2	=	K_3FeCy_6Aq	+	2KClAq
{ $4K_2MnO_4Aq$	+	O_2	=	$4KMnO_4Aq$	+	$2K_2O$
(In the three cases in the bracket, KCl and K_2O may be regarded as reduced Cl and O respectively.						
$3SO_2Aq$	+	$2HNO_3Aq + 2H_2O$	=	$3H_2SO_4Aq$	+	2NO

Any element or compound which frequently reacts to produce substances containing relatively more negative radicle than the original substance acted on, is called an *oxidiser* or *oxidising agent*. Among the substances commonly used in the laboratory to effect oxidations are oxygen, ozone, chlorine, hypochlorites, nitric acid, potassium permanganate, potassium chlorate, molten potash, and chromium trioxide. The conditions under which oxidation occurs vary much; thus Hg is oxidised by ozone at the

ordinary temperature, but by O only at temperatures near the B.P. of Hg; $KMnO_4Aq$ oxidises $H_2C_2O_4Aq$ completely only in the presence of H_2SO_4, and at a moderately high temperature; O does not oxidise SO_2 under ordinary conditions, but if the gases are passed over hot spongy Pt, SO_3 is produced rapidly. When O is absorbed by charcoal, and the charcoal is then brought into contact with H_2S, PH_3, C_2H_6O, &c., oxidation proceeds rapidly (*v.* Calvert, *C. J.* [2] 5, 293). The products of oxidation obtained from a specified substance often vary according to the oxidiser employed; thus ozone produces Hg_2O from Hg at ordinary temperatures, but HgO is formed by the action of O on hot Hg; carbohydrates generally give $H.CO_2H$ when oxidised by CrO_3, but $H_2C_2O_4$ when oxidised by HNO_3; phthalic acids, $C_6H_4(CO_2H)_2$, are obtained by oxidising naphthalene, $C_{10}H_8$, by CrO_3 in glacial acetic acid, but the chief product of the oxidation of the same compound by K_2CrO_4 and H_2SO_4Aq (which is essentially a solution of CrO_3) is naphthaquinone, $C_{10}H_6O_2$. There are some compounds the presence of which in a solution of an oxidisable body hastens the oxidation when O is passed into the solution; thus, $H_2C_2O_4Aq$ is oxidised by CrO_3Aq in presence of $MnSO_4$ (Harcourt, *B. A.* 1864. 34); SO_2Aq is rapidly oxidised by O in the presence of certain salts, especially $MnSO_4$, $CuSO_4$, $FeCl_3$, $CoCl_2$, &c. (*v.* L. Meyer, *B.* 20, 3058; Roessler, *D. P. J.* 242, 278; *cf.* Mendelejeff, *B.* 19, 2656). M. M. P. M.

OXIDES. *Binary compounds of oxygen.* For the purposes of this definition, those compounds of O with organic radicles which react similarly to oxides of elements must be classed among binary compounds (*e.g.* the ethers); in the present article, however, only the binary compounds of O with elements are considered. Oxides of all elements except Br and F have been isolated.

Oxides are frequently prepared by the direct union of O with other elements; O unites directly with all the elements except Br, Cl, F, I, Au, and Pt. Metallic oxides are formed by the action of heat on carbonates, nitrates, and other salts of volatilisable acids; but the alkali oxides cannot be thus prepared. Most (?all) metals decompose water or steam, forming oxides or hydroxides, and evolving H. Many metallic sulphides yield oxides when roasted in air or O. Those oxides or hydroxides of metals which are not easily soluble in water are generally formed by the reaction of alkalis or alkaline oxides with solutions of metallic salts. The higher oxides of metals are often obtained by the action of hypochlorites, or Cl and KOHAq, on the lower oxides, sometimes by the action of conc. HNO_3 on the lower oxides or the metals, and sometimes by reacting on salts of the metals in solution with H_2O_2Aq in presence of an alkali.

Fusion of metallic oxides with KOH or KNO_3 generally results in the formation of alkali salts of metal-containing acids in the cases of those metals which are capable of forming such salts. The higher oxides of metals are generally more or less easily reduced to lower oxides; this reduction occurs sometimes by heating, in other cases by the action of such reducers as H, CO, SO_2Aq, or H_2S. The oxides of non-metals are frequently formed by combining O with the non-metal, *e.g.* B_2O_3, SO_2, SO_3, CO, CO_2, H_2O, NO_2, P_2O_3, P_2O_5; sometimes they are produced by such indirect methods as decomposing oxyacids or salts of oxyacids of the non-metals, *e.g.* N_2O_5 from HNO_3, I_2O_5 from HIO_3, ClO_2 from $KClO_3$; sometimes they are formed by very indirect methods, *e.g.* Cl_2O by the reaction of Cl with HgO.

Oxides may be divided into classes in accordance with their empirical composition; thus, monoxides, M_2O and MO; sesquioxides, M_2O_3; dioxides, MO_2; trioxides, MO_3; tetroxides, MO_4; pentoxides, M_2O_5; heptoxides, M_2O_7.

A better classification is that based primarily on chemical properties; on this system, oxides are classified as *basic*, *acidic*, *indifferent* or *neutral*, and *peroxides*. None of these terms can be defined with strictness. The term *basic* is applied to those *oxides* which react with acids or with oxides more negative than themselves to form salts. *Acidic oxides* are those which react with water to produce acids, or are formed by removing water from acids, or react with oxides more positive than themselves to form salts. Acidic oxides are sometimes called *anhydrides*. *Peroxides* react with acids to form salts which correspond with oxides containing less O than the peroxides. Some peroxides also form acids when dissolved in water, or react with acidic oxides to produce salts. Peroxides which exhibit acidic functions may be called *acidic peroxides*, *e.g.* CrO_3; peroxides which exhibit no acidic functions may be called *basic peroxides*, *e.g.* BaO_2. Certain other oxides are sometimes included in the class peroxides (*v. infra*). The class of *indifferent* or *neutral* oxides includes all oxides not belonging to one or other of the three preceding classes.

Basic oxides. Most of the lower oxides of metals belong to this class. The characteristic reactions of the class are shown by the following two typical changes:—$BaO + H_2SO_4Aq = BaSO_4 + H_2OAq$; $PbO + SO_3 = PbSO_4$. None of the oxides of any undoubted non-metal is distinctly basic. Oxides of non-metals, however, exist which form salts by reacting with certain strong acids, or the anhydrides of certain strong acids, and which also form salts by reacting with oxides more basic than themselves; thus, B_2O_3 reacts with H_2SO_4 containing SO_3 to form $B(HSO_4)_3$, and B_2O_3 also reacts with K_2O to form $K_2B_2O_4$; similarly As_2O_3 reacting with SO_3 forms compounds belonging to the salt type, $xAs_2O_3.ySO_3$, and with K_2OAq it forms $KAsO_2$.

Some metallic oxides are basic, and nevertheless also form compounds with water which react as weak acids towards the more positive oxides; thus Al_2O_3 is distinctly basic, $Al_2O_3.H_2O$ is also basic, yet it reacts with K_2OAq to form the unstable salt $K_2Al_2O_4$; similarly $Au_2O_3.3H_2O$ dissolves in HNO_3Aq to form the salt $Au(NO_3)_3$, and $Au_2O_3.3H_2O$ also dissolves in K_2OAq to form $K_2Au_2O_4$. The term basic oxide is sometimes widened to include oxides which correspond with salts, although these salts may not be formed directly from the oxides; thus, no salts have been obtained by the action of oxyacids on OsO, but a few salts corresponding with this oxide are produced by indirect methods, *e.g.* $OsSO_3$ is formed by reacting on OsO_4Aq with SO_2Aq. The *alkali-forming oxides* constitute a

division of the basic oxides; these oxides are distinctly and markedly basic; they also dissolve in water to form alkalis (*v.* ALKALI, vol. i. p. 111; *v.* also BASE, vol. i. p. 445).

Acidic oxides or *anhydrides.* The greater number of the oxides of non-metals belong to this class. SO_3 is a typical acidic oxide; it reacts with water to form the acid H_2SO_4; it is obtained by removing H_2O from H_2SO_4, by heating the acid; it reacts with basic oxides to form salts, *e.g.* with BaO it produces $BaSO_4$. All acidic oxides do not exhibit the three characteristic reactions; some yield acids with water, but are not obtained by removing water from their acids, *e.g.* P_2O_3; some are obtained by removing water from acids, but do not react with water to form acids, *e.g.* Sb_2O_3; some do not form acids with water, are not obtained by removing water from acids, but react with oxides more positive than themselves to produce salts, *e.g.* As_2O_3. Those acidic oxides which do not form corresponding acids by reacting with water generally show basic functions when they react with strong acids. Should an oxide form no acid with water, nor be obtained by removing water from an acid, but yet react with basic oxides to form salts, this oxide, although classed as acidic, will be found, almost certainly, to react as a basic oxide towards strong acids, or the anhydrides of strong acids. Thus, As_2O_3 does not form an acid with water, nor is it obtainable from a corresponding acid, it does, however, react with strongly basic oxides, *e.g.* with K_2OAq, to form salts; now As_2O_3 combines with SO_3 to form $As_2O_3.2SO_3$, a compound in which As_2O_3 acts as a basic oxide. Some of the higher oxides of metals react as feebly acidic oxides; the salts corresponding with these oxides are generally obtained by fusing the oxides with KOH or NaOH (*v.* ANHYDRIDES, vol. i. p. 267).

Peroxides. This class includes those oxides which react with acids to produce salts that correspond with oxides containing less O than the peroxides. The following reactions exhibit this typical property of peroxides:—

$BaO_2 + H_2SO_4Aq = BaSO_4 + H_2OAq + O$;

$2CrO_3 + 12HClAq = 2CrCl_3Aq + 6H_2O + 3Cl_2$.

Some oxides which react in this way also dissolve in water to form acids, *e.g.* $CrO_3 + H_2O + Aq = H_2CrO_4Aq$; others do not form acids with water, but react with strongly basic oxides to produce salts, *e.g.* $PbO_2 + K_2O$ (molten) $= K_2PbO_3$. Peroxides which exhibit acidic functions may be called *acidic peroxides*, *e.g.* CrO_3, PbO_2; peroxides which do not exhibit acidic functions, *i.e.* which do not form acids with water, nor salts by reacting with basic oxides, may be called *basic peroxides*, *e.g.* CaO_2, K_2O_4. The more important *basic peroxides* are Na_2O_2, K_2O_4, CaO_2, SrO_2, BaO_2 (?)CdO_2, CuO_2, (?)Bi_2O_5. Among the *acidic peroxides* may be mentioned CrO_3, PbO_2, and MnO_2. Several highest oxides of metals cannot be assigned with certainty to the class of acidic peroxides, or to that of basic peroxides; *e.g.* Bi_2O_5 reacts with acids as a basic peroxide, and probably forms salts by fusion with a large excess of KOH, but the salts have not been isolated; UO_3 is distinctly acidic, with acids it forms uranyl salts, *e.g.* $UO_2.SO_4$; OsO_4 is slightly acidic, no corresponding salts have been obtained by the reaction of acids, but these reactions have not been examined sufficiently.

The term *peroxide* is used sometimes to include any oxide of a specified element which contains more O than the highest definitely basic or acidic oxide of that element. This statement does not define peroxide, because no formal definitions of the terms 'definitely basic oxide' and 'definitely acidic oxide' can be given. Such oxides as S_2O_7, Cr_2O_7 (if it exists), MnO_3, and Mn_2O_7, would thus be classed as peroxides (*v. infra*).

Indifferent or neutral oxides. Oxides which do not form acids with water, are not obtained by removing water from acids, and do not form salts by reacting with either basic or acidic oxides, or with acids, are generally called *neutral* or *indifferent oxides*. Examples of such oxides are H_2O, NO, P_4O, (?)Fe_3O_4, Pb_2O, Ag_4O, (?)Mn_3O_4.

None of the qualifying terms applied to oxides can be defined with strictness; such an oxide as MnO_2 is basic, because it forms salts by reacting with acids; MnO_2 is also acidic, because when fused with K_2O, in presence of O, it forms a salt (K_2MnO_4); it is also a peroxide, because the salts which it forms with acids correspond with the lower oxide MnO; and lastly, it may be classed as an indifferent oxide, because it does not form an acid with water, is not obtained by removing water from an acid, and does not form *corresponding* salts by the action of acids, acidic oxides, or basic oxides. When it is remembered that the properties expressed by the terms basic oxide, acidic oxide, and peroxide, are properties which come into play only when the oxides react with other substances, it is evident that these properties must depend to some extent on those of the other substances. Keeping this in mind, one sees how difficult, if not impossible, it must be to define the properties in question.

Oxides have been classified as *indifferent* and *salt-forming*; and the salt-forming oxides have been subdivided into those which form corresponding salts by reacting with acids or negative oxides, those which form corresponding salts by reacting with basic oxides, and those which form salts, but not corresponding salts, by one or other of these reactions. This classification is practically the same as that which has been sketched already, although it is expressed in somewhat different terms.

What is the composition of the basic oxides? Which elements form acidic oxides? Can the composition of peroxides be stated in general terms? Alkali-forming oxides are oxides of the most positive metals. The following are usually included in this group:—Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O; Tl_2O; MgO, CaO, SrO, BaO; (?Ag_2O, ?PbO). Basic oxides, which are not alkali-forming, are oxides of fairly positive metals: *e.g.* BeO, ZnO, CdO, HgO, Sc_2O_3, La_2O_3, Al_2O_3, Ga_2O_3, Fe_2O_3, NiO, CoO, TiO_2, ZrO_2, SnO, SnO_2, PbO, Bi_2O_3. Acidic oxides are oxides of negative elements, or they are compounds of elements, which on the whole are positive, with relatively much O; *e.g.* N_2O_3, N_2O_5, P_2O_3, P_2O_5, Cl_2O, I_2O_5, SiO_2, CO_2, CrO_3, UO_3, Ta_2O_5. Peroxides, in the sense explained above, are usually the highest oxides of metals: *e.g.* CrO_3, PbO_2; in the widest sense, peroxides

also include some of the highest oxides of non-metals, *e.g.* S_2O_7. Two oxides of the same element may exist, and one of these may be a basic, and the other an acidic, oxide; thus Cr_2O_3 is basic, but CrO_3 is acidic. Hence, whether an oxide is basic or acidic seems to depend not only on the general chemical character of the element combined with O, but also on the relative quantities of O and the other element. None of the elements whose lower oxides are alkali-forming forms an acidic oxide, but some of these elements form basic peroxides; in other words, the association of much O with a very distinctly positive element does not produce an acidic oxide, but does produce a basic peroxide. It is impossible to divide the elements into two classes, and say all on one side of the division-line generally form basic oxides, but may also form acidic oxides. All that can be said is, the lower oxides of the metallic elements, as a class, are basic, but many of these elements also form higher oxides, some of which are distinctly acidic, and some are acidic peroxides; the oxides of the non-metallic elements as a class, are acidic, but some of these elements also form indifferent oxides, and a few oxides of non-metals are peroxides.

The peroxides have been divided by Mendelejeff into two classes (*J. R.* 1881, [1] 561; abstract in *B.* 15, 242; *v.* also Traube, *B.* 19, 1111, 1115, 1117; Richarz, *B.* 21, 1675). Mendelejeff distinguishes peroxides belonging to the type H_2O from those which belong to the type H_2O_2; the latter class he calls *superoxides*, the former *polyoxides*. In the polyoxides, according to M., the O is all in direct union with the other element, and none of the O atoms is directly united with any other; whereas the O atoms of superoxides are regarded as in direct union with each other, as well as with the other element. BaO_2 is a typical superoxide, and is supposed to have the structure $Ba\!<\!\begin{smallmatrix}O\\|\\O\end{smallmatrix}$; MnO_2 is a typical polyoxide, and is supposed to have the structure O.Mn.O. The views of Traube (*l.c.*) and Richarz (*l.c.*) are practically the same as those expressed by Mendelejeff. The superoxides yield H_2O_2Aq by reacting with dilute acids, and therefore reduce $KMnO_4Aq$ in presence of H_2SO_4; the polyoxides do not yield H_2O_2, but H_2O and O. Peroxides formed by the action of alkaline oxidisers, *e.g.* KClOAq, seem always to belong to the class of polyoxides. The peroxides K_2O_4, Na_2O_2, CaO_2, SrO_2, BaO_2, ZnO_2, CdO_2, CuO_2, Di_2O_5, and some others, are superoxides; *i.e.* they give H_2O_2Aq when acted on by dilute acids. According to Mendelejeff, S_2O_7 is a superoxide; it gives H_2O_2 when dissolved in much water; the constitution is probably $\begin{matrix}O.SO_2\\|\\O.SO_2\end{matrix}\!>\!O$.

Mendelejeff (*l.c.*) says that the power possessed by any element of forming a characteristic basic or acidic oxide, from which salts are obtained, is connected with the position of the element in the periodic scheme of classification. But besides forming a salt-forming oxide, or more than one such oxide, some elements are also capable of producing superoxides belonging to the type HO.OH. Glancing at the groups of elements, as the elements are arranged in the periodic scheme of classification (*v.* CLASSIFICATION, vol. ii. p. 204), and expressing the composition of the highest characteristic oxides of each group in a general formula, we have the result shown in the table on p. 661.

The molecular weights of very few oxides have been determined with certainty; on this subject *v.* Henry, *P. M.* [5] 20, 81; *cf.* Carnelley a. Walker, *C. J.* 53, 59. M. M. P. M.

OXIDO-DI-NAPHTHYL-AMINE *v.* IMIDO-DI-NAPHTHYL OXIDE.

OXIMIDO-ACETIC ETHER $C_4H_7NO_3$ *i.e.* $CH(NOH).CO_2Et$. *Nitroso-acetic ether.* Formed, together with oxalic acid, by the action of fuming HNO_3 on aceto-acetic ether (Pröpper, *A.* 222, 48). Oil. Yields oxalic acid and hydroxylamine when heated with HClAq at 140°. Cold KOHAq yields KCy, K_2CO_3, and alcohol.—$(NH_4)C_4H_6NO_3$ aq: silky needles.—$C_4H_6NaNO_3$ $\frac{1}{2}$aq: needles (from water).

OXIMIDO-ACETOACETIC ETHER *v.* NITROSO-ACETOACETIC ETHER.

OXIMIDO- compounds *v.* NITROSO- compounds.

OXIMIDO-ETHER *v.* OXALIMIDO-ETHYL ETHER.

TRI-OXIMIDO-METHYLENE $C_3H_9N_3O_3$ *i.e.* $CH_2\!<\!\begin{smallmatrix}N(OH).CH_2\\N(OH).CH_2\end{smallmatrix}\!>\!N(OH)$. Formed from formic aldehyde and hydroxylamine (Scholl, *B.* 24, 574). White amorphous solid, insol. water, alcohol, and ether. At 133° it passes directly into a gas.

OXIMIDO-NAPHTHOL *v.* AMIDO-NAPHTHO-QUINONE.

OXIMS or **OXIMES.** Compounds containing the group C:N.O.H, obtained by the action of hydroxylamine on aldehydes, ketones, and ketonic compounds, by the reaction $RR'CO + H_2N.OH = RR'C(NOH) + H_2O$ (V. Meyer, *B.* 15, 1164, 1324, 1525, 2784; 16, 822, 2992; 19, 1613) (*v.* ALDOXIMS, vol. i. p. 111). The reaction is best performed with hydroxylamine hydrochloride (1 mol.) and aqueous NaOH (3 mols.) in the cold (Auwers, *B.* 22, 604). Oxims are split up by boiling HClAq into hydroxylamine and the original aldehyde or ketonic compound. The oxims do not exhibit Liebermann's reaction with phenol and H_2SO_4. The oxims yield acetyl, alkyl, and sodium derivatives. Ketoxims (*i.e.* oxims of ketones) are converted by warming with conc. H_2SO_4 at 100° into the isomeric amides; thus Ph_2C:NOH becomes Ph.CO.NHPh, while PhMeC:NOH yields acetanilide (Beckmann, *B.* 20, 1507; Wegerhoff, *A.* 252, 1; Günther, *A.* 252, 44). PCl_5 acts like H_2SO_4. Oxims are readily reduced, in alcoholic solution by means of sodium amalgam and acetic acid, to the corresponding amines, thus: $XYC:NOH + 2H_2 = XYCH.NH_2 + H_2O$ (Goldschmidt, *B.* 19, 3232). Benzoic aldehyde gives two oxims and two sets of alkyl-oxims (Beckmann, *B.* 22, 1534), and benzil also gives a greater number of oxims and alkyl-oxims than the ordinary formulæ indicate. These isomerisms may perhaps be explained by considering the arrangement in space of the atoms in the molecule (Beckmann, 20, 2766; *B.* 23, 1680; Auwers a. V. Meyer, *B.* 21, 784; 22, 1996; 23, 2403; Hantzsch, *B.* 24, 31, 1192).

Groups.	I.	II.	III.
Elements in group	H, Li, Na, K, Cu, Rb, Ag, Cs, Au	Be, Mg, Ca, Zn, Sr, Cd, Ba, Hg	B, Al, Sc, Ga, Y, In, La, Yb, Tl
Composition of highest basic or acidic oxide characteristic of the group	M_2O	MO	M_2O_3
Character of highest basic or acidic oxide characteristic of the group	Basic	Basic	Basic except B_2O_3 which is a weak anhydride
Superoxides, type of HO.OH	H_2O_2, Na_2O_2, K_2O_4, CuO_2, Ag_2O_2	CaO_2, ZnO_2, SrO_2, CdO_2, BaO_2	(? TlO_3)

Groups.	IV.	V.	VI.	VII.
Elements in group	C, Si, Ti, Ge, Zr, Sn, Ce, Pb, Th	N, P, V, As, Nb, Sb, Di, Er, Ta, Bi	(O), S, Cr, Se, Mo, Te, W, U	F, Cl, Mn, Br, I (group very incomplete)
Composition of highest basic or acidic oxide characteristic of the group	MO_2	M_2O_5	MO_3	M_2O_7; represented only by Mn_2O_7. [Cl_2O, ClO_2, I_2O_3; no oxide of F or Br]
Character of highest basic or acidic oxide characteristic of the group	Acidic when M = C or Si; acidic and basic when M = Ti, Ge, Zr, Sn (? Ce), Pb (becoming more basic as M increases); basic when M = Th	Acidic, except Bi_2O_5 which acts as a feebly acidic peroxide (*polyoxide*)	Acidic; becoming less acidic as M increases; UO_3 shows some basic properties	Acidic
Superoxides, type of HO.OH	TiO_3, CeO_3	(? NO_3, ? Di_2O_5)	S_2O_7(? Cr_2O_7, ?UO_4)	none

Group VIII.

	Family 1. Fe, Ni, Co.	Family 2. Ru, Rh, Pd.	Family 3. Os, Ir, Pt.
Highest characteristic oxide	M_2O_3	MO_4; represented only by RuO_4	MO_4; represented only by OsO_4
Character of oxide	Basic	Feebly acidic. (These elements also form MO, M_2O_3, and MO_2, which are feebly basic)	Feebly acidic. (These elements also form MO, M_2O_3, and MO_2, which are feebly basic)
Superoxides, type of HO.OH	? FeO_3, ? $Ni_2O_3.xO$, ? $Co_2O_3.xO$	none	none

Oxims of ketones may be changed to phenyl-hydrazides by heating with phenyl-hydrazine (Just, *B.* 19, 1205).

OXINDOLE C_8H_7NO *i.e.* $C_6H_4<\begin{smallmatrix}CH_2\\NH\end{smallmatrix}>CO$ or $C_6H_4<\begin{smallmatrix}CH_2\\N\end{smallmatrix}>C.OH$ (Baeyer a. Comstock, *B.* 16, 1704). *Anhydride of o-amido-phenyl-acetic acid.* Mol. w. 133. [120°]. Formed by reducing *o*-nitro-phenyl-acetic acid with tin and HCl. Obtained also by reducing dioxindole with sodium-amalgam (Knop, *J. pr.* 97, 65; Baeyer a. Knop, *A.* 140, 1; Baeyer, *B.* 11, 583; 12, 457). If the mixture of isomeric nitro- acids got by heating phenyl-acetic acid with fuming HNO_3 on the water-bath be reduced with tin and HClAq, and, after removal of tin by H_2S, be boiled with $BaCO_3$, only the *m-* and *p*-nitro-phenyl-acetic acids will form barium salts, and the oxindole may be extracted by ether.

Properties.—Long colourless needles (from water). Oxidised slowly by moist air, forming dioxindole. Reduces ammoniacal silver nitrate, forming a mirror. Extracted by ether from its alkaline solution. Not affected by boiling baryta-water, but at 150° it yields barium amido-phenyl-acetate. Nitrous acid forms nitroso-oxindole which is an oxim of ISATIN. PCl_5 yields $C_6H_4<\begin{smallmatrix}CHCl\\N\end{smallmatrix}>CCl$ [104°] reduced by iron-filings and KOH to indole.

Salts.—AgC_8H_6NO.—B'HCl: deliquescent spicules.

Acetyl derivative [126°]. Long colour-

less needles. Sl. sol. cold water and ligroïn, v. sol. alcohol (Suida, *B.* 12, 1326). Converted by dilute NaOHAq into $C_6H_4(NHAc).CH_2.CO_2H$ [142°].

Bromo-oxindole C_8H_6BrNO. [176°]. Formed, together with tri-bromo-oxindole $C_8H_4Br_3NO$ 2aq, by the action of bromine-water on oxindole. Both compounds form feathery crystals.

Nitro-oxindole $C_8H_6(NO_2)NO$. Prepared by nitration. Yellow needles, sol. alcohol. Begins to decompose at 175°.

Amido-oxindole $\left[4\frac{1}{2}\right] C_6H_3(NH_2)<^{CH_2}_{NH}>CO$. [c. 200°]. Prepared by reduction of (4,2,1)-di-nitro-phenyl-acetic acid (Gabriel a. Meyer, *B.* 14, 832). Long spikes, v. sol. hot water.

Exo-**amido-oxindole** $C_6H_4<^{CH(NH_2)}_{NH}>CO$. The hydrochloride, formed by reducing isatin-oxim with tin and HClAq, is decomposed by water, yielding a red resin.

Methyl-oxindole *v.* p. 351.

Ethyl-oxindole $C_6H_4<^{CH_2}_{NEt}>CO$. Formed by heating oxindole with EtI and NaOEt. Liquid, sl. sol. water. Very difficult to saponify by acids or alkalis.

Dioxindole $C_8H_7NO_2$ *i.e.* $C_6H_4<^{CH(OH)}_{NH}>CO$. *Isatin dihydride. Anhydride of Hydrindic acid.* Mol. w. 149. [180°]. S. 8·5 in the cold; 17 at 100°. S. (alcohol) 7 in the cold; 10 at 78°. Formed by reducing an aqueous solution of isatin with zinc-dust and HClAq, and extracting with ether (Baeyer, *B.* 12, 1309). Yellowish mono-clinic prisms (from water) or colourless crystals (from alcohol). Forms a violet liquid on melting. Its aqueous solution becomes red on exposure to the air, forming isatyde and isatin. In acid solution it may be reduced to oxindole. Chlorine forms chloro-dioxindole $C_8H_6ClNO_2$ and dichloro-dioxindole $C_8H_5Cl_2NO_2$. The corresponding bromo- derivatives melt at 165° and 170° respectively. PCl_5 yields $C_8H_5Cl_2N$. Ammonia colours its solution violet, and on boiling throws down a violet colouring matter, sol. HClAq. Potash and baryta produce a dark-violet colour, changing to red and finally yellow.

Salts. — $C_8H_7NO_2HCl$: nodular crusts.— $C_8H_7NO_2H_2SO_4$ aq: ppd. by adding water to its solution in H_2SO_4.—$NaC_8H_6NO_2$ 2aq: silvery scales, v. sol. water, insol. alcohol.—BaA'_2 4aq: white cubes, sl. sol. water. Gives off aniline on heating.—PbA'_2 2aq: ppd. by lead subacetate.—AgA': crystalline pp. Gives off benzoic aldehyde at 60°.

Acetyl derivative $C_8H_6AcNO_2$. [127°]. Short prisms, sl. sol. cold water (Suida, *B.* 12, 1326). Cold baryta-water converts it into acetyl-hydrindic acid $C_6H_4(NHAc).CH(OH).CO_2H$ [142°] which is also formed by reducing acetyl-isatic acid with 3 p.c. sodium-amalgam in acid solution (Suida, *B.* 11, 586).

Nitroso-dioxindole $C_8H_6(NO)NO_2$. [300°-310°]. Formed by passing nitrous acid vapour into an alcoholic solution of dioxindole. Yellowish crystals, sl. sol. water. May be sublimed. On boiling with $FeSO_4$ and KOHAq it yields 'azodi-oxindole' $C_8H_6N_2O_2$ which is ppd. by HClAq in white needles [300°], yielding with $AgNO_3$ and NH_3 a white pp. of $Ag_2C_8H_4N_2O_2$. Sodium-amalgam and a little water reduce nitroso-dioxindole to 'azoxindole' $C_8H_6N_2O$, ppd. by HClAq as an amorphous powder (containing $\frac{1}{2}$aq) and crystallising from alcohol in cubes. Bromine-water converts nitroso-dioxindole into $C_8H_4Br_2N_2O_3$ 3aq [275°].

Salts.—$NH_4C_8H_5(NO)NO_2$ $1\frac{1}{2}$aq: white silky laminæ.—$BaC_8H_4N_2O_3$.—$AgC_8H_5N_2O_3$: yellowish-white pp.

OXOCTENOL $C_8H_{16}O_2$ *i.e.* $CMe_3.C(OH)<^{CMe_2}_{O}$? [49·5°]. (178°). V.D. 4·8 (at 185°). A product of the oxidation of isodibutylene by $KMnO_4$ (Butleroff, *J. R.* 14, 203; *C. J.* 42, 936; *Bl.* [2] 38, 553). Long thin prisms, smelling like camphor; sl. sol. water, v. sol. alcohol and ether. Does not react with hydroxylamine (Meyer a. Nägeli, *B.* 16, 1622). Not attacked by hot bromine.

Acetyl derivative $C_8H_{15}AcO_2$. (201°). Formed by heating with Ac_2O at 150°.

OXOCTYLIC ACID *v.* Oxy-octoic acid.

OXONIC ACID $C_4H_5N_3O_4$. A salt of this acid is formed by the atmospheric oxidation of an alkaline solution of uric acid (Strecker; Medicus, *A.* 175, 230; *B.* 10, 546). The free acid splits up at once into glyoxyl-urea, CO_2, and NH_3. — NH_4HA''aq. — KHA''. — K_2A'' $1\frac{1}{2}$aq. — $Ba(HA'')_2\frac{1}{2}$aq: minute needles.

OXYACANTHINE $C_{18}H_{19}NO_3$. Occurs in the root of *Berberis vulgaris*, together with berberine, berbamine, and at least one other alkaloid. Needles (from alcohol or ether), or amorphous solid. In the amorphous state it melts at [138°-150°], in the crystalline state at [208°-214°]. V. sol. benzene and chloroform, scarcely in petroleum spirit. In chloroform $[\alpha]_D = +131·6$. Conc. H_2SO_4, or conc. H_2SO_4 and molybdic acid, gives no colour at first, but on standing or heating, a yellow colour. From iodic acid it separates iodine.

Salts. — B'HCl 2aq: small colourless needles; in aqueous solution $[\alpha]_D = +163·6$.— $B'HNO_3$ 2aq; colourless needles.—$B'_2H_2SO_4$ 2aq: microscopic plates.—$B'_2H_2SO_4$ 6aq: small prisms. —$B'_2H_2Cl_2PtCl_4$ 5aq: yellow pp. (Hesse, *B.* 19, 3190; *cf.* Polex, *Ar. Ph.* 6, 265; Wacker, *J.* 1861, 545).

DIOXY-ACENAPHTHENE $C_{10}H_6<^{CH(OH)}_{CH(OH)}$. *Acenaphthylene-glycol.* [205°]. Formed by saponifying its acetyl derivative, which is obtained from di-bromo-acenaphthene $C_{10}H_6<^{CHBr}_{CHBr}$ (Ewan a. Cohen, *C. J.* 55, 578). Long colourless needles, sl. sol. cold MeOH and hot water. On treatment with Na and alcohol it yields the ketone $C_{10}H_6<^{CH_2}_{CO}$ [119°].

Mono-acetyl derivative $C_{12}H_9AcO_2$. [112°]. Long needles, v. sol. alcohol.

Di-acetyl derivative $C_{12}H_8Ac_2O_2$. [130°].

Benzoyl derivative $C_{12}H_9BzO_2$. [190°].

OXY-ACETIC ACID *v.* Glycollic acid.

Di-oxy-acetic acid *v.* Glyoxylic acid.

Tri-oxy-acetic acid *v.* Oxalic acid.

DI-OXY-ACETOACETIC ETHER.

Di-ethyl derivative $C_{10}H_{18}O_5$ *i.e.* $CH_2(OEt).CO.CH(OEt).CO_2Et$. (245°). Formed by the action of Na on a solution of $CH_2(OEt).CO_2Et$ in benzene (Conrad, *B.* 11, 58).

Liquid; gives a violet colour with $FeCl_3$. Forms Na and Ba derivatives. Split up by alkalis into alcohol and $CH_2(OEt).CO_2H$.

OXY-ACETONE *v.* ACETYL-CARBINOL.

s-**Di-oxy-acetone.** *Di-ethyl derivative* $C_7H_{14}O_3$ *i.e.* $CO(CH_2OEt)_2$. (195°). S.G. $\frac{17.5}{}$ ·98. V.D. 4·95. Formed by allowing the ether $CH_2(OEt).CO.CH(OEt).CO_2Et$ (*v.* the preceding article) to stand for three days with cold dilute (2·5 p.c.) KOH, neutralising with H_2SO_4, extracting with ether, and distilling (Grimaux a. Lefèvre, *C. R.* 107, 914). Sweet aromatic liquid, sl. sol. Aq, sol. alcohol, volatile with steam. Combines with $NaHSO_3$. Reduces Fehling's solution and yields a mirror with warm ammoniacal $AgNO_3$.

u-**Di-oxy-acetone** *v.* PYRUVIC ALDEHYDE.

p-**OXY-ACETOPHENONE** $C_6H_4(OH).CO.CH_3$ [1:4]. [107°]. Obtained by diazotising *p*-amido-acetophenone and boiling the solution (Klingel, *B.* 18, 2691). Formed also by heating phenol with $ZnCl_2$ and HOAc (Michael a. Palmer, *Am.* 7, 277). White needles. Sol. water, alcohol, and ether. $FeCl_3$ gives a dark-brown colouration.

Methyl derivative $C_6H_4(OMe).CO.CH_3$. [39°] (Gattermann, *B.* 23, 1201). (258°) (G.); (221°) (O.). Formed by heating anisic aldehyde with Na and MeI in ethereal solution (Oliveri, *G.* 13, 275).

Ethyl derivative. [61°]. (above 260°).

ω **Oxy-acetophenone** *v.* BENZOYL-CARBINOL. The *phenyl derivative* $Bz.CH_2(OPh)$ [72°] and the *p-nitro-phenyl derivative* $Bz.CH_2(OC_6H_4NO_2)$ [144°] may be obtained from ω-bromo-acetophenone (Möhlau, *B.* 15, 2497). The phenyl-hydrazides $C_6H_5.C(N_2HPh).CH_2OH$ [112°] and $C_6H_5.C(N_2HPh).CH:N_2HPh$ [152°] have been prepared by Laubmann (*A.* 243, 247).

(4:2:1)-**Di-oxy-acetophenone** [4:2:1]$C_6H_3(OH)_2.CO.CH_3$. *Resacetophenone.* [142°]. Formed by fusion of β-methyl-umbelliferon with KOH (Pechmann a. Duisberg, *B.* 16, 2123). Prepared by heating resorcin (1 pt.) with HOAc (1½ pts.) and $ZnCl_2$ (1½ pts.) at 150° (Nencki a. Sieber, *J. pr.* [2] 23, 147, 546). Fine white needles. Gives a red colouration with Fe_2Cl_6. With HOAc, $ZnCl_2$, and $POCl_3$ it gives $C_6H_2(OH)_2Ac_2$ [180°] (Crépieux, *Bl.* [3] 6, 152).

Acetyl derivative $C_6H_3(OAc)_2.CO.CH_3$. [73°]. (303°). White needles.

Phenyl hydrazide $C_6H_3(OH)_2.CMe:N_2HPh$. [139°]. Tables (from xylene) (Michael a. Palmer, *Am.* 7, 276).

Methyl derivative [2:4:1] $C_6H_3(OH)(OMe).CO.CH_3$. [47°]. Occurs in Japanese peonies (Will, *B.* 19, 1776).

Di-ethyl derivative. [68°] (G.).

(5,2,1)-**Di-oxy-acetophenone.** [202°]. Made in like manner from hydroquinone (Nencki).

Tri-oxy-acetophenone $C_8H_8O_4$ *i.e.* $C_6H_2(OH)_3.CO.CH_3$. *Gallacetophenone.* [168°]. Formed by heating pyrogallol (1 pt.) with HOAc (1½ pts.) and $ZnCl_2$ (1½ pts.) at 150° (Nencki a. Sieber, *J. pr.* [2] 23, 147, 538). Pearly plates. Alcoholic KOH ppts. $C_8H_8O_4KOH$.

OXY-ACETOPHENONE-CARBOXYLIC ACID. *Phenyl derivative* $C_{15}H_{12}O_4$ *i.e.* $C_6H_4(CO_2H).CO.CH_2OPh$. [110°]. Prepared by dissolving $C_6H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>CH.OPh$ in alkalis and acidifying the solution. Needles (Gabriel, *B.* 14, 923).—A'Ag: white flocculent pp.

β-**OXY-ACETYL-PROPIONIC ACID** $C_5H_7(OH)O_3$. *β-Oxy-levulic acid.* Formed in chief quantity, together with acetacrylic acid, by the action of aqueous Na_2CO_3 upon β-bromo-levulic acid. Yellowish oil. V. sol. water and alcohol, sl. sol. other solvents. Very prone to enter into reactions. Reduces alkaline silver solutions. Hydroxylamine gives an oxim [145°]. By heating with NH_3 it yields tetra-methyl-pyrazine (di-methyl-ketine), with evolution of CO_2. The salts are amorphous and easily decomposable (Wolff, *B.* 20, 426; *A.* 264, 234). On heating it yields two anhydrides [240°] and [263°].

The isomeric α-oxy-acetyl-propionic acid $CH_2Ac.CH(OH).CO_2H$ [104°] is crystalline.

OXYACIDS *v.* vol. i. p. 57.

OXY-ACRYLIC ACID *v.* GLYCIDIC ACID and PYRUVIC ACID.

OXY-ADIPIC ACID $C_6H_{10}O_5$ *i.e.* $CO_2H.CHMe.CMe(OH).CO_2H$. Formed by treating methyl-acetoacetic ether with HCy and boiling the product with HClAq (König, *B.* 12, 768). Crystalline mass.—Na_2A''.—Ag_2A''.

Isomeride *v.* ADIPOMALIC ACID.

Di-oxy-adipic acid $C_6H_{10}O_6$. Formed by the action of Ag_2O on the di-bromo-adipic acid prepared from hydromuconic acid (*v.* p. 443) (Limpricht, *A.* 165, 267). Syrup, sol. alcohol and ether.—BaA'' 4aq: hygroscopic powder.

Di-oxy-adipic acid. Got from its nitrile, which is formed by warming the anhydride $C_4H_6O_2$ of erythrite with dry HCy at 55° (Przybytek, *B.* 17, 1094). Crystalline. — KHA''.—CdA'' 4aq. — PbA'' 2aq: amorphous pp.

Tri-oxy-adipic acid $C_6H_{10}O_7$. Prepared by boiling tri-bromo-adipic acid with baryta-water (Limpricht). Prisms (from alcohol-benzene).—BaA'' ¾aq: v. sol. water.

Tri-oxy-adipic acid $C_6H_{10}O_7$. [147°]. Formed by oxidising metasaccharin with HNO_3 (S.G. 1·2) at 50° (Kiliani, *B.* 18, 644, 1555). Small monoclinic plates, v. sol. water, v. sl. sol. alcohol and ether. Reduced by HI to adipic acid [149°].—CaA'' 4aq.—ZnA'' 3½aq.—CuA'' 4aq.—Ag_2A''.

Tetra-oxy-adipic acid *v.* MUCIC ACID and SACCHARIC ACID.

OXY-ALDEHYDO-BENZOIC ACID *v.* ALDEHYDO-OXY-BENZOIC ACID.

OXY-ALDEHYDO-CYMENE *v.* CARVACROTIC ALDEHYDE.

OXY-ALDEHYDO-PHENOXY-ACETIC ACID *Methyl derivative* $C_6H_3(OMe)(CHO).O.CH_2.CO_2H$ [2:4:1]. [188°]. Prepared by melting chloro-acetic acid with vanillin, adding aqueous KOH (S.G. 1·2), and heating on the water-bath (Elkan, *B.* 19, 3054). Slender needles (from water), v. sol. alcohol and ether.—AgA': white pp.

OXY-TRI-ALDINE *v.* ALDEHYDE.

OXYAMENYL-NAPHTHOQUINONE *v.* LAPACHIC ACID.

OXY-AMIDO-ACETIC ACID $C_2H_5NO_3$ *i.e.* $CH(NH_2)(OH).CO_2H$. Formed by the action of alcoholic NH_3 on glyoxylic acid (Böttinger, *A.* 198, 217). Syrup.—CaA'_2: insol. cold water. Yields pyrrole on distillation.

OXY-AMIDO-ACETOPHENONE-OXIM *v.* OXAMIDO-ACETOPHENONE-OXIM.

(α)-**OXY-AMIDO-ANTHRAQUINONE** $C_6H_4:C_2O_2:C_6H_2(OH)(NH_2)$ [1:2:4:3]. Formed, together with a smaller quantity of the (β)-iso-

meride by heating alizarin with NH_3Aq for 3 hours at 200° (Liebermann a. Troschke, *A.* 183, 202). Brown needles (from alcohol) with green lustre, insol. water. Yields alizarin on fusing with potash, and on heating with HClAq at 250°.—BaA'_2.

Acetyl derivative $C_{14}H_6O_2(OH)(NHAc)$. [170°]. Formed by heating with Ac_2O for 2 hours at 120° (Von Perger, *J. pr.* [2] 18, 143). Yellow needles (from HOAc); insol. water, sol. alkalis.

Ethyl ether $C_{14}H_6O_2(OEt)(NH_2)$. [182°]. Red plates (Liebermann a. Hagen, *B.* 15, 1796).

(β)-Oxy-amido-anthraquinone $C_6H_4{:}C_2O_2{:}C_6H_2(OH)(NH_2)$ [1:2:3:4]. Formed by boiling di-amido-anthraquinone with KOHAq (Von Perger, *J. pr.* [2] 18, 139). Brown needles (from alcohol), insol. water, sol. H_2SO_4. Begins to sublime at 150°. On boiling with baryta it yields an insoluble Ba salt (difference from the (α)-isomeride). Its solution in KOHAq deposits the K salt on standing. Potash fusion forms alizarin. Elimination of NH_2 yields erythro-oxy-anthraquinone.

Acetyl derivative $C_{14}H_6O_2(OH)(NHAc)$. [242°]. Small brownish needles (from alcohol).

Oxy-amido-anthraquinone $C_{14}H_6O_2(OH)(NH_2)$. [301°]. Prepared by heating sodium anthraquinone sulphonate with NH_3Aq at 180° (Bourchart, *B.* 12, 1418). Red needles. Yields the tri-acetyl derivative $C_{10}H_6Ac_3NO_3$ [257°].

Oxy-amido-anthraquinone $C_{14}H_6O_2(NH_2)(OH)$. Formed by heating purpuroxanthin with NH_3Aq (Liebermann, *A.* 183, 217). Brown needles with green lustre.

Di-oxy-amido-anthraquinone $C_{14}H_5(OH)_2NH_2$. (α)-*Amido-alizarin.* Formed by reducing (α)-nitro-alizarin with sodium-amalgam (Perkin, *C. J.* 30, 578). Crystallises from alcohol in black needles with green lustre. Its alcoholic and alkaline solutions are crimson.

Di-oxy-amido-anthraquinone $C_{14}H_5(OH)_2NH_2$. (β)-*Amido-alizarin.* [above 300°]. Formed by reducing (β)-nitro-alizarin with zinc-dust and KOH, or with glucose and H_2SO_4 (Schunck a. Roemer, *B.* 12, 588; Brunner a. Chuard, *B.* 18, 445). Lustrous red prisms, sl. sol. alcohol, forming a reddish-yellow solution. Its alkaline solution is blue. Dyes iron mordants grey, and alumina red.

Acetyl-ethenyl derivative

$$C_6H_4{<}^{CO}_{CO}{>}C_6H(OAc){<}^{O}_{N}{>}C.CH_3. \quad [240°].$$

Formed by heating amidoalizarin with acetic anhydride. Yellowish-brown crystals (from benzene or acetic anhydride); sublimes in small yellow plates. By boiling with HCl it is reconverted into amidoalizarin.

Di-acetyl derivative

$$C_6H_4{<}^{CO}_{CO}{>}C_6H(OH)(OAc)(NHAc). \quad [268°-271°].$$

Formed by boiling the preceding body with dilute acetic acid till dissolved. Red-brown crystals; soluble in alcohol with a yellow colour. Alcoholic $Pb(OAc)_2$ gives a violet pp., alcoholic $Cu(OAc)_2$ a red solution. It dissolves in aqueous Na_2CO_3 with a violet, in KOH with a blue, colour. Alumina-mordants are dyed a deep red.

Benzoyl-benzenyl derivative

$$C_6H_4{<}^{CO}_{CO}{>}C_6H(OBz){<}^{O}_{N}{>}C.CH_3. \quad [above 300°].$$

Formed by heating amidoalizarin with benzoyl chloride. Small glistening needles; sublimes in yellow needles; nearly insol. all solvents. Alcoholic KOH gives a blue solution on boiling (Roemer, *B.* 18, 1666).

Di-oxy-amido-anthraquinone $C_{14}H_5O_2(OH)_2(NH_2)$. *Amidoisoanthraflavic acid.* Formed by heating anthrapurpurin with ammonia at 150°–180° (Perkin, *C. J.* 33, 216). Dark-green crusts (from alcohol), almost insol. water. Its alkaline solution is purple. Nitrous acid converts it into isoanthraflavic acid.

Tetra-amido-di-oxy-anthraquinone $C_{14}H_2O_2(NH_2)_4(OH)_2$. *Hydrochrysamide.* Formed by reducing tetra-nitro-di-oxy-anthraquinone (chrysammic acid) (Schunck, *A.* 65, 234; Stenhouse a. Miller, *A.* 142, 91; Liebermann, *A.* 183, 182). Bluish-black needles with coppery lustre, insol. boiling water, sl. sol. hot alcohol. Its alkaline solution is blue.

(α)-OXY-AMIDO-ANTHRAQUINONE SULPHONIC ACID $C_{14}H_5O_2(OH)(NH_2)SO_3H$. Formed from (α)-oxy-amido-anthraquinone and H_2SO_4 at 130° (Von Perger, *J. pr.* [2] 18, 182). Brick-red crystalline aggregates (from alcohol). V. sol. water, giving it a reddish-brown colour. Insol. ether. Forms a violet solution with NaOH, a violet-blue pp. with baryta water, and a reddish-brown pp. with $BaCl_2$. Dyes, with iron mordant, a pale brown. With N_2O_3 it gives oxy-anthraquinone sulphonic acid.

β-Oxy-amido-anthraquinone sulphonic acid. Formed from amido-erythro-oxy-anthraquinone and H_2SO_4 at 115°. Crystals obtained from water exhibit a green metallic lustre. Aqueous solutions are red. Insol. ether. Forms a purple solution with NaOH, a reddish-violet pp. with baryta-water and a violet-red pp. with $BaCl_2$. Dyes, with iron mordants, yellow. With N_2O_3 it gives erythro-oxy-anthraquinone sulphonic acid.

Oxy-amido-anthraquinone sulphonic acid. Got by heating sodium anthraquinone disulphonate with NH_3Aq at 180° (Bourchart, *B.* 12, 1419). Violet pp., forming a red solution in ammonia.—$NH_4A'\,2\tfrac{1}{2}aq$.

Di-oxy-amido-anthraquinone sulphonic acid $C_{14}H_4(OH)_2(NH_2)SO_3H$. Formed by the action of boiling alkali upon the anhydride $C_{28}H_{16}N_2S_2O_9$ or the sulphate, which are got by heating (α)-nitro-anthraquinone sulphonic acid with H_2SO_4 at 200° (Claus, *B.* 15, 1522; 16, 903; Lifschütz, *B.* 17, 902). Red powder with green lustre. Decomposed by heat. Its alkaline solution is bluish-violet.

OXY-AMIDO-AZO- *v.* Azo-.

OXY-AMIDO-BENZENE *v.* Amido-phenol.

Di-oxy-amido-benzene *v.* Amido-hydroquinone, Amido-pyrocatechin, and Amido-resorcin.

Di-oxy-di-amido-benzene *v.* Di-amido-hydroquinone and Di-amido-resorcin.

Tri-oxy-tri-amido-benzene *Tribenzoyl derivative* $C_6(OH)_3(NHBz)_3$[1:3:5:2:4:6] *Tribenzoyl-tri-amido-phloroglucin.* [c. 156°]. Got by the action of NaOEt on hippuric ether (Rügheimer, *B.* 21, 3329). Needles (containing $1\tfrac{1}{2}aq$), v. sl. sol. water.—$Cu_3A'''_2$.—$Pb_3A'''_2$.

Tetra-oxy-amido-benzene $C_6H(OH)_4(NH_2)$[1:2:4:5:6]. Formed from nitro-di-oxy-quinone, $SnCl_2$, and HCl (Nietzki a. Schmidt, *B.* 22, 1661).—B'HCl aq: needles.

Penta-acetyl derivative. [242°].

Tetra-oxy-di-amido-benzene $C_6(NH_2)_2(OH)_4$. Formed by reduction of nitranilic acid or of nitro-amido-tetra-oxy-benzene with an excess of $SnCl_2$; the yield is 90 p.c. of the theoretical. The base could not be isolated, being readily oxidised to di-imido-di-oxy-quinone $C_6(NH)_2(OH)_2O_2$. By HNO_3 it is converted into benzene-tri-quinone C_6O_6. By boiling with KOH, NH_3 is evolved with separation of a black crystalline substance; if this is boiled with water and evaporated with a little KOH, it yields croconic acid $C_5H_2O_5$. Distillation with zinc-dust yields *p*-phenylene-diamine. *Hydrochloride*: $C_6(OH)_4(NH_2)_2H_2Cl_2$: colourless needles.

Di-acetyl derivative. Needles.

Hexa-acetyl derivative $C_6(NHAc)_2(OAc)_4$: [c. 240°]; small colourless tables (Nietzki a. Benckiser, *B.* 18, 502; 19, 2727; 21, 1852).

OXY-AMIDO-BENZENE SULPHONIC ACID *v.* AMIDO-PHENOL SULPHONIC ACID.

Di-oxy-amido-benzene sulphonic acid $C_6H_2(OH)_2(NH_2)(SO_3H)$. *Amido-resorcin sulphonic acid.* Formed by reducing the nitro-acid (Hazura, *M.* 4, 613; Brünner a. Krämer, *B.* 17, 1870). Plates, with greenish lustre, sl. sol. hot water. Its alkaline solution soon becomes blue, then green, and finally black.

OXY-AMIDO-BENZOIC ACID $C_7H_7NO_3$ *i.e.* $C_6H_3(OH)(NH_2).CO_2H$ [2:5:1]. *Amido-salicylic acid.* Mol. w. 153. Obtained by reducing the nitro- acid (Beilstein, *A.* 130, 243; Hübner, *A.* 195, 18). Obtained also by reducing $C_{10}H_7.N_2.C_6H_3(OH)CO_2H$ (P. F. Frankland, *C. J.* 37, 748) and $C_6H_5.N_2.C_6H_3(OH).CO_2H$ (Limpricht, *B.* 22, 2908). Satiny needles, insol. alcohol, sl. sol. hot water. $FeCl_3$ colours its aqueous solution cherry-red.

Reactions.—1. *Distillation* produces *p*-amido-phenol.—2. *Nitrous acid* forms diazo-salicylic acid $C_6H_3(OH)\langle{}^{N_2}_{CO}\rangle O$, which is converted by conc. HI into iodo-salicylic acid $C_6H_3I(OH)CO_2H$ [193·5°] (Frankland).—3. *Urea* forms, on heating, crystalline uramidosalicylic acid $C_8H_8N_2O_4$, which at 200° forms 'carboxamidosalicylic' acid $C_{15}H_{12}N_2O_7$ (Griess, *J. pr.* [2] 1, 235).

Salts.—HA'HCl.—HA'HSnCl$_3$ (Goldberg, *J. pr.* [2] 19, 362).—HA'HI (Schmitt, *J.* 1864, 383, 423).—$H_2A'_2H_2SO_4$ aq: prisms.—CaA'_2 $5\frac{1}{2}$aq.—BaA'_2 4aq. Needles, v. sol. water.—MgA'_2 8aq.—ZnA'_2 10aq: needles (Wattenberg, *B.* 8, 1221).

Acetyl derivative $C_6H_3(OH)(NHAc)CO_2H$. [218°]. Thick needles (containing $\frac{1}{2}$aq); v. sol. water.

Benzoyl derivative $C_6H_3(OH)(NHBz)CO_2H$. [252°]. Yields the salts BaA'_2 6aq and CaA'_2 (Dabney, *Am.* 5, 22).

Oxy-amido-benzoic acid $C_6H_3(OH)(NH_2)(CO_2H)$ [2:3:1]. Formed by reducing the nitro- acid (Hübner, *A.* 195, 17).—HA'HCl aq: needles, v. sol. water.

Benzoyl derivative. [189°]. Needles.

Oxy-amido-benzoic acid $C_6H_3(OH)(NH_2)CO_2H$ [5:2:1]. [235°]. Formed from benzene-azo-*m*-oxy-benzoic acid and $SnCl_2$ (Limpricht, *A.* 263, 234). Prisms, v. sl. sol. water.—HA'HCl: white needles.

Oxy-amido-benzoic acid $C_6H_3(OH)(NH_2)CO_2H$ [4:3:1]. Got by reducing nitro-*p*-oxy-benzoic acid (Barth, *Z.* 1866, 648; Deninger, *J. pr.* [2] 42, 553). Needles.—$H_2A'_2H_2SO_4$: needles, m. sol. water.

Ethyl ether EtA'. Plates.

Methyl derivative $C_6H_3(OMe)(NH_2)CO_2H$. *Amido-anisic acid.* [181°]. S. ·125 at 100°. Formed by reducing $C_6H_3(OMe)(NO_2)CO_2H$ (Zinin, *A.* 92, 327; Cahours, *A. Ch.* [3] 53, 322).—AgA': curdy pp.—HA'HCl.—$H_2A_2'H_2PtCl_6$.—HA'HNO$_3$.—$H_2A'_2H_2SO_4$.—*Ethers* MeA'.—$(MeA')_2H_2PtCl_6$: reddish prisms.—EtA'.—EtA'HCl.—$(EtA')_2H_2PtCl_6$: brownish-red prisms.

Oxy-amido-benzoic acid. *Methyl derivative* $C_6H_3(OMe)(NH_2)(CO_2H)$ [4:2:1]. Formed from $C_6H_2Br(OMe)(NH_2)CO_2H$ by treatment with zinc and HCl (Balbiano, *G.* 14, 247). It melts at 204°.

Oxy-di-amido-benzoic acid $C_6H_2(OH)(NH_2)_2CO_2H$ [2:3:5:1]. Formed by reducing $C_6H_2(OH)(NO_2)_2CO_2Me$ with HI and P (Saytzeff, *A.* 133, 321). Small needles, sl. sol. cold water. — HA'H$_2$Cl$_2$. — HA'H$_2$I$_2$ $1\frac{1}{2}$aq. — HA'H$_2$SO$_4$ aq: dimetric prisms, sl. sol. water.

Di-oxy-amido-benzoic acid. *Di-methyl derivative* $C_6H_2(NH_2)(OMe)_2CO_2H$. Formed with evolution of CO_2 by reduction of nitro-hemipic acid $C_6H(NO_2)(OMe)_2(CO_2H)_2$ with tin and HCl (Grüne, *B.* 19, 2305).—A'HHCl: white needles.

Di-oxy-amido-benzoic acid. *Di-methyl derivative* [4:3:*x*:1] $C_6H_2(OMe)_2(NH_2)CO_2H$. *Amido-veratric acid.* Formed by reducing nitro-veratric acid (Tiemann a. Matsmoto, *B.* 9, 942; 11, 135). Tables. *Ethyl ether* EtA'. [89°].

Di-oxy-amido-benzoic acid. *Di-methyl derivative* $C_6H_2(OMe)_2(NH_2)CO_2H$ [5:3:4:1]. [182°]. Got by reduction (Meyer, *M.* 8, 432). Six-sided prisms (from alcohol).—CuA'_2 2aq.—HA'HCl: needles, m. sol. cold water.

Di-oxy-amido-benzoic acid. *Acetyl-methylene derivative* of the *Nitrile* $C_6H_2(O_2CH_2)(NHAc).CN$. [216°]. Formed from the oxim of amido-piperonal, Ac_2O, and NaOAc (Haber, *B.* 24, 626). Yellow needles (from chloroform).

Reference.—BROMO-OXY-AMIDO-BENZOIC ACID.

DI-OXY-AMIDO-BENZOIC ALDEHYDE *Oxim of the methylene derivative* $C_6H_2(O_2CH_2)(NH_2).CH:NOH$. [175·5°]. Got by reducing the oxim of o-nitro-piperonal with ammonium sulphide (Haber, *B.* 24, 625). Yellow plates. Yields a di-acetyl derivative [188°].

OXY-AMIDO-BENZYLAMINE. *Methyl derivative* $C_6H_3(OMe)(NH_2)CH_2NH_2$ [1:2:4]. Formed from $C_6H_3(OMe)(NO_2).CH_2NHAc$, tin, and HClAq (Goldschmidt a. Polonowska, *B.* 20, 2412).—B'HCl: needles.—$B'_2H_2PtCl_6$: plates.

Di-acetyl derivative. [185°]. Needles.

α-OXY-β-AMIDO-BUTYRIC ACID $C_4H_9NO_3$ *i.e.* $CH_3.CH(NH_2).CH(OH).CO_2H$. S. 4 at 15°. Formed by heating β-methyl-glycidic acid in sealed tubes with NH_3Aq at 100° (Pavloff, *Bl.* [2] 43, 115; Melikoff, *J. R.* 16, 525). Prisms, with sweet taste.

Oxy-amido-isobutyric acid. S. ·55 at 15°. Formed from α-methyl-glycidic acid and NH_3.

OXY-AMIDO-CINNAMIC ACID

Methyl derivative [5:2:1] $C_6H_3(NH_2)(OMe).CH:CH.CO_2H$. [189°]. Formed by reduction of nitro-methoxy-cinnamic

acid with $FeSO_4$ and NH_3 (Schnell, *B.* 17, 1384). Colourless needles. V. sol. alcohol and ether, almost insol. cold water. An aqueous solution of the ammonium salt gives pps. with $AgNO_3$, $CuSO_4$, $Pb(OAc)_2$, and $ZnSO_4$.

Anhydride $C_6H_3(NH_2)<\begin{matrix}O.CO\\CH:CH\end{matrix}$. *Amido-coumarin.* [170°] (Frapolli a. Chiozza, *A.* 95, 253); [161°] (Taege, *B.* 20, 2110). Got by reduction of nitro-coumarin.—$B'_2H_2PtCl_6$.

Di-oxy-amido-cinnamic acid. *Methylene derivative.*

$CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_2(NH_2).CH:CH.CO_2H$. [207°].

Formed by reducing the nitro- acid with NH_3 and hot aqueous $FeSO_4$ (F. M. Perkin, *C. J.* 59, 158). Brownish needles, v. sol. HOAc.

DI-OXY-AMIDOETHYL-BENZOIC ACID. *Methylene derivative* $C_{10}H_{11}NO_4$ *i.e.* $C_6H_2(O_2CH_2)(CH_2.CH_2NH_2)CO_2H$. '*ω-Amido-ethylpiperonylcarboxylic acid.*' [182°]. Formed, together with hemipic acid, by boiling anhydro-berberilic acid with water (W. H. Perkin, jun., *C. J.* 57, 1055). Needles, sl. sol. alcohol, m. sol. cold water.—$(HA')_2H_2SO_4$ 2aq. [203°]. Colourless prisms.—HA'HCl.—$HA'H_2C_2O_4$. [203°].—$(HA')_2H_2PtCl_6$. [222°].—$HA'HAuCl_4$.

Di-benzoyl derivative $C_{24}H_{19}NO_6$. [150°].

Anhydride $CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_2<\begin{matrix}CO.NH\\CH_2.CH_2\end{matrix}$.

Formed by heating the acid, and, along with its ψ-opianate and ψ-opianic acid by the action of alkalis on berberal. It is also a product of the oxidation of berberine with $KMnO_4$. Yields the compound $C_{10}H_8BrNO_3$. [240°].—*Opianate* $B'C_6H_2(OMe)_2(CO_2H)_2$. [132°]. — *ψ-Opianate.* $C_{20}H_{19}NO_8$. [149°]. Needles, sl. sol. cold water. Yields berberal when heated.

OXY-AMIDO-GLUTAMIC ETHER $C_7H_{14}N_2O_4$ *i.e.* $CO(NH_2).CH_2.C(OH)(NH_2).CH_2.CO_2Et$. [86°]. Formed from acetone dicarboxylic ether and conc. NH_3Aq (Stokes a. Von Pechmann, *B.* 19, 2694). Needles, sl. sol. cold water, insol. alkalis. $FeCl_3$ gives a red colour. Dilute HClAq yields a body melting at 61° turned purple by $FeCl_3$. Nitrous acid yields a nitroso- derivative [178°]. Boiling alkaline carbonates yield glutazine (*v.* DI-OXY-AMIDO-PYRIDINE).

OXY-AMIDO-HEPTOIC ACID $C_7H_{15}NO_3$ *i.e.* $CMe_2(NH_2).CH_2.CMe(OH).CO_2H$. *Amidotri-methylbutyllactic acid.* [210°]. Formed by the action of boiling baryta-water on its anhydride which is obtained by the action of boiling conc. HClAq upon the product of the union of HCy with diacetonamine (Heintz, *A.* 189, 231; 192, 329; Weil, *A.* 232, 208). Prisms (from water); insol. alcohol and ether. Neutral to litmus. Yields its anhydride when heated.—*Salts* $CuC_7H_{13}NO_3$ 2aq: minute greenish-blue prisms. —$(HA')_2H_2SO_4$.—HA'HCl: crystalline.

Anhydride $CMe(OH)<\begin{matrix}CO.NH\\CH_2.CMe_2\end{matrix}$. *Di-oxy-tri-methyl-pyrrole.* Prisms (by sublimation). Melts above 180°.

OXY-AMIDO-HYDRO-ISATIN *v.* ISATIN.

OXY-AMIDO-IMIDO-DI-PHENYL SULPHIDE $C_{12}H_8N_2SO$ *i.e.* $N<\begin{matrix}C_6H_3(NH_2)\\ \big| \\ O{-}C_6H_3\end{matrix}>S$.

Thionoline. Formed by adding H_2S and FeCl successively to an aqueous solution of *p*-amido-phenol hydrochloride (Bernthsen, *A.* 230, 202). Yellowish-brown plates or needles with green lustre (from alcohol).

OXY-AMIDO-DI-ISATIN-DIAMIDE *v.* ISATIN.

DI-OXY-DI-AMIDO-TETRAMETHENYL.

Di-benzoyl derivative $\begin{matrix}C(NHBz):C(OH)\\ \mid \qquad\qquad \mid \\ C(OH) = C(NHBz)\end{matrix}$. [138°]. Formed by heating hippuric ether with NaOEt, or with Na, at 160° (Rügheimer, *B.* 21, 3325; 22, 114). Needles, m. sol. alcohol, v. e. sol. benzene. $FeCl_3$ colours its alcoholic solution violet. Decomposed by acids into benzoic acid and di-amido-acetone. Hydroxylamine does not affect it. Methyl alcohol and gaseous HCl form a body ($C_{11}H_{10}N_2O_3$?) crystallising in plates [200°].

Oxy-tetra-amido-pentamethenyl hydride $CH(OH)<\begin{matrix}C(NH_2):C(NH_2)\\C(NH_2):C(NH_2)\end{matrix}$. *Tetra-amido-pentol.* Formed from the tetra-oxim of leuconic acid $SnCl_2$, and HClAq (Nietzki a. Rosemann, *B.* 22, 923).—$B^{iv}3HCl$: octahedra.—$B^{iv}(H_2SO_4)_2$ aq.

Tetra-oxy-tetra-amido-octomethenyl.

Tetra-benzoyl derivative $C_{36}H_{28}N_4O_6$ *i.e.* $C(OH)<\begin{matrix}C(NHBz):C(OH).C(NHBz)\\C(NHBz).C(OH):C(NHBz)\end{matrix}>C(OH)$. A product of the action NaOEt on hippuric ether (Rügheimer, *B.* 22, 1962). Small yellow needles. Does not melt below 270°.—$BaC_{36}H_{26}N_4O_6$: pp.

Anhydride $C_{36}H_{24}N_4O_6$.

OXY-AMIDO-METHYL-ANTHRAQUINONE $C_{15}H_{11}NO_3$ *i.e.* $C_{14}H_5Me(OH)(NH_2)O_2$. Formed by heating chrysophanic acid with NH_3Aq at 200° (Liebermann, *A.* 183, 218). Brown plates.

Oxy-di-amido-methyl-anthraquinone $C_{15}H_{12}N_2O_3$. *Di-amido-chrysophanic acid.* Formed by heating chrysophanic acid with excess of NH_3Aq at 150°. With Ac_2O it yields $C_{15}H_{11}AcN_2O_3$ crystallising from chloroform in lustrous violet needles.

OXY-DIAMIDO-METHYL-DIPHENYL

Ethyl derivative

$C_6H_4(NH_2).C_6H_2Me(OEt)(NH_2)$ [1:2:5:4]. [107°]. Formed from the hydrazo- derivative $C_6H_5.NH.NH.C_6H_3Me(OEt)$ by dissolving in cold HClAq (Noelting a. Werner, *B.* 23, 3263). Needles, v. sl. sol. water.

Oxy-di-amido-methyl-diphenyl [3:4:1] $C_6H_3Me(NH_2).C_6H_3(OH)(NH_2)$ [1:3:4]. [177°]. Formed by the action of water at 180° on the sulphonic acid $C_6H_3Me(NH_2).C_6H_2(OH)(NH_2)SO_3H$ [1:3:4:6], got by reducing the dye from diazotised *o*-toluidine and *p*-phenol sulphonic acid (Weinberg, *B.* 20, 3174). Plates, v. sl. sol. water.

Ethyl derivative

$C_6H_3Me(NH_2).C_6H_3(OEt)(NH_2)$. [117·5°]. Formed in like manner from $C_{13}H_8(OEt)(NH_2)_2SO_3H$, which yields HA'HCl 4aq and BaA'_2 8aq.

OXY-AMIDO-METHYL-QUINOLINE $C_9H_4(OH)(NH_2)MeN$. Formed by reducing nitro-(*Py.* 1)-oxy-(*Py.* 3)-methyl-quinoline (Conrad a. Limpach, *B.* 20, 950). Prisms, decomposing at 225° without melting.—B'HCl aq.

OXY-AMIDO-NAPHTHALENE *v.* AMIDO-NAPHTHOL.

(1,2,3)-Di-oxy-amido-naphthalene

$C_6H_4<\begin{matrix}C(OH):C(OH)\\ \qquad\quad \mid \\ N\ \ :C(NH_2)\end{matrix}$? *Di-oxy-naphthylamine*

Obtained by reduction of nitro-(β)-naphtho-

quinone (Korn, *B.* 17, 906). Reduces cold $AgNO_3$. Fe_2Cl_6 gives a blue-black pp.

(2,2′,1)-**Di-oxy-amido-naphthalene** $\begin{matrix}C(OH):CH.C.C(NH_2):C(OH)\\ CH{=\!=}CH.C.CH{=\!=}CH\end{matrix}$. Formed by reducing the (α)-oxim of (2′)-oxy-(β)-naphthoquinone with $SnCl_2$ (Clausius, *B.* 23, 521).—B′HCl: needles, turning blue in air.

Di-oxy-amido-naphthalene. Got by reducing amido-(α)-napthoquinone (Graebe a. Ludwig, *A.* 154, 320). Tables, v. e. sol. water. Blackens in moist air.

Tri-oxy-amido-naphthalene $C_6H_4<\begin{matrix}C(OH):C(NH_2)\\ C(OH):C(OH)\end{matrix}$. Formed by reducing nitro-oxy-(α)-naphthoquinone with $SnCl_2$ (Kehrmann, *B.* 21, 1780; *J. pr.* [2] 40, 179). Monoclinic crystals. Cold conc. HNO_3 appears to form $C_6H_4<\begin{matrix}CO.C(N.NO)\\ CO.CO\end{matrix}$ crystallising in reddish yellow needles. Yields a tetra-acetyl derivative [145°].

OXY-AMIDO-NAPHTHALENE SULPHONIC ACID *v.* Amido-naphthol sulphonic acid.

Oxy-di-amido-naphthalene sulphonic acid $C_6H_4(NH_2)_2(OH)(SO_3H)$ [*x*:4′:1:4]. The hydrochloride B′HCl is formed by reducing di-nitro-naphthol sulphonic acid with $SnCl_2$ and HCl (Nietzki a. Zübelen, *B.* 22, 455). It crystallises in colourless needles.

OXY-*m*-AMIDO-NAPHTHOIC ACID $C_{10}H_5(OH)(NH_2)CO_2H$. Formed by reducing the nitro- acid (Schmitt a. Burkard, *B.* 20, 2700). Decomposes above 200°.

Acetyl derivative [185°].

Oxy-*p*-amido-naphthoic acid. Got by reducing $C_6H_4(SO_3H).N_2.C_{10}H_5(OH)CO_2H$ with tin and HCl (S. a. B.). Decomposes above 200°.

Acetyl derivative [195°].

Oxy-amido-naphthoic acid $C_{10}H_5(OH)(NH_2)(CO_2H)$ [1:4:2 ?]. [above 200°]. Formed from (α)-oxy-naphthoic acid by combining it with diazobenzene chloride and warming the product with $SnCl_2$ and HCl (Nietzki a. Guitermann, *B.* 20, 1275). Crystalline powder, insol. water. Decomposes above 230° into CO_2 and (α)-amido-(α)-naphthol.

OXY-AMIDO-(α)-NAPHTHOQUINONE $C_6H_4<\begin{matrix}CO.C(NH_2)\\ CO.C(OH)\end{matrix}$. *Amido-naphthalic acid.* Formed by reduction from nitro-oxy-naphthoquinone (Diehl a. Merz, *B.* 11, 1319) and from di-nitroso-di-oxy-naphthalene (Kostanecki, *B.* 22, 1346). Formed also by oxidising tri-oxy-amido-naphthalene with aqueous $FeCl_3$ (Kehrmann, *B.* 21, 1781). Red prisms, sl. sol. water. Its alkaline solutions are blue.—BaA'_2: violet pp.—AgA′: grey pp.

Acetyl derivative $C_{10}H_4O_2(OH)(NHAc)$. [220°]. Formed from $C_{10}H_4(OAc)_3(NHAc)$ and KOHAq (Kehrmann a. Weichardt, *J. pr.* [2] 40, 182). Yellow needles, insol. water.—KA′: blue-black needles.

Oxim $C_6H_4<\begin{matrix}CO{-\!-\!-}C.NH_2\\ C(NOH).C.OH\end{matrix}$. Greenish flocculent pp.—B′HCl: yellow needles.

Acetyl derivative of the oxim $C_6H_4<\begin{matrix}CO{-\!-\!-}C.NHAc\\ C(NOH).C.OH\end{matrix}$. Golden needles, sl. sol. alcohol. Decomposes at 190°-200°.

OXY-DIAMIDO-DIPHENYL $C_{12}H_{12}N_2O$ *i.e.* [4:1] $C_6H_4(NH_2).C_6H_3(NH_2)(OH)$ [1:4:2]. [185°]. Formed by the action of water at 180° on the hydrochloride of its sulphonic acid, which is got by reducing $C_6H_5.N_2.C_6H_3(OH)SO_3H$ with $SnCl_2$ at 30° (Weinberg, *B.* 20, 3173; Noelting a. Werner, *B.* 23, 3256). Plates, sl. sol. water.—$HA'H_2SO_4$: insol. water. — HA′HCl.—$(HA')_2H_2PtCl_6$ 5aq: sl. sol. water.

Ethyl derivative $C_6H_4(NH_2).C_6H_3(NH_2)(OEt)$. [135°]. Needles, sl. sol. water.—$HA'H_2SO_4$: prisms.

Di-oxy-di-amido-diphenyl. *Di-ethyl-derivative* [4:3:1] $C_6H_3(NH_2)(OEt).C_6H_3(NH_2)(OEt)$ [1:4:3]. *Di-ethoxy-benzidine.* [117°]. Formed from [2:1] $C_6H_4(OEt)NH.NH.C_6H_4(OEt)$ [1:2] and conc. HClAq (Möhlau, *J. pr.* [2] 19, 381). Needles or plates, sol. hot water.—$B''H_2Cl_2$.—$B''2HSnCl_3$.—$B''H_2PtCl_6$.—$B''H_2SO_4$: needles, sol. hot water.

Di-oxy-di-amido-diphenyl [3:4:1] $C_6H_3(NH_2)(OH).C_6H_3(NH_2)(OH)$ [1:3:4]. [above 300°]. Formed by reducing di-nitro-di-oxy-diphenyl (Kunze, *B.* 21, 3332; Schütz, *B.* 21, 3531). Needles or plates. Ac_2O yields the di-acetyl derivative. AcCl forms the di-ethenyl derivative [195°].—$B''H_2Cl_2$: needles.—$B''H_2SO_4$.

Di-acetyl derivative $C_{12}H_6(OH)_2(NHAc)_2$. [210°]. Needles, sol. alkalis, insol. acids.

Tetra-acetyl derivative $C_{12}H_8Ac_4N_2O_2$. [225°]. White needles (K.).

Di-oxy-tetra-amido-diphenyl $C_6H_2(NH_2)_2(OH).C_6H_2(NH_2)_2(OH)$. Formed from tetra-nitro-di-oxy-diphenyl (Kunze). Colourless needles or silvery plates, turning blue in air. AcCl converts it into a compound $C_{16}H_{14}N_4O_2$.—$B^{iv}H_4Cl_4$ 4aq.—$B^{iv}H_2SO_4$: white needles.

Tetra-acetyl derivative $C_{12}H_4(NHAc)_4(OH)_2$. [280°]. Got by boiling the hexa-acetyl derivative with NaOHAq.

Hexa-acetyl derivative $C_{12}H_4(NHAc)_4(OAc)_2$. [300°]. Formed from the base and boiling Ac_2O.

Tetra-oxy-di-amido-diphenyl $C_6H_2(OH)_2(NH_2).C_6H_2(OH)_2NH_2$.

Tetra-methyl derivative $C_{12}H_4(OMe)_4(NH_2)_2$. [210°]. Formed by molecular change from tetra-methoxy-hydrazobenzene under the influence of acids (Baessler, *B.* 17, 2128). Silky white needles; v. sol. chloroform, CS_2, hot alcohol, and hot benzene, sl. sol. water and ligroin.—$B''H_2Cl_2$: small white, easily soluble needles.—$B''H_2Cl_2PtCl_4$: yellow pp. The di-acetyl derivative forms white needles [251°], sol. hot alcohol, benzene, chloroform, and CS_2.

Tetra-ethyl derivative $C_{12}H_4(NH_2)_2(OEt)_4$. [129°]. Formed, in like manner, from the hydrazo- compound got by reducing the di-ethyl ether of nitro-hydroquinone with powdered zinc and alcoholic potash (Nietzki, *B.* 12, 39). Leaflets.—$B''H_2Cl_2$.—$B''H_2PtCl_6$: yellow crystalline pp.

Tetra-oxy-tetra-amido-diphenyl. *Tetra-acetyl derivative* $C_6H_2(NHAc)_4(OH)_4$. White needles, formed by reduction of the corresponding quinone $(C_6H(NHAc)_2OH)_2O_2$ [268°] which is formed by oxidation of tri-acetyl-tri-amido-phenol (Bamberger, *B.* 16, 2403).

α-OXY-*o*-AMIDO-PHENYL-ACETIC ACID. *Hydrindic acid.*

Acetyl derivative $C_6H_4(NHAc).CH(OH).CO_2H$. [142°]. Got by reducing acetyl-isatic acid with sodium-amalgam in presence of acetic acid (Suida, *B.* 11, 586). Needles, v. sol. water.

Anhydride v. Di-oxindole.

p-Oxy-α-amido-phenyl-acetic acid. *Methyl derivative* $C_6H_4(OMe).CH(NH_2).CO_2H$. [225°]. Formed from anisic aldehyde by successive treatment with HCy, alcoholic NH_3, and HCl (Tiemann a. Köhler, *B.* 14, 1979). Needles (from dilute alcohol).—CuA'_2 : blue amorphous pp.

Di-oxy-α-amido-phenyl-acetic acid. *Methylene derivative* $CH_2O_2{:}C_6H_3.CH(NH_2).CO_2H$. [210°]. Formed from piperonal by successive treatment with HCy, alcoholic NH_3, and HCl (Lorenz, *B.* 14, 794). Needles, sl. sol. water.

OXY-AMIDO-PHENYL-ACRIDINE *v.* Chrysophenol.

OXY-AMIDO-DI-PHENYL-AMINE $C_6H_5.NH.C_6H_3(OH)(NH_2)$ [1:3:4]. [135°]. Formed by reducing nitroso-oxy-di-phenyl-amine (Köhler, *B.* 21, 910). Plates, v. sol. chloroform.

OXY-AMIDO-PHENYL-CARBAMIC ETHERS. Formed from the nitro- compounds (Köhler, *J. pr.* [2] 29, 263).

[4:3:1].$C_6H_3(OEt)(NH_2).NH.CO_2Et$. [88°]. Small needles.—B'HCl. [156°]. Needles.

[4:3:*x*:1] $C_6H_2(OEt)(NH_2)_2NHCO_2Et$. Needles. —B'HCl. [238°]. Six-sided plates, sol. water.

$C_6H(OEt)(NH_2)_3NHCO_2Et$. Small needles, rapidly oxidising in air.—B'HCl. [233°]. Needles.

OXY-AMIDO-DI-PHENYL-METHANE *v.* Amido-benzyl-phenol.

Oxy-di-amido-tri-phenyl-methane. *Methyl derivative* $C_6H_4(OMe).CH(C_6H_4NH_2)_2$. Formed by heating anisic aldehyde with aniline and HClAq (Mazzara a. Possetto, *G.* 15, 57). Crystalline crust (containing C_7H_8) melting at 65°.

Di-oxy-tri-amido-tri-phenyl-methane. *Di-methyl derivative* $C_6H_4(NH_2).CH(C_6H_3(NH_2).OMe)_2$. [183°]. Obtained by reduction of the di-methyl derivative of nitro-di-amido-di-oxy-tri-phenyl-methane (Fischer, *B.* 15, 681). Plates or tables. Yields on oxidation 'rosanidine,' a bluish-red colouring matter with blue fluorescence.

OXY-AMIDO-PHENYL-METHYL-PYRAZOLE $C_{10}H_{11}N_3O$ *i.e.* $C_6H_5N\left<\begin{array}{l}CO.CH(NH_2)\\ N\ {:}CMe\end{array}\right.$. Formed by reducing the nitro- compound (Knorr, *A.* 238, 189). Rapidly oxidised by air.—B'HCl.

OXY-DI-AMIDO-PHENYL-METHYL-PYRIMIDINE $C_{11}H_{12}N_4O$. [232°–240°]. Formed from $C_6H_5CH\left<\begin{array}{l}N.C(OH)\\ N{:}CMe\end{array}\right>CH$ by nitration and reduction (Pinner, *B.* 20, 2364). Golden needles, sol. NaOHAq.—$B''H_2PtCl_6$.—$B''H_2I_2$: prisms.

OXY-DI-AMIDO-PHENYL-NAPHTHALENE. *Ethyl derivative* [2:1:4] $C_{10}H_5(OEt)(NH_2).C_6H_4NH_2$ [1:4]. [72°]. Formed by reducing $C_6H_5.N_2.C_{10}H_6OEt$ in alcoholic solution with $SnCl_2$ and HCl (Weinberg, *B.* 20, 3177). White flakes.—B''HCl.—$B''H_2SO_4$: sl. sol. water.

OXY-AMIDO-PHENYL-PROPIONIC ACID $C_6H_5.CH(NH_2).CH(OH).CO_2H$ [190°] (P.). Formed from sodium phenyl-glycidate and NH_3 (Plöchl, *B.* 16, 2822; Erlenmeyer, jun., *B.* 22, 1482). Decomposes at 221° (E.).

α-Oxy-o-amido-phenyl-propionic acid. *Anhydride* $C_6H_4\left<\begin{array}{l}CH_2.CH(OH)\\ \quad\quad\ |\\ NH.CO\end{array}\right.$. *Oxyhydrocarbostyril.* [198°]. Got by reducing the product of the nitration of α-oxy-phenyl-propionic acid (Erlenmeyer a. Lipp, *A.* 219, 229). White plates (from alcohol). Sl. sol. ether, v. sol. hot water.

α-Oxy-*p*-amido-phenyl-propionic acid $C_6H_4(NH_2).CH_2.CH(OH).CO_2H$. [189°]. Got by reducing the nitrate of nitro-oxy-phenyl-propionic acid (Erlenmeyer a. Lipp, *A.* 219, 227). Slender needles (containing ½aq) from diluto (93 p.c.) alcohol. More sol. alcohol or ether than tyrosine. Readily soluble in alkalis or acids. Unlike tyrosine, its solution is acid and it does not give Piria's reaction. Boiled with $Hg(NO_3)_2$ it forms a yellow flocculent pp., which, on adding HNO_2, turns red. HA'HCl. V. sol. water or alcohol, without decomposition.

p-Oxy-α-amido-phenyl-propionic acid *v.* Tyrosine.

αβ-Di-oxy-o-amido-phenyl-propionic acid $C_6H_4(NH_2).CH(OH).CH(OH).CO_2H$. [218°]. Produced in the reduction of o-nitro-cinnamic acid by tin and HClAq (Morgan, *J.* 1877, 788). Yellow needles (from alcohol). Its solutions fluoresce green.

Di-oxy-amido-propionic acid. *Anhydride of the methylene derivative* $CH_2\left<\begin{array}{l}O\\ O\end{array}\right>C_6H_2\left<\begin{array}{l}NH.CO\\ CH_2.CH_2\end{array}\right.$. '*Ethylamidopiperonyl-ω-carboxylic anhydride.*' [235°]. Formed by reducing $(CH_2O_2)C_6H_2(NO_2).CH{:}CH.CO_2Et$ in alcoholic solution with tin and gaseous HCl (F. M. Perkin, *C. J.* 59, 159). Crystalline pp.

OXY-AMIDO-PHENYL-PYRAZOLE CARBOXYLIC ACID.

Benzoyl derivative $NPh\left<\begin{array}{l}CO.CH.NHBz\\ N=C.CO_2H\end{array}\right.$. [185°–190°]. Formed from its ether and NaOH (Wislicenus, *B.* 24, 1261). Yellowish needles, sl. sol. water.

Ethyl ether EtA'. [195°]. Formed by boiling the phenyl-hydrazide of benzoyl-amido-oxalacetic ether with HOAc. Yellow crystals.

OXY-*m*-AMIDO-PHENYL-PYROTARTARIC ACID. *Anhydride* $C_{11}H_{11}NO_4$ *i.e.* $C_6H_4(NH_2).CH\left<\begin{array}{l}CH(CO_2H)\\ O.CO.CH_2\end{array}\right>$. *Amidophenylparaconic acid.* Formed by reducing the correspondiug nitro- compound (Salomonson, *R. T. C.* 6, 18).—B'HCl: prisms.—$B'_2H_2PtCl_6$. Tho isomeric oxy-*p*-amido-phenyl-pyrotartaric anhydride yields a similar hydrochloride.

(*B.* 2)-OXY-*p*-AMIDO-(*Py.* 3)-PHENYL-QUINOLINE $\begin{array}{l}C(OH){:}CH.C.CH{:}CH\\ CH{=\!=}CH.C.N\ \ {:}C.C_6H_4.NH_2\end{array}$. [294°]. Formed by passing oxygen over a mixture of (*B.* 2)-oxy-quinoline hydrochloride, aniline hydrochloride, aniline, and platinised asbestos at 220° (Weidel a. Georgievitch, *M.* 9, 146). Needles (from amyl alcohol), sl. sol. alcohol and ether.—B'HCl ½aq.—$B'_2H_2SO_4$ 1½aq.

Acetyl derivative $C_{15}H_{10}Ac_2N_2O$. Scales.

(*Py.* 4:1:2)-Oxy-amido-phenyl-isoquinoline $C_{15}H_{12}N_2O$ *i.e.* $C_6H_4<\begin{matrix}C(NH_2):CPh \\ | \\ C(OH):N\end{matrix}$. *Amido-iso-benzal-phthalimidine.* [c. 190°]. Formed by reduction of the nitro- derivative with P and HI (Gabriel, *B.* 19, 833). Fine yellow needles. V. sol. acetic acid and hot alcohol.

DI-OXY-DI-AMIDO-DI-PHENYL SULPHONE $C_{12}H_{12}N_2SO_4$ *i.e.* $SO_2(C_6H_3(NH_2)OH)_2$. Formed by reducing the nitro- compound (Annaheim, *B.* 7, 436; 8, 1063). Crystals (from water). Alcoholic isoamyl nitrite forms golden plates of $C_{12}H_6N_4SO_4$. Salts.—$B''H_2Cl_2$ 2aq.—$B''H_2I_2$ 2aq. — $B''H_2SO_4$ 2aq: thick prisms. — $C_{12}H_{10}Me_2N_2SO_4H_2I_2$. Forms long needles.—$C_{12}H_{10}Et_2N_2SO_4H_2I_2$: needles.

OXY-DI-AMIDO-DIPHENYL SULPHONIC ACID [4:1]$C_6H_4(NH_2).C_6H_2(NH_2)(OH)SO_3H$. [1:4:3:6]. Prepared by reducing the azo- compound $C_6H_5.N_2.C_6H_3(OH)SO_3Na$ with aqueous $SnCl_2$ (Weinberg, *B.* 20, 3172; Feer a. Müller, *C. C.* 1888, 1358). Needles, v. sol. water.—B'HCl: transparent crystals.

Ethyl derivative $C_6H_4(NH_2).C_6H_2(NH_2)(OEt)SO_3H$. Got in like manner. Needles.—B'HCl 2aq: needles, v. sol. water.

OXY-AMIDO-DIPHENYL DISULPHONIC ACID $C_6H_3(NH_2)(SO_3H).C_6H_3(OH)(SO_3H)$. Formed from benzidine disulphonic acid by the diazo- reaction (Limpricht, *A.* 261, 315). Light-yellow crystalline mass, v. e. sol. water, insol. ether.—BaA''8aq: reddish-yellow crystals.

OXY-AMIDO-PHENYL-TOLYL KETONE $C_{14}H_{13}NO_2$ *i.e.* $C_6H_4(NH_2).CO.C_6H_3Me(OH)$ or $C_6H_4(OH).CO.C_6H_3Me(NH_2)$. A product of the action of water at 270° on commercial rosaniline (Liebermann, *B.* 16, 1927). Small colourless needles, sol. acids and alkalis.

Di-benzoyl derivative. [193°]. Needles.

DI-OXY-AMIDO-PHTHALIC ACID. *Methyl derivative of the anhydride* $C_6H(OMe)(OH)(CO_2H)<\begin{matrix}CO \\ NH\end{matrix}$ [4:3:2:$\frac{1}{6}$]. *Nor-methylazoopianic acid.* [175°]. Formed by reducing $C_6H(NO_2)(OMe)(OH)(CHO)CO_2H$ with conc. $SnCl_2$ and HCl (Elbel, *B.* 19, 2307). Colourless needles, nearly insol. ether. Yields an acetyl derivative $C_8H_3NO_3(OMe)(OAc)$ [198°], and a di-acetyl derivative [105°].

Di-methyl derivative of the anhydride v. Amido-hemipic acid, vol. ii. p. 672.

DI-OXY-AMIDO-PHTHALIDE. *Di-methyl derivative v. Amido-*Meconin (p. 198) and *Amido-ψ-*Meconin (p. 199).

α-OXY-β-AMIDO-PROPIONIC ACID $CH_2(NH_2).CH(OH).CO_2H$. *Amido-lactic acid.* S. 1·5 at 20°. Formed from $CH_2Cl.CH(OH).CO_2H$ and conc. NH_3Aq (Melikoff, *C. C.* 1881, 354; *B.* 13, 958, 1266; Erlenmeyer, *B.* 13, 1077). Monoclinic prisms.—B'HCl: needles.

OXY-AMIDO-ISOPROPYL-BENZOIC ACID $CMe_2(OH)C_6H_3(NH_2).CO_2H$ [4:2:1]. [158°]. Got from the nitro- acid (Widman, *B.* 19, 271). Prisms. Yields amido-propenyl-benzoic acid on boiling with HClAq.

Acetyl derivative [174°]. Tables.

Exo-oxy-amido-isopropyl-benzoic acid $CMe_2(OH)C_6H_3(NH_2)(CO_2H)$ [4:3:1]. Does not melt below 270° (Widman, *B.* 16, 2571). Its acetyl derivative is not melted at 280°.

OXY-AMIDO-PYRIDINE $C_5H_3N(OH)(NH_2)$. [214°]. Got by reducing oxy-comazine (Krippendorff, *J. pr.* [2] 32, 162). Pyramids (containing aq), v. e. sol. hot water.—B'HCl.—$B'_2H_2PtCl_6$.

Di-oxy-amido-pyridine $NH<\begin{matrix}CO.CH_2 \\ CO.CH_2\end{matrix}>C:NH$ or $N<\begin{matrix}C(OH).CH \\ C(OH):CH\end{matrix}>C.NH_2$. *Glutazine.* [c. 300°]. Formed by boiling β-oxy-β-amido-glutamic ether $CO_2Et.CH_2.C(OH)(NH_2).CH_2.CONH_2$ with aqueous Na_2CO_3 (Stokes a. Von Pechmann, *B.* 19, 2694; 20, 2655; *Am.* 8, 375). Rectangular plates, m. sol. hot water, almost insol. hot alcohol. Gives a deep-red colour with $FeCl_3$ turning dark green on warming.

Reactions.—1. Hot HClAq yields tri-oxy-pyridine. — 2. *Bromine* in excess forms $CBr_3.CO.CBr_2.CONH_2$ [c. 148°].—3. By heating with PCl_5 (6 to 7 pts.) it is converted into a mixture of tri-chloro-oxy-amido-pyridine [282°] and tetra-chloro-amido-pyridine [212°], together with small quantities of di-chloro-di-oxy-amido-pyridine [242°] and tri-chloro-amido-pyridine [158°].—4. Yields nitro-glutazine [170°–180°] and crystalline di-nitro-glutazine on treatment with nitrous acid gas. With $NaNO_2$ and acetic acid there is formed the nitro-nitrosamine $C_5H_4N_2O_2(NO_2)(NO)$ whence $NaC_5H_3N_4O_5$ crystallising in yellow needles, which on warming with $NaNO_2$ and HOAc yields the di-nitro-nitrosamine salt $NaC_5H_2N_5O_7$, a scarlet powder.

Salts.—B'HCl aq: prisms, v. sol. alcohol.—AgA': plates.

Acetyl derivative $C_5N_2H_5AcO_2$ [285°–290°]. Tables; not attacked by hydroxylamine.—NH_4A' aq.

Di-benzoyl derivative $C_5N_2H_4Bz_2O_2$. [216°]. Brownish plates, insol. water.

DI-OXY-AMIDO-PYRIMIDINE CARBOXYLIC ACID $NH<\begin{matrix}CO.NH \\ CO.C(NH_2)\end{matrix}>C.CO_2H$. Formed by reducing the nitro- acid (Behrend, *A.* 240, 21). Not affected by boiling potassium cyanate.—KA' aq.

Ethyl ether EtA'. [260°] (Köhler, *A.* 236, 32).

OXY-AMIDO-PYROTARTARIC ACID $CH_3.C(OH)(CO_2H).CH(NH_2).CO_2H$ or $CH_3.C(NH_2)(CO_2H).CH(OH)(CO_2H)$. *Amido-citramalic acid.* S. 31 at 18°. Formed from oxycitraconic acid and NH_3Aq at 100° (Melikoff a. Feldmann, *A.* 253, 92). Monoclinic prisms.—B'HCl: prisms, v. sol. water.

DI-OXY-AMIDO-PYRROLE. *Benzoyl derivative* $N<\begin{matrix}CH{=\!=}C(OH) \\ C(OH).CH.NHBz\end{matrix}$. [200·5°]. Got by heating at 140° the product of the action of NaOEt on hippuric ether (Rügheimer, *B.* 22, 1957). Plates (from MeOH), v. sol. warm water.

OXY-AMIDO-QUINIZINE-CARBOXYLIC ACID ? $C_{10}H_9N_3O_3$. *Anhydride of amido-oxal-acetic-acid-phenyl-hydrazide.* Formed by warming the phenyl-hydrazide of amido-oxalacetic acid (vol. i. p. 169) with conc. H_2SO_4. White glistening plates. Insol. hot water and ether, v. sl. sol. hot alcohol. Dissolves in alkalis and in conc. H_2SO_4. Reduces Fehling's solution on gently warming. Mercuric salts are reduced in

the cold with formation of a deep orange-red colouration (Tafel, *B.* 20, 246).

(*B.* 4:1)-**OXY-AMIDO-QUINOLINE** $C_9H_5(OH)(NH_2)N$ *i.e.* $\begin{matrix} CH:C(NH_2).C.CH:CH \\ CH:C(OH)\ .C.N\ :CH \end{matrix}$ Formed by reduction of sulpho-benzene-azo-oxy-quinoline (from diazotised sulphanilic acid and (*B.* 4)-oxy-quinoline) (Fischer a. Renouf, *B.* 17, 1643). Crystalline solid. Very oxidisable. On oxidation it gives quinoline-quinone. Salts.—$B''H_2Cl_2$.—$B''H_2SO_4$: sparingly soluble needles.

(*B.* 2, 4)-**Oxy-amido-quinoline** $\begin{matrix} C(OH):CH\ .C.CH:CH \\ CH:C(NH_2).C.\ N\ :CH \end{matrix}$ Obtained by reducing (*B.* 4, 2)-nitro-oxy-quinoline (Altschal, *B.* 21, 2255). Needles (containing 2aq) becoming yellowish-green on drying at 100°. Its acetyl derivative yields at 235° a crystalline ethenyl derivative.

(*B.* 2, 1)-**Oxy-amido-quinoline** $\begin{matrix} C(OH):C(NH_2).C.CH:CH \\ CH{=\!=}CH{-\!-}C.\ N\ :CH \end{matrix}$ [143°]. Got by reducing the nitroso- compound with $SnCl_2$ and HCl (Von Kostanecki, *B.* 24, 153). Radiating needles.—$B''H_2SO_4$ 2aq: needles.

(*Py.* 3)-**Oxy-amido-quinoline** *v.* AMIDO-CARBOSTYRIL.

Oxy-amido-quinoline dihydride *v.* AMIDO-HYDROCARBOSTYRIL.

OXY-AMIDO-QUINONE. *Acetyl derivative* $\begin{matrix} C(NHAc):CH.C.O \\ C(OH)\ \ :CH.C.O \end{matrix}$ [170°]. Formed from tetra-acetyl-di-amido-hydroquinone, NaOHAq, and $FeCl_3$ (Nietzki a. Schmidt, *B.* 22, 1657). Golden plates (by sublimation).

Di-oxy-di-amido-quinone $C_6O_2(OH)_2(NH_2)_2$ [1:4:2:5:3:6]. Formed from tetra-oxy-di-amido-benzene hydrochloride by atmospheric oxidation in presence of aqueous NaOAc (Nietzki, *B.* 21, 1850). Reddish-brown needles. Yields a crystalline di-acetyl derivative.

OXY-AMIDO-SULPHOBENZOIC ACID $C_6H_2(OH)(NH_2)(SO_3H).CO_2H$ [2:5:x:1]. Obtained by reducing the nitro- acid (Hübner, *B.* 10, 1701). Needles (containing aq). An isomeric acid, crystallising in needles (containing 3aq) is got by sulphonating (2, 5, 1)-oxy-amido-benzoic acid. It yields CaA'_2 5aq crystallising in nodules.

OXY-AMIDO-THYMOQUINONIMIDE *v.* vol. i. p. 186.

OXY-AMIDO-TOLUIC ACID $C_6H_2Me(OH)(NH_2)CO_2H$ [1:2:5:3]. Formed from o-cresotic acid by combining it with diazobenzene and reducing the azo- compound (Nietzki a. Ruppert, *B.* 23, 3476). Plates, melting above 300°. Yields an acetyl derivative [275°].

OXY-DI-AMIDO-DITOLYL. *Ethyl derivative* [1:3:4]$C_6H_3Me(NH_2).C_6H_2Me(OEt)(NH_2)$ [1:2:5:4]. [75°]. Formed from the hydrazo-derivative and H_2SO_4 (Noelting a. Werner, *B.* 23, 3264). Needles: sl. sol. water.

OXY-ISOAMYL-AMINE $C_5H_{10}(OH).NH_2$. (158°). S.G. $\frac{14}{}$ ·9265. Formed from amylene chlorhydrin (chiefly consisting of tri-methyl-ethylene chlorhydrin) and NH_3Aq (Wurtz, *A. Suppl.* 7, 89; Radziszewski a. Schramm, *B.* 17, 838). Oil, v. sol. water. Alkaline in reaction. P_2O_5 forms some terpene.—$B'_2H_2PtCl_6$: orange crystals.

Di-oxy-di-isoamyl-amine $NH(C_5H_{10}.OH)_2$. (250°). S.G. $\frac{14}{}$ ·950. Accompanies the preceding base. Strongly alkaline syrup, sol. alcohol and ether.

OXY-AMYL-ANTHRACENE $C_6H_4\!<\!\begin{matrix} CO{-\!-\!-\!-} \\ CH(C_5H_{11}) \end{matrix}\!>\!C_6H_4$. *Amyl-hydroanthronc.* [253°]. Formed by boiling anthranol with KOHAq, and isoamyl iodide (Hallgarten, *B.* 21, 2508). Yellowish crystals.

DI-OXY-AMYL-BENZENE $CHPr(OH).CH(OH).C_6H_5$. [82°]. Formed from isobutyric aldehyde, benzoic aldehyde, and alcoholic potash (Fossek, *M.* 5, 120). Crystals.

DI-OXY-DI-AMYL KETONE ANHYDRIDE $CH_2\!<\!\begin{matrix} CH_2{-\!-} \\ CHEt.O \end{matrix}\!>\!C\!<\!\begin{matrix} {-\!-}CH_2 \\ O.CHEt \end{matrix}\!>\!CH_2$. (209° i.V.). S. ·26 at 15°. Obtained by boiling its carboxylic acid with water (Fittig, *A.* 256, 141). Oil. Yields $C_{11}H_{20}Br_2O$ [35°].

Carboxylic acid $CH_2\!<\!\begin{matrix} CH_2{-\!-} \\ CHEt.O \end{matrix}\!>\!C\!<\!\begin{matrix} CH(CO_2H) \\ O.CHEt \end{matrix}\!>\!CH_2$. [106°]. Got by the action of warm NaOHAq on 'di-hexolactone,' an oil formed by boiling the lactone of oxyhexoic acid with alcoholic NaOEt. Prisms.—NaA'.—CaA'_2.—BaA'_2 (dried at 100°). —AgA': white flocculent pp.

OXY-AMYL-PHOSPHINIC ACID *v.* OXY-PENTANE PHOSPHONIC ACID.

Di-oxy-di-isoamyl hypophosphorous acid $(C_4H_9.CH(OH))_2PO.OH$. [160°]. Formed by heating isovaleric aldehyde with hypophosphorous acid in a current of CO_2 at 95° (Ville, *Bl.* [3] 2, 202; *C. R.* 109, 73). Globular masses of slender needles, v. sl. sol. water. Gives off PH_3 and isovaleric aldehyde on heating.—KA' 3aq.—BaA'_2 aq.—PbA'_2 5aq: granules, v. sl. sol. water.

OXY-ISOAMYL-SUCCINIC ACID. *Lactone.* $PrCH_2.CH\!<\!\begin{matrix} CH(CO_2H) \\ O.CO \end{matrix}\!>\!CH_2$. *Isobutyl paraconic acid.* [124°]. Formed by reducing, with sodium-amalgam, the isobutaconic acid $PrCH_2.CH\!<\!\begin{matrix} C(CO_2H) \\ O.CO \end{matrix}\!>\!CH$ [168°] which is got by the action of boiling water on brominated isobutylitaconic acid. Prepared by heating valeric aldehyde with Ac_2O and sodium succinate at 110° (Fittig, *A.* 255, 97; 256, 103). Thin needles (from water). Boiling baryta-water yields $C_9H_{14}BaO_5$ whence $C_9H_{14}Ag_2O_5$.—CaA'_2 2aq. —BaA'_2 3aq.—ZnA'_2 1½aq.—AgA'.

Ethyl ether EtA'. [17°]. (293°).

OXY-ANGELIC ACID. *Ethyl derivative* $CH_3.C(OEt):CMe.CO_2H$. [133°]. Formed by heating chlorotiglic acid with NaOEt at 130°–160° (Friedrich, *A.* 219, 357). Prisms.

Oxy-angelic acid $CH_3.CH:CH.CH(OH).CO_2H$. Formed by saponifying with HClAq the product of the union of liquid HCy and crotonic aldehyde (Lobry de Bruyn, *Bl.* [2] 42, 159).—BaA'_2: crystalline.

Oxy-angelic lactones *v.* ANGELICO-LACTONES.

OXY-ANTHRACENE *v.* ANTHRANOL and ANTHROL.

Di-oxy-anthracene $C_{14}H_8(OH)_2$. *Chrysazol.* Formed by fusing anthracene (α)-disulphonic acid with KOH (Liebermann, *B.* 12, 185). Yellow needles. Gives a bluish-green colouration with $FeCl_3$ or bromine.

Acetyl derivative [184°]. Needles.

Di-oxy-anthracene $C_{14}H_8(OH)_2$. *Flavol.* [c. 270°]. Formed by fusing anthracene (α)-disulphonic acid with KOH at a high temperature (Schüler, *B.* 15, 1808). Yellow crystalline powder, v. sol. alcohol and ether with blue fluorescence. Its alkaline solution exhibits intense green fluorescence.

Acetyl derivative $C_{14}H_8(OAc)_2$. [255°].

Di-ethyl ether $C_{14}H_8(OEt)_2$. [229°].

(β)-Di-oxy-anthracene $C_6H_3(OH){:}C_2H_2{:}C_6H_3(OH)$. *Rufol.* Got by fusing anthracene (β)-disulphonic acid with KOH (Liebermann a. Boeck, *B.* 11, 1615). Needles, v. sol. alcohol with blue fluorescence. Its alkaline solution is yellow.

Di-acetyl derivative [198°]. Colourless leaflets. Yields anthrarufin on oxidation.

Di-benzoyl derivative [263°]. Needles.

Isomerides *v.* OXANTHRANOL and OXY-ANTHRANOL.

***m*-OXY-ANTHRACOUMARIN** $C_{16}H_8O_4$ *i.e.* $C_6H_4<\begin{matrix}\overline{C\ .\ C\ .\ C} & :CH\\ CO.C\ . & CH:C(OH)\end{matrix}$ (with CH.CO.O above) [325°]. Formed from *s*-di-oxy-benzoic acid, cinnamic acid, and H_2SO_4 at 60° (Von Kostanecki, *B.* 20, 3142). Yellow needles, sol. HOAc.

Acetyl derivative [255°]. Needles.

Di-oxy-anthracoumarin $C_6H_4<\begin{matrix}C\ .C\ .C & :C(OH).\\ CO.C & .CH:C(OH)\end{matrix}$ (with CH.CO.O above). *Styrogallol.* Formed by heating a mixture of cinnamic acid, gallic acid, and H_2SO_4 (Jacobsen a. Julius, *B.* 20, 2588; Von Kostanecki, *B.* 20, 3143). Minute yellow needles (from alcohol), not melted at 350°.

Di-acetyl derivative [260°]. Needles.

(α)-OXY-ANTHRANOL $C_6H_4<\begin{matrix}CH\\C(OH)\end{matrix}>C_6H_3OH$. [202°–206°]. Formed by boiling oxy-anthraquinone (1 pt.), zinc-dust (2 pts.), and NH_3Aq (8 pts.) with water (5 pts.) (Liebermann a. Simon, *A.* 212, 28). Slender needles (from dilute alcohol). Yields a di-acetyl derivative [155°].

Oxy-anthranol dihydride $C_6H_4<\begin{matrix}CH_2\\CH(OH)\end{matrix}>C_6H_3OH$. [99°]. Got by boiling quinizarin with HIAq (Liebermann a. Giesel, *A.* 212, 15). Plates (from alcohol). Its solutions fluoresce greenish-yellow. Yields o-oxy-anthraquinone on oxidation. $FeCl_3$ colours its alcoholic solution green. Ethylamine forms $C_{14}H_{10}(OH)(NHEt)$ [172°].—$KC_{14}H_{11}O_2$: yellow needles.—$Ba(C_{14}H_{11}O_2)_2$ (dried at 100°).—$PbC_{14}H_{10}O_2$.

Acetyl derivative $C_{14}H_{11}AcO_2$. [138°].

(*A.*)-Oxy-anthranol $C_6H_4<\begin{matrix}C(OH)\\C(OH)\end{matrix}>C_6H_4$ *v.* OXANTHRANOL.

Di-oxy-anthranol $C_6H_4<\begin{matrix}C(OH)\\CH\end{matrix}>C_6H_2(OH)_2$. *Deoxyalizarin.* Prepared by reducing an ammoniacal solution of alizarin with zinc-dust (Römer, *B.* 14, 1259). Yellow crystals, sl. sol. water. In solution it is slowly oxidised in the air to alizarin. The alkaline solution is greenish-yellow.

Tri-acetyl derivative [188°]. Needles. Exhibits blue fluorescence in solution.

Di-oxy-anthranol $C_6H_3(OH)<\begin{matrix}C(OH)\\CH\end{matrix}>C_6H_3(OH)$. *Deoxyisoanthraflavic acid.* [above 330°]. Got in like manner from isoanthraflavic acid (Römer a. Schwarzer, *B.* 15, 1040). Golden needles. Its alkaline solution fluoresces greenish-blue.

Di-acetyl derivative $C_6N_3(OAc)<\begin{matrix}CO\\CH_2\end{matrix}>C_6H_3(OAc)$. [173°]. White needles, insol. alkalis.

Di-oxy-anthranol $C_6H_3(OH)<\begin{matrix}C(OH)\\CH\end{matrix}>C_6H_3(OH)$. Formed by heating anthraflavic acid with HOAc and tin, and slowly adding HClAq (Liebermann, *B.* 21, 445). Needles. Yields a tri-acetyl derivative [165°] which fluoresces blue in alcoholic solution.

Tri-oxy-anthranol $C_6H_3(OH)<\begin{matrix}C(OH)\\CH\end{matrix}>C_6H_2(OH)_2$. Formed in like manner from flavopurpurin (L.). Yellow needles. Its alkaline solution exhibits greenish fluorescence. It yields a tetra-acetyl derivative [105°].

Tri-oxy-anthranol $C_6H_4<\begin{matrix}C(OH)\\CH\end{matrix}>C_6H(OH)_3$. '*Anthragalanthranol.*' Formed in like manner from anthragallol (L.). Yellowish needles. Yields a tetra-acetyl derivative [205°].

Tri-oxy-anthranol. *Tetra-acetyl derivative* $C_6H_4<\begin{matrix}C(OAc)\\C(OAc)\end{matrix}>C_6H_2(OAc)_2$. [219°]. Formed by boiling hystazarin (1 pt.) with NaOAc (1½ pts.), Ac_2O (12 pts.), and zinc-dust (3 pts.) (Schoeller, *B.* 22, 683). Colourless crystals (from alcohol).

Tri-oxy-anthranol. *Tetra-acetyl derivative* $C_6H_3(OAc)<\begin{matrix}C(OAc)\\C(OAc)\end{matrix}>C_6H_3(OAc)$. Two isomeric compounds of this constitution [274°] and [c. 240°] are formed from anthraflavic acid, NaOAc, Ac_2O, and zinc-dust (L.).

Tri-oxy-anthranol $C_{14}H_6(OH)_4$. '*Anthrapurpuranthranol.*' Formed by reduction of anthrapurpurin with HOAc, tin, and HClAq (Liebermann, *B.* 21, 443). Minute leather-yellow needles, Yields a tetra-acetyl derivative [167°].

Tetra-oxy-anthranol $C_6H_4<\begin{matrix}C(OH)\\C(OH)\end{matrix}>C_6H(OH)_3$. *Tri-oxy-oxanthranol.* Formed by atmospheric oxidation of an alkaline solution of 'anthragalanthranol' (L.). Violet crystals. The penta-acetyl derivative [203°] is formed by reducing anthragallol with NaOAc, Ac_2O, and zinc-dust (Liebermann, *B.* 21, 1172).

Tetra-oxy-anthranol. *Penta-acetyl derivative* $C_6H_3(OAc)<\begin{matrix}C(OAc)\\C(OAc)\end{matrix}>C_6H_2(OAc)_2$. [240°]. Formed from flavopurpurin, HOAc, Ac_2O, and zinc-dust. When the operation is protracted the tetra-acetyl derivative [250°–260°] is the chief product.

Hexa-oxy-anthranol. *Hepta-acetyl derivative* $C_{14}H_4(OAc)_7$. Obtained from rufigallol (L.). Yellowish crystals, sol. alcohol, with blue fluorescence.

OXYANTHRAQUINONES. Oxyanthraquinones having two hydroxyls in the position occupied by them in alizarin possess tinctorial properties (Liebermann a. Wense, *B.* 20, 862).

Erythro - **oxyanthraquinone** $C_{14}H_8O_3$ *i.e.* $C_6H_4<\begin{matrix}CO.C.C(OH):CH\\ CO.C.CH{=}CH\end{matrix}$. Mol. w. 224. [191°].

Formation.—1. By fusing o-bromo-anthraquinone with KOH at 150° (Pechmann, *B.* 12, 2127).—2. Together with its isomeride by heating phenol with phthalic anhydride and H_2SO_4 (Baeyer a. Caro, *B.* 7, 968).—3. By the action of nitrous acid on o-amido-anthraquinone (Roemer, *B.* 15, 1793).—4. By passing nitrous acid gas into an alcoholic solution of di-amido-anthraquinone or (β)-oxy-amido-anthraquinone (Von Perger, *J. pr.* [2] 18, 148).—5. Together with three isomeric di-oxy-anthraquinones, by heating a mixture of benzoic acid (120 grms.) and *m*-oxy-benzoic acid (60 grms.) with 1200 grms. of H_2SO_4 and 120 grms. of water for 10 hours at 180°–200° (Liebermann a. Kostanecki, *B.* 19, 329).—6. By oxidation of oxy-anthranol dihydride (Liebermann, *A.* 212, 20).

Properties.—Orange feathery needles (from alcohol), insol. water, sol. ether and benzene. Yields alizarin on fusion with KOH. Insol. cold baryta-water, but boiling baryta yields a violet salt. Insol. NH_3Aq, sol. HOAc. Its ethereal solution shaken with baryta-water forms a violet pp., while the isomeric oxyanthraquinone gives a red solution. KOHAq dissolves it with difficulty, forming a brown solution. May be sublimed at 140° in a current of gas.

Acetyl derivative $C_{14}H_7AcO_3$ [176°–179°].

Oxy-anthraquinone $C_6H_4<\begin{matrix}CO.C.CH:C(OH)\\ CO.C.CH:CH\end{matrix}$. [302°].

Formation. — 1. A by-product in the preparation of alizarin by fusing anthraquinone sulphonic acid with KOH or NaOH (Liebermann, *B.* 4, 108; 5, 868; *A.* 160, 141; Simon, *B.* 14, 464). Occurs also in the product of the dry distillation of sodium anthraquinone sulphonate (A. G. a. W. H. Perkin, *C. J.* 47, 680).—2. Obtained also from *m*-bromo-anthraquinone by careful potash fusion (Graebe a. Liebermann, *A.* 212, 25; *Suppl.* 7, 290).—3. By the action of nitrous acid on *m*-amido-anthraquinone.

Properties.—Yellow needles (by sublimation). Readily soluble in excess of baryta-water. Its alkaline solution is reddish-brown. Potash-fusion yields alizarin. HIAq reduces it to anthrol and anthracene hexahydride. Sol. NH_3Aq, forming a reddish-yellow liquid.—$Ba(C_{14}H_7O_3)_2$. —$Ba(C_{14}H_7O_3)_2$ aq.

Acetyl derivative [158°]. Small needles. Formed by acetylation and also by oxidation of the acetyl derivative of anthrol.

Ethyl ether $C_{14}H_7O_2(OEt)$. [135°]. Sol. alcohol. Very difficult to saponify (Liebermann a. Hagen, *B.* 15, 1798).

Di-oxy-anthraquinone $C_6H_4<\begin{matrix}CO.C.C(OH):C(OH)\\ CO.C.CH{=}CH\end{matrix}$. *Alizarin.* Mol. w. 240. [290°]. S. ·034 at 100° (Plessy a. Schutzenberger, *C. R.* 43, 167). Occurs in madder, the root of *Rubia tinctoria*, which contains its glucoside $C_{26}H_{28}O_{14}$ (ruberythric acid), and the glucosides of purpurin, purpurin carboxylic acid, purpuroxanthin, and purpuroxanthin carboxylic acid (Robiquet a. Colin, *A. Ch.* [2] 34, 225; Runge, *J. pr.* 5, 362; Schunck, *A.* 66, 174, 201; 81, 336; 87, 344; *P. M.* [4] 5, 410, 495; 12, 200, 270; *J. pr.* 59, 465; Rochleder, *A.* 80, 321; 82, 205; Debus, *A.* 66, 351; Wolff a. Strecker, *A.* 75, 1; Wartha, *B.* 3, 545, 673; Willigk, *A.* 82, 339; Rosenstiehl, *A. Ch.* [5] 18, 235; *C. R.* 88, 1194; Wurtz, *C. R.* 96, 465; Liebermann, *B.* 20, 2241; Bergami, *B.* 20, 2247).

Formation.—1. By fusing di-bromo-anthraquinone with potash (Graebe a. Liebermann, *Bl.* [2] 11, 516; *A. Suppl.* 7, 300).—2. By fusing anthraquinone sulphonic acid with potash (Perkin, *C. J.* 23, 133; *B.* 9, 281). The yield may be improved by addition of $KClO_3$.—3. By heating pyrocatechin with phthalic anhydride and H_2SO_4 at 140° (Baeyer a. Caro, *B.* 7, 972).

Purification.—1. By repeated solution in NaOHAq and ppn. by CO_2; the pp. being decomposed by HCl (Liebermann a. Troschke, *B.* 8, 379).—2. Crude commercial alizarin, a mixture of alizarin, flavo-purpurin, and isopurpurin, is fractionally sublimed when the alizarin comes over from 100° to 160°, and a mixture of flavo-purpurin and isopurpurin from 160° to 170°; the crystals of these two bodies can be distinguished in the sublimate with a microscope and can be separated by means of benzene, in which isopurpurin is only slightly soluble, but the flavo-purpurin very soluble (Schunck a. Römer, *B.* 13, 41).

Properties.—Red trimetric needles, v. sol. alcohol and ether. Sometimes crystallises in golden scales (containing 2aq (Schunck). Its solutions in alkalis and alkaline carbonates are purple. $BaCl_2$ and $CaCl_2$ give purple pps. in these solutions. Alumina decolourises its alcoholic solution forming a red lake. Salts of Mg, Fe, Cu, and Ag give purple pps. in the ammoniacal solution.

Reactions.—1. Yields phthalic acid on oxidation with HNO_3.—2. Distillation with *zinc-dust* yields anthracene (G. a. L.).—3. *Zinc-dust and ammonia* reduce it to di-oxy-anthranol.—4. Aqueous *ammonia* at 200° gives oxy-amido-anthraquinone, di-amido-anthraquinone, and other bodies (Von Perger, *J. pr.* [2] 18, 129).

Salts.—CaA″aq.—BaA″aq (dried at 100°). —PbA″: violet-brown pp.

Di-acetyl derivative [160°] (P.); [179°–183°] (Baeyer, *B.* 9, 1232). Pale-yellow crystals (Perkin, *C. J.* 26, 21).

Methyl ether $C_{14}H_6O_2(OH)(OMe)$. From alizarin, KOH, and MeI (Schunck, *C. N.* 27, 171).

Di-ethyl ether $C_{14}H_6O_2(OEt)_2$. Got by heating alizarin with $KEtSO_4$ and KOH at 170° (Habermann, *M.* 5, 228). Needles.

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Nitro-alizarin *v.* NITRO-DI-OXY-ANTHRAQUINONE.

Amido-alizarin *v.* DI-OXY-AMIDO-ANTHRAQUINONE.

Alizarin blue. $C_{17}H_9NO_4$ *i.e.* $C_6H_4<\begin{matrix}CO.C\text{———————}C.CH:CH\\ CO.C.C(OH):C(OH).C.N{=}CH\end{matrix}$ [270°]. Formed by heating (β)-nitro-alizarin (1 pt.) with glycerin ($1\frac{1}{2}$ pts.) and H_2SO_4 (5 pts.) at 107°–200° (Prudhomme, *Bl.* [2] 28, 62; Auerbach, *C. J.* 35, 799; Graebe, *A.* 201, 333; *B.* 12, 1416). Brown needles. Alkalis form a blue solution, but excess of alkali throws it down again. Dyes chromium acetate mordant blue. Yields $C_{17}H_7NO_2(OH)NH_2$ [255°]. Gives anthraquinol-

ine when distilled with zinc-dust.—B'HCl.—B'HOAc.—$B'C_6H_2(NO_2)_3OH$. [245°].—$Ba_2OC_{17}H_7NO_4$ ½aq : greenish-blue pp.

Di-acetyl derivative $C_{17}H_7Ac_2O_4$. [225°].

Di-benzoyl derivative [244°].

Alizarin-blue S $C_{17}H_{11}NO_4(SO_3Na)_2$. Prepared by dissolving alizarin-blue in a cold concentrated solution of $NaHSO_3$ (Brunck a. Graebe, *B.* 15, 1783). Reddish-brown crystalline powder. V. sol. water, sl. sol. 95 p.c. of alcohol. At 60° it begins to decompose into its constituents.

Isoalizarin occurs in madder that has been heated with HClAq or dilute H_2SO_4 (Rochleder, *B.* 3, 292). Its alkaline solutions are blood-red, and it forms a red solution with baryta-water. It does not dye mordants.

p-**Di-oxy-anthraquinone**
$C_6H_4\!<\!\begin{matrix}CO.C.C(OH):CH\\CO.C.C(OH):CH\end{matrix}$. *Quinizarin.* [195°].
Formed by heating hydroquinone or *p*-chlorophenol with H_2SO_4 and phthalic anhydride at 140° (Grimm, *B.* 6, 506). Red needles (from alcohol). Its alkaline solutions are blue. Yields anthracene on distillation with zinc-dust. Its ethereal solution shows greenish-yellow fluorescence. Baryta gives a bluish-violet lake. Oxidised by MnO_2 and H_2SO_4 at 140° to purpurin (Baeyer a. Caro, *B.* 8, 152).

Reactions.—1. HI (S.G. 1·7) and a little red P give a dihydride, $C_6H_4\!<\!\begin{matrix}C(OH)\\|\\C(OH)\end{matrix}\!>\!C_6H_2(OH)_2$, which forms golden plates or needles (from alcohol). It forms with NaOH a yellow solution, turned blue by air. $SnCl_2$ and HCl also reduce quinizarin to this dihydride (Liebermann, *A.* 212, 11).—2. A longer treatment with HI forms hydroquinizarol, $C_{14}H_{12}O_3$. It forms orange needles (from alcohol). This body is probably $C_6H_4\!<\!\begin{matrix}CH(OH)\\CH_2\end{matrix}\!>\!C_6H_2(OH)_2$.—3. Conc. HI (S.G. 1·9) and red P after an hour's boiling reduce quinizarin to oxy-anthranol dihydride (*q. v.*).

Di-acetyl derivative [200°]. Prisms.

Ethyl ether $C_{14}H_6O_2(OH)(OEt)$. [151°].

Di-ethyl ether $C_{14}H_6O_2(OEt)_2$. [177°]. Yellow needles (Liebermann, *B.* 21, 1168).

m-**Di-oxy-anthraquinone**
$C_6H_4\!<\!\begin{matrix}CO.C.C(OH):CH\\CO.C.CH{=}C(OH)\end{matrix}$. *Purpuroxanthin.*
Xanthopurpurin. [265°]. Occurs, together with its carboxylic acid, in madder (Schützenberger, *Bl.* 4, 12). May be got by reducing purpurin with HIAq or with $SnCl_2$ and NaOH. Formed also by dissolving P in a hot alkaline solution of purpurin (Rosenstiehl, *C. R.* 79, 764); by the action of nitrous acid on purpuramide (di-oxy-amido-anthraquinone) (Liebermann a. Fischer, *B.* 8, 974); and, together with anthrachrysone, by heating a mixture of *s*-di-oxy-benzoic acid (1 pt.), benzoic acid (5 pts.), and H_2SO_4 at 105°-110° (Noah, *B.* 19, 332).

Properties.—Yellow needles, sol. alcohol, HOAc, and benzene, insol. water. May be sublimed. Its alkaline solution is red. Its barium salt is easily soluble. Gives purpurin on fusion with KOH. Nitric acid oxidises it to phthalic acid. Reduced by HI and P to a dihydride, which dyes alumina mordants like quercitron (Rosenstiehl, *A. Ch.* [5] 18, 224; *C. R.* 79, 764). Yields anthracene on distillation with zinc-dust. NH_3Aq at 150° yields brown needles of $C_{14}H_6O_2(OH)(NH_2)$ (Liebermann, *A.* 183, 217).

Acetyl derivative $C_{14}H_6O_2(OAc)_2$. [184°].

Di-methyl ether. [180°] (Plath, *B.* 9, 1204).

Di-ethyl ether $C_{14}H_6O_2(OEt)_2$. [170°].

(*B.* 1, 4')-**Di-oxy-anthraquinone**
$\begin{matrix}CH:CH{-}C.CO.C.C(OH):CH\\CH:C(OH).C.CO.C.CH{=}CH\end{matrix}$. *Anthrarufin.*
[280°]. Formed in small quantity (2 g.), together with anthraflavic acid (30 g.) and *m*-'benzdioxyanthraquinone' (5 g.), by the action of H_2SO_4 on *m*-oxy-benzoic acid (100 g.) (Schunck a. Römer, *B.* 11, 1176, 1616). Formed also by potash-fusion from anthraquinone (ρ)-disulphonic acid (Liebermann a. Dehnst, *B.* 12, 1287), and by the action of nitrous acid on the di-amido-anthraquinone. Obtained by reduction of di-nitro-anthraquinone [above 300°] (Römer, *B.* 16, 369).

Properties.—Yellow tables, insol. water, sl. sol. alcohol, HOAc, ether, and CS_2, v. sol. benzene. Forms oxyanthrarufin on fusion with KOH. Almost insol. baryta-water, Na_2CO_3, and NH_3Aq, sol. KOHAq. Its solution in H_2SO_4 is cherry red with scarlet fluorescence. Its Ca and Ba salts are crimson and insoluble.

Acetyl derivative $C_{14}H_6O_2(OAc)_2$. [244°]. Got by oxidising (β)-di-oxy-anthracene with CrO_3 in HOAc. Yellow needles.

Di-oxy-anthraquinone $C_{14}H_8O_4$. *Anthraflavic acid.* [above 330°]. S. (95 p.c. alcohol) 1·18 at 10° (Rosenstiehl, *Bl.* [2] 29, 401, 434). A by-product in the preparation of alizarin, being formed by fusing anthraquinone (α)-disulphonic acid with KOH (Schunck, *B.* 4, 360; 8, 1628; 9, 379, 679; Perkin, *C. J.* 24, 1109; 26, 19; 29, 851). Formed also from *m*-oxy-benzoic acid and H_2SO_4 (*v. supra*). Radiating yellow needles (from alcohol), insol. ether and benzene, sl. sol. HOAc. Its solution in H_2SO_4 is yellow. Its solution in alkalis is yellowish-red. Its Ba and Ca salts are sl. sol. water. It does not dye mordanted cotton. Potash-fusion forms flavopurpurin. Distillation with zinc-dust forms anthracene. Boiling with zinc-dust and NH_3Aq forms $C_{14}H_{10}O_3$, whence $C_{14}H_7(OAc)_3$ [165°] (Liebermann, *B.* 21, 445).

Salts.—Na_2A'' 5aq : sl. sol. water.—$BaA''x$aq : reddish-brown needles.

Di-acetyl derivative $C_{14}H_6O_2(OAc)_2$. [229°].

Di-benzoyl derivative $C_{14}H_6O_2(OBz)_2$. [275°].

Di-methyl ether $C_{14}H_6O_2(OMe)_2$. [248°].

Di-ethyl ether [232°]. Yellow needles.

Di-oxy-anthraquinone $C_{14}H_8O_4$. [above 330°]. *Isoanthraflavic acid.* Occurs in crude commercial alizarin, being formed by fusing anthraquinone (β)-disulphonic acid with potash (Schunck a. Römer, *B.* 9, 379; 15, 1041; Perkin, *C. J.* 29, 851). Yellow needles (containing aq), almost insol. benzene and ether, sl. sol. HOAc and alcohol. It dissolves in cold baryta-water and in KOHAq with dark-red colour. Does not possess tinctorial properties. Its solution in H_2SO_4 is red. Yields anthrapurpurin on fusion with KOH.—$BaA''x$aq : red needles, v. sol. Aq.

Di-acetyl derivative [c. 195°]. Crystals.

Di-ethyl ether [194°]. Yellow needles.

(B. 1, 1′ or 3′)-**Di-oxy-anthraquinone** $C_6H_3(OH);C_2O_2:C_6H_3OH$. *Chrysazin.* [192°]. Formed by eliminating amidogen from di-oxy-tetra-amido-anthraquinone (hydrochrysamide) (Liebermann a. Giesel, *B.* 8, 1643; 9, 329; *A.* 183, 184). Formed also by fusing anthraquinone χ-disulphonic acid with potash (Liebermann a. Dehnst, *B.* 12, 1287). Golden laminæ or reddish-brown needles; m. sol. alcohol and HOAc. Insol. cold NH_3Aq and Na_2CO_3Aq. Its solution in KOHAq is yellowish-red, and that in H_2SO_4 is red. Potash-fusion yields oxychrysazin, and *o*- and *m*- oxy-benzoic acid. Yields anthracene when distilled with red-hot zinc-dust. Baryta- and lime- water give red pps. Does not dye mordanted cotton.

Di-acetyl derivative [232°]. Prepared by oxidising di-acetyl-chrysazol $C_{14}H_8(OAc)_2$ with CrO_3 (Liebermann, *B.* 12, 186).

Di-oxy-anthraquinone $C_{14}H_8O_4$. *Isochrysazin.* [175°–180°]. Formed, together with *m*-'benzdioxyanthraquinone,' by the action of nitrous acid and alcohol on the dye $C_{28}H_{17}N_3O_9$ got from o-di-nitro-anthraquinone and H_2SO_4 (Lifschütz, *B.* 17, 897). Deep-red needles (from alcohol); readily sublimed. Its solutions in NH_3Aq and KOHAq are violet-red; that in H_2SO_4 is reddish-yellow. Its Ba salt is insoluble. It does not dye mordants.

Di-acetyl derivative [160°–165°]. Needles.

Di-oxy-anthraquinone $C_{14}H_8O_4$. '*m-Benzdioxyanthraquinone.*' [293°]. A product of the action of H_2SO_4 on *m*-oxy-benzoic acid (Schunck a. Römer, *B.* 11, 969). Formed also as above. Yellow needles, insol. water and CS_2, sol. alcohol, HOAc, ether, and benzene. Its alkaline solution is yellow. Gives purpurin by potash-fusion. Its solution in H_2SO_4 is brownish-yellow. When freshly ppd. it dissolves in hot baryta-water, and on cooling the Ba salt separates in red needles, which, after drying, are insoluble. Has no tinctorial power.

Di-acetyl derivative [199°]. Needles.

Di-oxy-anthraquinone $C_{14}H_8O_4$. *Frangulic acid.* [254°]. Obtained, together with glucose, by hydrolysing frangulin which occurs in the bark of *Rhamnus Frangula* (Faust, *A.* 165, 229). Orange needles (containing $1\frac{1}{2}$aq), sl. sol. hot water, m. sol. alcohol. Its solution in KOHAq is cherry-red. Its ammoniacal solution gives a red pp. with $BaCl_2$. Distillation over zinc-dust gives anthracene.

Di-acetyl derivative [184°]. Prisms.

Di-oxy-anthraquinone
$C_6H_4<\begin{matrix}CO.C.CH:C(OH)\\CO.C.CH:C(OH)\end{matrix}$. *Hystazarin.* [282°]. Formed by heating pyrocatechin (5 g.) with phthalic anhydride (6·8 g.) and H_2SO_4 (75 g.) at 145° for 5 hours (Liebermann a. Schöller, *B.* 21, 2503; 22, 683). Orange-yellow needles (from acetone), almost insol. benzene, v. sl. sol. alcohol, ether, and HOAc. Its solution in KOHAq is blue; that in NH_3Aq is violet; and that in H_2SO_4 blood-red. The Ba salt is blue, the Ca salt violet and insol. water. It dyes mordants slightly. Yields anthracene on distillation with zinc-dust.

Di-acetyl derivative [207°]. Needles.

Ethyl ether $C_{14}H_6O_2(OH)(OEt)$. [234°–240°]. Yellow needles, forming a crimson solution in alkalis.

Di-ethyl ether $C_{14}H_6O_2(OEt)_2$. [160°–163°]. From hystazarin, KOH, and EtI. Yellow needles.

Eleven di-oxy-anthraquinones have been described, but ten only are indicated by theory.

Tri-oxy-anthraquinone
$C_6H_4<\begin{matrix}CO.C.C(OH):C(OH)\\CO.C.C(OH):CH\end{matrix}$. *Purpurin.* [253°]. Occurs in madder-root, probably as glucoside (Colin a. Robiquet, *A. Ch.* [2] 34, 244; Gaulthier de Claubry a. Persoz, *A. Ch.* [2] 48, 69; 51, 110; Runge, *A. Ch.* [2] 63, 282; Schiel, *A.* 60, 74; Debus, *A.* 66, 351; 86, 117; Wolff a. Strecker, *A.* 75, 1; Rochleder, *A.* 80, 321; 82, 205; Stenhouse, *Pr.* 12, 633; 13, 145; Schützenberger, *J.* 1864, 542; *Bl.* [2] 4, 12). Formed by the action of MnO_2 and H_2SO_4 at 150° on alizarin (De Lalande, *C. R.* 79, 669) and on quinizarin (Baeyer a. Caro, *B.* 8, 152); and also by heating tri-bromo-anthraquinone with H_2SO_4 at 200° (Diehl, *B.* 11, 184). It may be separated from alizarin by repeatedly dissolving in boiling alum solution and ppg. by acid. Orange prisms containing aq (from dilute alcohol) or dark-red anhydrous needles (from absolute alcohol). May be sublimed. Sl. sol. boiling water, forming a yellow liquid. Its ethereal solution is yellow and shows two absorption bands (Stokes, *C. J.* 12, 220; Vogel, *B.* 9, 1641). Its solution in H_2SO_4 is rose-red and shows three absorption bands. Aqueous KOH, Na_2CO_3, and NH_3 yield purple-red solutions. Almost insol. alcoholic potash. Baryta-water forms an insoluble purple lake. Its alkaline solution is oxidised in daylight by the air becoming yellow (unlike alizarin) the product containing phthalic acid (Schunck a. Römer, *C. J.* 31, 665; Dralle, *B.* 17, 376). Boiling alum forms a pink solution with yellow fluorescence. Lead acetate gives in an alcoholic solution a dark-crimson pp., soluble in excess, forming a crimson liquid with three absorption bands (the lead compound of alizarin is insol. alcoholic lead acetate). Dyes cotton, mordanted with alumina, red.

Reactions.—1. Yields anthracene on heating with *zinc-dust.*—2. Forms some quinizarin when heated in sealed tubes at 300°.—3. Phosphorus and NaOHAq reduce it to purpuroxanthin.—4. *Nitric acid* oxidises it to phthalic acid.—5. Aqueous ammonia forms brown purpuramide $C_{14}H_5O_2(NH_2)(OH)_2$.

Acetyl derivative $C_{14}H_5O_2(OAc)_3$. [193°] (L.); [200°] (S. a. R.). Yellow needles.

Ethyl ether $C_{14}H_5O_2(OEt)_3$. Red crystals.

Tri-oxy-anthraquinone $C_{14}H_5O_2(OH)_3$. *Anthrapurpurin. Isopurpurin.* [above 330°]. A by-product in the preparation of artificial alizarin, being formed by fusing anthraquinone (β)-disulphonic with potash (Perkin, *C. J.* 25, 659; 26, 425; 29, 851; Caro, *B.* 9, 682). Formed also by potash-fusion from isoanthraflavic acid, from *m*-benzdioxyanthraquinone (Schunck a. Römer, *B.* 9, 679; 11, 972), and from (α)-di-bromo-anthraquinone (Perkin, *C. J.* 37, 557). Orange needles (from alcohol), v. sol. hot alcohol, sl. sol. hot water and ether. Conc. H_2SO_4 forms a red solution; potash, NH_3Aq, and Na_2CO_3Aq give a violet solution. Sl. sol. hot baryta-water, forming

a violet solution. Alcoholic lead acetate gives a purple pp., sol. excess. It colours mordants.

Reactions.—1. *Nitric acid* gives no phthalic acid.—2. Aqueous *ammonia* at 100° forms an unstable blue dye, decomposed by HCl or KOH with regeneration of anthrapurpurin.—3. Aqueous ammonia at 170° forms anthrapurpuramide $C_{14}H_5O_2(OH)_2(NH_2)$ which does not dye mordants (Perkin, *C. J.* 33, 216).

Tri-acetyl derivative [222°]. Yellow scales.

Tri-benzoyl derivative [185°]. Crystals.

Mono-ethyl ether $C_{14}H_5O_2(OH)_2(OEt)$. [265°]. Orange-red needles (Liebermann a. Jellinek, *B.* 21, 1170).

Di-ethyl ethers $C_{14}H_5O_2(OH)(OEt)_2$. [162°] and [170°]. Yellow needles (L. a. J.).

Tri-oxy-anthraquinone $C_{14}H_8O_5$. *Flavopurpurin.* [above 330°]. Formed by potash fusion from anthraflavic acid and from anthraquinone (α)-disulphonic acid. Purified by means of its lead salt (S. a. R.; C.; Liebermann, *B.* 21, 441, 2524). Golden needles (from alcohol), v. sol. cold alcohol. Its solution in conc. H_2SO_4 is red; that in KOHAq is purple, becoming red on dilution. Sl. sol. baryta-water, forming a red solution. Its solution in NH_3Aq and Na_2CO_3Aq is yellowish-red. Alcoholic lead acetate forms a reddish-brown pp., v. sl. sol. excess. On heating with phenyl cyanate at about 160° it forms $C_{14}H_6O_3(O.CO.NHPh)_2$ crystallising in yellowish plates (Tesmer, *B.* 18, 2610).

Di-acetyl derivative [238°]. Golden plates.

Tri-acetyl derivative [196°]. Yellow needles.

Di-benzoyl derivative [210°]. Needles.

Ethyl ether $C_{14}H_5O_2(OH)_2(OEt)$. V. sol. ether.

Di-ethyl ether [209°]. Needles.

Tri-oxy-anthraquinone
$C_6H_4{<}\begin{matrix}CO.C.C(OH){:}C(OH)\\ CO.C.CH{=}C(OH)\end{matrix}$. *Anthragallol.* [310°] (Cahn, *B.* 19, 2335). Formed by heating a mixture of benzoic acid, gallic acid, and H_2SO_4 at 70° (Seuberlich, *B.* 10, 38). Formed also from pyrogallol, phthalic anhydride, and H_2SO_4. Orange needles (by sublimation), nearly insol. water. Its alkaline solution is green. Dilute HNO_3 forms phthalic acid. Distillation over zinc-dust gives anthracene. Dyes alumina mordants brown. Alcoholic lead acetate ppts. violet-brown $C_{14}H_5O_5Pb_2OAc$. Boiling alcoholic NH_3 forms anthragallolamide $C_{14}H_5O_2(NH_2)(OH)_2$ crystallising in black needles with green reflex. HCl and HOAc form $C_{14}H_{10}O_4$ whence $C_{14}H_6Ac_4O_4$ [205°] (L.).

Tri-acetyl derivative [173°]. Needles.

Ethyl ether $C_{14}H_5O_2(OH)_2OEt$. [175°]. From the K salt and EtI at 80°. The Pb salt and EtI at 220° yields an isomeride [245°].

Di-ethyl ether [134°]. Formed from the K salt (L. a. J.). The Pb salt yields an isomeride [198°].

Tri-oxy-anthraquinone $C_{14}H_8O_5$. *Oxychrysazin.* Formed by potash-fusion from chrysazin and from anthraquinone ρ and χ disulphonic acids (Liebermann, *A.* 183, 191; 12, 1289). Probably identical with oxyanthrarufin. Red needles (from alcohol). Its alkaline solutions are blue. Baryta-water gives a blue insoluble pp. Dyes mordants.

Tri-acetyl derivative [193°]. Yellow needles.

Tri-oxy-anthraquinone
$C_6H_3(OH){:}C_2O_2{:}C_6H_2(OH)_2$. *Oxyanthrarufin.* Prepared by fusing anthrarufin with KOH (Liebermann a. Boeck, *B.* 11, 1617). Red needles (by sublimation). Its alkaline solutions are blue. Dyes mordants like alizarin.

Tetra-oxy-anthraquinone $C_{14}H_8O_6$ *i.e.*
$\begin{matrix}C(OH){:}CH.C.CO.C.CH{=}C(OH)\\ CH{:}C(OH).C.CO.C.C(OH){:}CH\end{matrix}$. *Anthrachrysone.* Mol. w. 272. Formed by heating *s*-di-oxy-benzoic acid alone or with H_2SO_4 (Barth a. Senhofer, *A.* 164, 109; Noah, *B.* 19, 754). Silky needles (containing 2aq), not melted at 360°. V. sol. alcohol, v. sl. sol. water and ether. Yields anthracene on distilling with zinc-dust. Its solution in KOHAq is reddish-yellow.—$Ba(C_{14}H_7O_6)_2$ 11aq: red needles.

Tetra-acetyl derivative [253°]. Needles.

Tetra-oxy-anthraquinone $C_{14}H_8O_6$. *Oxypurpurin.* Formed by heating purpurin with KOH at 240° (Diehl, *B.* 11, 185). Brown nodules, not melted at 290°. Almost insol. alcohol. Its alkaline solution is brownish-red. Its acetyl derivative melts above 240°.

Tetra-oxy-anthraquinone
$\begin{matrix}CH{:}C(OH).C.CO.C.C(OH){:}C(OH)\\ CH{:}C(OH).C.CO.C.CH{=}CH\end{matrix}$. *Quinalizarin.* [above 275°]. Obtained by heating its di-methyl ether with HOAc and HCl at 200°. Formed also by heating alizarin with H_2SO_4 at 210° (Graebe, *B.* 23, 3739). Long red needles, sol. HOAc, sl. sol. alcohol. Dyes mordants well. Its solution in H_2SO_4 is blue. The Ba and Ca salts are insol. water. Yields anthracene on distillation with zinc-dust.

Tetra-acetyl derivative [201°]. Needles.

Di-methyl ethyl [225°–230°]. Obtained by heating hemipic acid $C_6H_2(OMe)_2(CO_2H)_2$ [6:5:2:1] with hydroquinone and H_2SO_4 at 130° (Liebermann a. Wense, *B.* 20, 864; *A.* 240, 298). Minute brownish-red plates. Forms a bluish-violet solution in alkalis and a blue solution in H_2SO_4. Does not dye. Yields $C_{14}H_4O_2(OMe)_2(OAc)_2$ [211°].

Tetra-oxy-anthraquinone $C_{14}H_8O_6$. *Rufiopin.* Formed by heating opianic acid with H_2SO_4 at 180° (Liebermann a. Chojnacki, *B.* 4, 194; *A.* 162, 322). Yellowish-red needles, sl. sol. boiling water, m. sol. hot alcohol. Its solution in KOHAq is violet-red; that in NH_3Aq is reddish-brown, and is ppd. by $BaCl_2$ and $CaCl_2$. Yields anthracene on distilling with zinc-dust. Conc. H_2SO_4 gives a violet-red solution. Dyes alumina mordants brownish-red.—$BaC_{14}H_6O_6$ aq.

Tetra-oxy-anthraquinone $C_{14}H_8O_6$. (α)-*Oxyanthragallol* [above 350°]. Formed, together with the (β)-isomeride and rufigallic acid, by heating pyrogallol with *m*-oxy-benzoic acid and H_2SO_4 at 150° (Noah; Liebermann a. Kostanecki, *A.* 240, 270). Golden needles (from alcohol) or red needles (from benzene). Conc. H_2SO_4 forms a violet solution. KOHAq gives a green solution. Insol. baryta-water. Dyes mordants.

Tetra-acetyl derivative [209°].

Tetra-oxy-anthraquinone $C_{14}H_8O_6$. (β)-*Oxyanthragallol.* [above 380°]. Formed as above.

Red needles (from alcohol), insol. benzene. Conc. H_2SO_4 gives a brownish-yellow solution. KOHAq forms a green solution. Dyes mordants.

Tetra-acetyl derivative [189°].

Of the two oxyanthragallols one should have the hydroxyls in the position 1,2,3,2′, and the other in 1,2,3,4′.

Penta-oxy-anthraquinone $\begin{matrix}C(OH):CH.C.CO.C.CH = C(OH)\\ CH:C(OH).C.CO.C.C(OH):C(OH)\end{matrix}$. Formed by heating gallic acid with *s*-di-oxy-benzoic acid H_2SO_4 for 15 minutes at 165° (Liebermann a. Noah, *B.* 19, 751; *A.* 240, 273). Small yellowish-red plates (by sublimation), not melted at 360°. V. sol. hot alcohol, sl. sol. ether, nearly insol. benzene and hot water. Its solution in KOHAq is green; that in H_2SO_4 is brownish-red. Dyes mordanted fabrics.

Penta-acetyl derivative [229°]. Needles.

Hexa-oxy-anthraquinone $\begin{matrix}C(OH):C(OH).C.CO.C.CH = C(OH)\\ C(OH) = CH.C.CO.C.C(OH):C(OH)\end{matrix}$. *Rufigallic acid.* Formed by heating gallic acid with H_2SO_4 (Robiquet, *A.* 19, 204; Wagner, *C. C.* 1861, 47; Löwe, *J. pr.* 107, 296; Jaffé, *B.* 3, 694; Widman, *B.* 9, 856; Klobulowski a. Nöltiug, *B.* 8, 819; 9, 1256; 10, 880). Red crystals (containing 2aq), v. sl. sol. alcohol and ether. Its solution in conc. KOHAq is blue, becoming violet-red on dilution. Couc. H_2SO_4 forms a red solution. Baryta-water forms a blue insoluble salt. Dyes fabrics, mordanted with alumina, brown; with iron salts, black.

Reactions.—1. Yields anthracene on heating with *zinc-dust.*—2. *Nitric acid* gives no phthalic acid.—3. Boiling HIAq and P form minute needles of $C_{14}H_{10}O_7$.—4. *Potash-fusion* yields *m*-oxy-benzoic acid, γ-oxy-isophthalic acid, and an anhydride of hexa-oxy-diphenyl $C_{24}H_{18}O_{11}$ 4aq, crystallising in colourless needles (Malin, *A.* 141, 346; Schreder, *M.* 1, 432).

Hexa-acetyl derivative. Needles.

Chloro-acetyl derivative $C_{16}H_9ClO_9$. Needles.

Tri-ethyl ether [195°]. Orange needles.

Tetra-methyl ether [c. 220°]. Needles.

Tetra-ethyl ether [above 180°]. Red needles.

Hexa-ethyl ether $C_{14}H_2O_2(OEt)_6$. [c. 140°]. Orange needles, sol. hot alcohol.

References.—Bromo-, Chloro-, and Nitro-oxyanthraquinone and Oxy-amido-anthraquinone.

OXY-ANTHRAQUINONE CARBOXYLIC ACID $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2(OH)CO_2H$. [260°]. Prepared by fusing anthraquinone carboxylic acid with caustic soda (Hammerschlag, *B.* 11, 83). Orange needles (by sublimation). Yields phthalic acid on oxidation with HNO_3. Its Ba salt is a blue pp. Its alkaline solutions are purple.

(*erythro*)-**Oxy-anthraquinone-carboxylic acid** [238°]. Formed by heating (*erythro*)-oxy-methyl-anthraquinone with H_2SO_4; a portion of the quinone probably oxidising the methyl of the rest (Birukoff, *B.* 20, 2438). Long yellow needles. V. sol. boiling water. Heated to about 270° it loses CO_2, and gives (*erythro*)-oxy-anthraquinone. The Ca and Ba salts are sparingly soluble.

Di-oxy-anthraquinone carboxylic acid $C_6H_2(OH)_2:C_2O_2:C_6H_3CO_2H$. *Alizarin carboxylic acid.* [305°]. Formed by soda-fusion from the sulphonic acid got by heating anthraquinone carboxylic acid with H_2SO_4 (Hammerschlag, *B.* 11, 86). Dull-red powder or red needles (by sublimation), v. sol. aqueous NaOAc. Decomposed by heat into CO_2 and alizarin. Its alkaline solutions are purple. Gives a red lake with alumina. Nitric acid oxidises it to trimellitic acid.—$Ba_3(C_{15}H_5O_6)_2$: blue pp.

Di-oxy-anthraquinone carboxylic acid $C_{15}H_8O_6$. *Munjistin. Purpuroxanthic acid.* [231°]. Occurs in madder (Schunck a. Römer, *B.* 10, 172; *C. J.* 31, 666; 33, 422) and in munjeet or East Indian madder (Stenhouse, *Pr.* 12, 633; 13, 86, 145). Golden scales (from HOAc), split up at 233° into CO_2 and purpuroxanthin. M. sol. boiling water and alcohol. Its alkaline solutious are red. Conc. H_2SO_4 forms an orange solution. Dilute nitric acid oxidises it to phthalic acid. Fuming HNO_3 gives a di-nitro-derivative. Dyes fabrics, mordanted with alumina, orange; with iron mordants, brownish-red. Forms a red insoluble Ba salt. Yields purpurin when boiled for a long time with conc. KOHAq. Ammonia at 100° forms purpurin-amide. Br in HOAc forms di-bromo-purpuroxanthin [231°].

Tri-oxy-anthraquinone carboxylic acid $C_{15}H_8O_7$. *Purpurin carboxylic acid. Pseudo-purpurin.* [220°]. Occurs in madder (Schützenberger a. Schiffert, *Bl.* 4, 13; Rosenstiehl, *C. R.* 84, 561; Liebermann, *B.* 10, 1618). Red plates, almost insol. water and alcohol. Split up by heat, or by boiling with water, potash, or alcohol into CO_2 and purpurin. Its alkaline solution is orange-red. Does not dye mordanted fabrics uuless the water is free from $CaCO_3$ (difference from purpurin). Bromine-water yields bromo-purpurin [275].

o-**OXY-ANTHRAQUINONE SULPHONIC ACID** $C_6H_4:C_2O_2:C_6H_2(OH)(SO_3H)$ [1:6:2:3 or 4]. *Erythro-oxy-anthraquinone sulphonic acid.* Formed from o-amido-anthraquinone sulphonic acid by the action of nitrous acid (Lifschütz, *B.* 17, 900). Yellow plates, v. sol. water, alcohol, and ether. Its alkaline solution is red. On fusion with potash it gives alizarin.—AgA′: yellow needles.

Anhydride $C_{14}H_6O_2<\begin{matrix}O\\SO\end{matrix}>O$. Grey needles, insol. water, alcohol, and ether, sl. sol. HOAc. Requires to be heated with alkalis before yielding the acid.

Oxy-anthraquinone sulphonic acid. Formed by sulphonating erythro-oxy-anthraquinone at 130°. Sol. water and alcohol, insol. ether. Its alkaline solution is reddish-yellow. Baryta gives a blood-red pp., crystallising from hot water. $BaCl_2$ gives a similar yellow pp. Lead acetate gives a yellowish-brown pp., sol. hot water. Gives neither alizarin nor purpurin on potash-fusiou.

m-**Oxy-anthraquinone sulphonic acid** $C_{14}H_6O_2(OH)(SO_3H)$. Formed by heating *m*-oxy-anthraquinone with H_2SO_4 at 120° (Von Perger, *J. pr.* [2] 18, 176). Crystals (from alcohol), m. sol. cold water, insol. ether. Its alkaline solu-

tion is reddish-brown. Lead acetate gives a brownish-yellow, and lime-water a brown, pp. Yields alizarin sulphonic acid on fusion with potash at 130°.—$BaC_{14}H_6SO_6$: orange crystals.

When (α)- or (β)- anthraquinone disulphonic acid is fused with moist potash, a mixture of anthraquinone disulphonic acid, oxyanthraquinone sulphonic acid, and tri-oxy-anthraquinone is got. The mono-sulphonic acid is obtained by stopping the fusion as soon as the blue colour begins to turn violet (Graebe a. Liebermann, *A.* 160, 139). According to Von Perger (*J. pr.* [2] 18, 168) it is doubtful whether the product is not a di-oxy-anthraquinone sulphonic acid. The acid prepared from (α)-anthraquinone disulphonic acid gives on fusion with potash anthraflavic acid and flavo-purpurin, and is therefore isomeric with that from (β)-anthraquinone disulphonic acid, which gives isoanthraflavic acid and anthrapurpurin on potash-fusion.

Di-oxy-anthraquinone sulphonic acids $C_{14}H_5O_2(OH)_2(SO_3H)$. Pure alizarin heated with strong H_2SO_4 at 120° forms at least three sulphonic acids. On adding water two sulphonic acids dissolve and another remains on the filter as a brown mass. The latter dissolves in alkalis, forming a cherry-red liquid. It is slightly soluble in water, but is slowly decomposed by boiling water, regenerating alizarin. Of the two sulphonic acids which are readily soluble, the one that is formed in greatest quantity is the most soluble, and it is decomposed by potash-fusion at 200° without forming either alizarin or purpurin. The other sulphonic acid is formed in very small quantity, but by potash-fusion it is converted at 140° into purpurin, the mass becoming crimson (Von Perger, *J. pr.* [2] 18, 173).

Di-oxy-anthraquinone sulphonic acid $C_{14}H_5O_2(OH)_2SO_3H$. *Quinizarin sulphonic acid.* Formed in small quantity in the preparation of quinizarin from hydroquinone, phthalic anhydride, and H_2SO_4 (Liebermann, *A.* 212, 11). Its Na salt forms a deep-orange solution, turned deep-blue by alkalis. It does not dye mordants.

OXY-AZELAIC ACID $C_7H_{13}(OH)(CO_2H)_2$. [91°]. Formed by the action of NaOHAq upon the product of the action of Br and a little red P upon azelaïc acid (Bujard a. Hell, *B.* 22, 68). Nodules (from water or ether).—BaA″ ½aq. S. 2·56 at 18°.—CaA″ 1½aq. S. ·65 at 20°.—ZnA″ 2aq. S. ·623 at 20°.—SrA″ 1½aq.—MgA″ 2aq.—CdA″ 2aq.—CuA′ 1½aq.—PbA″ ½aq.—Ag_2A''.

OXY-AZO- compounds *v.* Azo- compounds.

OXY-AZOPHENINE $C_{30}H_{24}N_4O$. [197°]. Formed by heating nitroso-*m*-oxy-diphenylamine with aniline and aniline hydrochloride on the water-bath (O. Fischer a. Hepp, *B.* 20, 2481; Kohler, *B.* 21, 910). Needles (from toluene), sol. alcoholic NaOH, insol. NaOHAq. Conc. H_2SO_4 forms a reddish-brown solution.

DI-OXY-BEHENIC ACID $C_{22}H_{42}(OH)_2O_2$. [127°] (H.); [133°] (H. a. G.). Formed by boiling oxy-erucic acid with potash (Haussknecht, *A.* 143, 53), or by oxidising erucic acid with alkaline $KMnO_4$ (Irwantzoff, *J. R.* 21, 13; *J. pr.* 39, 334; Hazura a. Grüssner, *M.* 9, 917). Plates (from alcohol), insol. water and ether. With PI_3 it gives iodobehenic acid reduced by zinc and HCl to behenic acid. NaA′: grains, sl. sol. water.—BaA'_2: insoluble pp.

Iso-di-oxy-behenic acid $C_{22}H_{42}(OH)_2O_2$. [99°]. Formed by oxidising brassic acid with alkaline $KMnO_4$ (Grüssner a. Hazura, *M.* 10, 197). Minute plates, insol. water and ligroïn, v. sol. hot alcohol.

DI-OXY-BEHENOLIC ACID $C_{22}H_{40}O_4$. [91°]. Formed by oxidising behenolic (benolic) acid with fuming HNO_3 (Haussknecht, *A.* 143, 46). Yellowish scales (from alcohol).—AgA′: white pp.

OXYBENZALDEHYDE *v.* Oxybenzoic aldehyde.

OXYBENZAMIDE *v.* *Amide* of Oxybenzoic acid.

o-OXY-BENZAMIDINE. *Ethyl ether.* $C_6H_4(OEt).C(NH).NH_2$. A product of the action of alcoholic HCl, followed by alcoholic NH_3, on $C_6H_4(OEt).CN$ (Pinner, *B.* 23, 2952). The hydrochloride B′HCl [218°] crystallises in short hexagonal columns, v. sol. water.

p-**Oxy-benzamidine.** *Ethyl ethyl.* The hydrochloride $C_6H_4(OEt).C(NH)NH_3Cl$ [260°] is formed by the action of alcoholic NH_3 on the hydrochloride of ethyl-*p*-oxy-benzimido-ether. It is converted by acetoacetic ether and NaOHAq into ethylated dioxy-phenyl-methyl-pyrimidine $C_6H_4(OEt)C\langle{}^{N.CMe}_{N:C(OH)}\rangle CH$.

OXY-BENZENE *v.* Phenol.

Di-oxy-benzene *v.* Hydroquinone, Pyrocatechin, and Resorcin.

u-**Tri-oxy-benzene** $C_6H_3(OH)_3$ [1:2:4]. *Oxy-hydroquinone.* [140·5°]. Formed, together with hexa-oxy-diphenyl, by fusing hydroquinone (1 pt.) with moist NaOH (9 pts.) (Barth a. Schreder, *M.* 4, 176; 5, 589). Monoclinic plates (from ether); $a:b:c = \cdot75:1:1\cdot01$; $\beta = 91°46'$. V. e. sol. water, alcohol, ether, and HOAc, almost insol. chloroform and benzene. Its alkaline solution rapidly becomes brown through absorption of oxygen. $FeCl_3$ gives a transient bluish-green colour. H_2SO_4 forms a green solution becoming cherry-red on warming. Bromine forms $C_6Br_3(OH)O_2$ [206°]. Nitric acid yields greyish-blue crystals of oxyquinhydrone.

Tri-acetyl derivative $C_6H_3(OAc)_3$. [96°].

Methyl ether $C_6H_3(OMe)(OH)_2$ [2:4:1]. [84°]. Got by reducing the methyl ether of oxyquinone with aqueous SO_2 (Will, *B.* 21, 606). Colourless plates. Turned yellow by $FeCl_3$ being reconverted into $C_6H_3(OMe)O_2$.

Tri-methyl ether $C_6H_3(OMe)_3$. (247°). Formed from the preceding ether, methyl iodide, and KOH (W.). Obtained also from asarone $C_6H_2(OMe)_3.CH:CHMe$ by oxidation to $C_6H_2(OMe)_3CO_2H$ and distillation of this acid with lime (Rizza a. Butlerow, *J. R.* 1887, 1). Oil, volatile with steam.

Mono-ethyl ether $C_6H_3(OH)_2(OEt)$ [1:4:3]. [112°]. Formed by reduction of the ethyl ether of oxy-quinone $C_6H_3(OEt)O_2$ with SO_2. Colourless prisms. Sublimes in fine plates. V. sol. water, alcohol, and ether, m. sol. benzene. Fe_2Cl_6 gives a dark-brown colouration.

Tri-ethyl ether $C_6H_3(OEt)_3$. [34°]. Formed by ethylation of the preceding body. Long white glistening needles; v. e. sol. alcohol and ether, insol. water; volatile with steam. This body is identical with that obtained from æsculetin, which is therefore a derivative of

u-tri-oxy-benzene (Will a. Pukall, *B.* 20, 1133; Herzig a. Zeisel, *M.* 10, 150).

Isomerides are described as PHLOROGLUCIN and PYROGALLOL.

s-Tetra-oxy-benzene $C_6H_2(OH)_4$ [1:2:4:5]. [c. 218°]. Formed by reducing di-oxy-quinone with $SnCl_2$ (Nietzki, *B.* 21, 2377). Colourless plates, v. e. sol. water, alcohol, and ether. Its aqueous solution rapidly turns brown, and its alkaline solution is oxidised by air or by $FeCl_3$ to di-oxy-quinone.

Acetyl derivative $C_6H_2(OAc)_4$. [217°]. Colourless plates.

Di-methyl ether $C_6H_2(OH)_2(OMe)_2$ [1:4:2:5]. [166°]. Formed by reducing $C_6H_2O_2(OMe)_2$ with stannous chloride (Nietzki a. Rechberg, *B.* 23, 1217). Colourless plates.

Di-ethyl ether $C_6H_2(OH)_2(OEt)_2$ [1:4:2:5]. [138°]. Got in like manner. Colourless needles (from hot water). Yields $C_6H_2O_2(OEt)_2$ on oxidation. Acetic anhydride forms the compound $C_6H_2(OAc)_2(OEt)_2$. [148°].

Tetra-ethyl ether $C_6H_2(OEt)_4$. [143°]. Formed from $C_6H_2(OH)_2(OEt)_2$, alcoholic NaOEt and EtBr at 100° (Nietzki, *B.* 23, 1214). Colourless plates, smelling like anise. May be sublimed.

u-Tetra-oxy-benzene. *Di-methyl ether* $C_6H_2(OH)_2(OMe)_2$ [1:4:3:5]. [158°]. Formed by reducing the corresponding $C_6H_2O_2(OMe)_2$ with Zn and HClAq, with $SnCl_2$, or with SO_2 (Hofmann, *B.* 8, 67; 11, 332; Will, *B.* 21, 609). Needles, reconverted into the quinone by $FeCl_3$. HOAc forms an acetyl derivative [133°] which forms a green solution in H_2SO_4. Ac_2O forms an acetyl derivative [128°] which does not give a green solution in H_2SO_4 (H.). Benzoyl chloride yields $C_6H_2(OMe)_2(OBz)_2$ [245°], v. sl. sol. alcohol.

Tri-methyl ether $C_6H_2(OH)(OMe)_3$. [146°]. Formed, together with the tetra-methyl ether by the action of methyl iodide and KOH on the di-methyl ether. Needles (from alcohol).

Tetra-methyl ether $C_6H_2(OMe)_4$. [47°]. (271°). Plates (from ether). Yields $C_6Br_2(OMe)_4$ [76°].

c-Tetra-oxy-benzene. *Di-methyl ether* $C_6H_2(OH)_2(OMe)_2$. *Di-methyl-apionol.* [106°]. (298°). Formed by heating apiolic acid $C_7H_3O_2(OMe)_2CO_2H$ with alcoholic potash, at 180° (Ciamician a. Silber, *B.* 22, 119, 2482; 23, 2291). Insol. water, sol. alcohol, ether, and benzene. Its solution in KOHAq becomes brownish-red. Ferric chloride gives a violet-black colour. Lead acetate gives a gelatinous pp. $AgNO_3$ forms minute needles, quickly turning black. Yields a crystalline acetyl derivative [144°].

Tetra-methyl ether $C_6H_2(OMe)_4$ [1:2:3:4]. [81°]. White needles, v. sol. ether.

Hexa-oxy-benzene $C_6(OH)_6$ (so-called '*tri-hydrocarboxylic acid*' of Lerch). Long nearly colourless needles. Soluble in hot water, slightly soluble in cold water, alcohol, ether, and benzene.

Formation.—1. By the action of dilute HCl upon freshly prepared carbonic-oxide potassium. 2. By reduction of tri-quinone C_6O_6 with stannous chloride.

Properties.—Reduces $AgNO_3$ in the cold. Is oxidised by HNO_3 to benzene-tri-quinone. Gives a violet colouration with Fe_2Cl_6. The solution in aqueous Na_2CO_3 is readily oxidised by the air to tetra-oxy-quinone $C_6(OH)_4O_2$. By distillation with zinc-dust it gives benzene and diphenyl. By evaporation in an open dish with dilute KOH it yields croconic acid $C_5H_2O_5$.

Salt $C_6(OK)_6$. Formed by combination of CO with K at 80°, occurring as a by-product in the preparation of K (Liebig, *A.* 11, 182; Brodie, *A.* 113, 358; Lerch, *A.* 124, 20). Grey mass, becoming explosive on exposure to air.

Hexa-acetyl derivative $C_6(OAc)_6$: [203°]; small colourless prisms; sl. sol. hot acetic acid, nearly insol. alcohol, ether, and benzene (Nietzki a. Benckiser, *B.* 18, 505, 1833).

OXY-BENZENE CARBOXYLIC ACID *v.* OXY-BENZOIC ACID.

Oxy-benzene dicarboxylic acid *v.* OXY-PHTHALIC, OXY-ISOPHTHALIC, and OXY-TEREPHTHALIC ACIDS.

Tri-oxy-benzene carboxylic acid *v.* GALLIC ACID.

Tri-oxy-benzene tri-carboxylic acid *v.* PHLOROGLUCIN TRICARBOXYLIC ACID.

Di-oxy-benzene tetra-carboxylic acid *v.* HYDROQUINONE TETRA-CARBOXYLIC ACID.

DI-OXY-BENZENE-DIQUINONE *v.* DI-OXY-DIQUINONE.

OXY-BENZENE SULPHONIC ACID *v.* PHENOL SULPHONIC ACID.

Di-oxy-benzene sulphonic acid $C_6H_3(OH)_2SO_3H$. [280°]. Formed by heating phenol 'β'-disulphonic acid with potash at 240° (Senhofer, *J.* 1879, 749). Crystallises from water in needles (containing aq). Coloured violet by $FeCl_3$.—BaA'_2 7aq.—ZnA'_2 27aq.—PbA'_2 8aq: long thin plates.

Isomerides. HYDROQUINONE, PYROCATECHIN, and RESORCIN SULPHONIC ACIDS.

OXY-BENZENYL-AMIDO-PHENYL MERCAPTAN $C_{13}H_9NSO$ *i.e.* $C_6H_4<^{N}_{S}>C.C_6H_4.OH$. [129°]. Formed by heating salicylic aldehyde with o-amido-phenyl-mercaptan (Hofmann, *B.* 13, 1237). Needles.—B'HCl.—*Platinochloride* $B'_2H_2PtCl_6$: pp.

***o*-OXY-BENZENYL-AMIDOXIM** $C_6H_4(OH).C(NOH).NH_2$. *Salicenyl-amidoxim.* [99°]. Formed from $C_6H_4(OH).CS.NH_2$, hydroxylamine hydrochloride, and Na_2CO_3Aq (Spilker, *B.* 22, 2774). Colourless needles, v. sol. alcohol and ether, m. sol. hot water. Gives a greenish pp. with $CuSO_4$ and a mirror with $AgNO_3$.

Reactions.—1. Ac_2O forms the acetyl derivative and, on further digestion, the azoxim $C_6H_4(OH).C<^{N.O}_{N}>CMe$ [77°] which yields an acetyl derivative [74°].—2. Concentrated sulphuric acid at 150° yields the sulphonic acid $C_6H_3(SO_3H)(OH).C(NOH)NH_2$, v. sl. sol. cold water, insol. alcohol.—3. $ClCO_2Et$ yields $C_6H_4(OH).C(NH_2):NO.CO_2Et$ [96°] (Miller, *B.* 22, 2799).—4. *Succinic anhydride* forms, on melting, the azoxim $C_6H_4(OH).C:(N_2O):C.C_2H_4.CO_2H$ [117°].—5. *Potassium cyanate* and HCl yield $C_6H_4(OH).C(NOH).NH.CO.NH_2$ [148°].— .

Phenyl cyanate forms by direct combination $C_6H_4(OH).C(NOH).NH.CO.NHPh$ [119°].

Salts.—$B'HCl$. [175°]. V. e. sol. water.—$B'_2H_2PtCl_6$.—$Na_2C_7H_6N_2O_2$.—$NaC_7H_7N_2O_2$.

Acetyl derivative $C_6H_4(OH).C(NOAc).NH_2$. [117°]. White plates, sl. sol. water.

Di-acetyl derivative. Formed from the Na salt and AcCl. Crystalline.

Benzoyl derivative $C_6H_4(OH).C(NOBz).NH_2$. [173°]. Needles, v. sol. ether. Yields $C_6H_4(OH).C{<}\genfrac{}{}{0pt}{}{N.O}{N}{>}CPh$ [128°], which forms a benzoyl derivative [120°].

Di-benzoyl derivative $C_6H_4(OBz).C(NOBz).NH_2$. [127°]. Formed from the amidoxim, NaOEt, and BzCl in ether. Indistinct crystals.

Ethyl ether $C_6H_4(OH).C(NOEt).NH_2$. (278°). Formed from the amidoxim, alcoholic NaOEt, and EtI. Oil. By HCl and $NaNO_2$ it is converted into $C_6H_4(OH).C(NOEt)Cl$ (234°).

Methyl derivative $C_6H_4(OMe).C(NOH)NH_2$. [123°]. Formed from $C_6H_4(OMe).CN$ and alcoholic hydroxylamine (Miller, *B.* 22, 2791). Needles (from hot water). Yields $B'HCl$ [168°]. With Ac_2O it yields $C_6H_4(OMe).C{<}\genfrac{}{}{0pt}{}{N.O}{N}{>}CMe$ [68°]. Aldehyde forms $C_6H_4(OMe).C{<}\genfrac{}{}{0pt}{}{N.O}{NH}{>}CHMe$ [127·5°]. $ClCO_2Et$ forms $C_6H_4(OMe).C(NH_2):NO.CO_2Et$ [120°], which on heating becomes $C_6H_4(OMe).C{<}\genfrac{}{}{0pt}{}{N.O}{NH}{>}CO$ [208°].

Methyl-acetyl derivative $C_6H_4(OMe).C(NOAc)NH_2$. [106°]. Formed from the oxim and AcCl in chloroform. Prisms.

Methyl-benzoyl derivative $C_6H_4(OMe).C(NOBz)NH_2$. [148°]. White granules, v. sol. alcohol.

Methyl-ethyl derivative $C_6H_4(OMe).C(NOEt).NH_2$. [52°]. Prisms, v. sol. alcohol.

Di-ethyl derivative $C_6H_4(OEt).C(NOEt).NH_2$. (195° at 160 mm.). Formed from the amidoxim, NaOEt, EtI, and alcohol. Oil, miscible with alcohol and ether.

m-**Oxy-benzenyl-amidoxim** $C_6H_4(OH).C(NH_2)(NOH)$. [71°]. Made by heating *m*-oxy-benzonitrile with hydroxylamine hydrochloride and Na_2CO_3 (Clemm, *B.* 24, 829). Groups of needles, v. sol. water.

Di-benzoyl derivative $C_6H_4(OBz).C(NH_2):NOBz$. [152·5°]. Crystals.

Acetyl derivative $C_6H_4(OH).C(NH_2):NOAc$. [90°]. Plates.

Di-ethyl ether $C_6H_4(OEt).C(NH_2):NOEt$ [109°]. Needles. *p*-Oxy-benzenyl-amidoxim. [153°]. Made in like manner (Krone, *B.* 24, 834.—$B'HCl$. [179°].

Acetyl derivative. [122·5°].

Benzoyl derivative. [166°].

Di-benzoyl derivative. [186°].

Di-ethyl ether. [84°].

o-**OXY-BENZENYL-*o*-PHENYLENE-DIAMINE** $C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{N}{>}C.C_6H_4OH$. [223°]. Formed by reducing the *o*-nitro-anilide of salicylic acid with tin and HCl (Hübner a. Mensching, *B.* 13, 463; *A.* 210, 345). Needles, v. sol. alcohol and ether. — $B'HCl$ aq. — $B'_2H_2SO_4$ 4aq: sparingly soluble needles.

o-**OXY-BENZENYL-DI-UREA** $C_9H_{12}N_4O_3$ *i.e.* $C_6H_4(OH).CH(NH.CO.NH_2)_2$. Formed from salicylic aldehyde and aqueous urea (Schiff, *A.* 151, 199). Nodular groups of needles (containing aq). V. sl. sol. water, sl. sol. alcohol, insol. ether.—$Cu(C_9H_{11}N_4O_3)_2$. Green pp.

Ethyl ether $C_6H_4(OEt).CH(N_2H_3CO)_2$aq. Crystals.

By fusing salicylic aldehyde with urea there is formed $(C_6H_4(OH).CH)_2(N_2H_3CO)_2$.

p-**Oxy-benzenyl-di-urea.** *Methyl ether* $C_6H_4(OMe).CH(NH.CO.NH_2)_2$. Formed from anisic aldehyde, an aqueous solution of urea, and a little HOAc. Yellow plates.

DI-OXY-BENZIL. *Di-methyl derivative* $C_6H_4(OMe).CO.CO.C_6H_4(OMe)$. *Anisil.* [133°]. Formed by oxidising anisoïn with alkaline copper solution (Boesler, *B.* 14, 327). Golden needles (from alcohol).

Hexa-oxy-benzil. *Hexa-methyl derivative* $C_6H_2(OMe)_3.CO.CO.C_6H_2(OMe)_3$. [189°]. Formed by the action of sodium-amalgam on an alcoholic solution of the tri-methyl derivative of the amide of gallic acid (Marx, *A.* 263, 253). Satiny needles, coloured bluish-green by H_2SO_4.

p-**OXY-BENZIMIDO-ETHER.** *Ethyl derivative* $C_6H_4(OEt)C(NH)(OEt)$. The hydrochloride is crystalline and is formed from $C_6H_4(OEt)CN$ and alcoholic HCl (Pinner, *B.* 23, 2953).

o-**OXY-BENZOIC ACID** $C_7H_6O_3$ *i.e.* $C_6H_4(OH).CO_2H$. *Salicylic acid.* Mol. w. 138. [156°] (Hübner, *A.* 162, 74); [159° cor.] (Reissert, *B.* 23, 2244); [157° cor.] (Dunstan a. Bloch, *Ph.* [3] 21, 429). S. ·09 at 0° (Ost, *J. pr.* [2] 17, 230); ·15 at 0°; ·225 at 15°; 7·925 at 100° (Bourgoin, *J. Pharm. Chim.* [4] 30, 488; *C. R.* 87, 62); H.C. 734,990 (Berthelot a. Recoura, *A. Ch.* [6] 13, 320); 729,500 (Stohmann, *J. pr.* [2] 40, 129). H.F. 106,000 (Von Rechenberg); 135,500 (S.). Occurs in the blossoms of the meadow-sweet (*Spiræa ulmaria*) (Löwig a. Weidmann, *P.* 46, 83), and in the leaves and stems of *Tulipa*, *Yucca*, and *Hyacinthus* (Griffiths, *C. J. Proc.* 5, 122). Occurs as methyl ether in the oil of wintergreen (from *Gaultheria procumbens*) (Cahours, *A.* 48, 60; Hartley, *C. J.* 53, 664). Methyl salicylate constitutes the essential oils of *Gaultheria punctata* and *G. leucocarpa* (Köhler, *B.* 12, 246).

Formation.—1. By oxidation of o-oxy-benzyl alcohol (saligenin), and of o-oxy-benzoic aldehyde (salicylic aldehyde).—2. By potash-fusion from salicin, coumarin, indigo, *o*-cresol (Barth, *A.* 154, 360), toluene *o*-sulphonic acid, *p*-chloro-toluene sulphonic acid (Vogt, *Z.* [2] 5, 577), and other bodies.—3. By heating cupric benzoate with water in sealed tubes for 3 hours at 180° (Smith, *Am.* 2, 338); *cf.* Ettling, *A.* 53, 83).—4. From *o*-amido-benzoic acid by the diazo-reaction (Hübner a. Petermann, *A.* 149, 129; *cf.* Gerland, *A.* 86, 147).—5. Together with *p*-oxy-benzoic acid by heating phenol with CCl_4 and alcoholic potash (Tiemann a. Reimer, *B.* 9, 1285).—6. By oxidising o-tolyl sulphuric acid $C_6H_4MeO.SO_3H$ with alkaline $KMnO_4$ (Heymann a. Königs, *B.* 19, 706).—7. By heating C_6H_5ONa with sodium carbonate in a current of carbonic oxide at 200°: $PhONa + Na_2CO_3 + CO$

$= C_6H_4(ONa).CO_2Na + HCO_2Na$ (Schroeder, *A.* 221, 41).—8. By oxidising toluene o-phosphonic acid with alkaline $KMnO_4$ (Heymann a. Königs, *B.* 19, 3306).—9. By distilling sodium phenyl carbonate with NaOEt in a current of CO_2 (Hentschel, *J. pr.* [2] 27, 39).—10. By heating phenyl ethyl carbonate with NaOPh at 200° in a current of hydrogen, PhOEt being also formed. 11. Together with PhOEt by heating Ph_2CO_3 with NaOEt in a current of hydrogen (H.).

Preparation.—By passing CO_2 over sodium-phenol heated at 180° $C_6H_4(ONa)CO_2Na$ being formed and phenol distilling over (Kolbe, *A.* 115, 201; *J. pr.* [2] 10, 93). CO_2 is first absorbed, and this can also take place at a lower temperature, and the resulting sodium phenyl carbonate $C_6H_5O.CO_2Na$ changes into the isomeric sodium salicylate $C_6H_4(OH).CO_2Na$. This change can take place at 130°. The sodium salicylate reacts upon excess of sodium phenol at 180°, setting free phenol, which distils over, leaving basic sodium salicylate behind $C_6H_4(OH).CO_2Na + PhONa = PhOH + C_6H_4(ONa).CO_2Na$ (R. Schmitt, *J. pr.* [2] 31, 404; *cf.* Baumann, *B.* 11, 1910). Salicylic acid is set free by acidifying the basic sodium salicylate. By using a measured quantity of CO_2, starting the operation at a low temperature and finishing it at 130°, the formation of basic sodium salicylate may be avoided, so that half the phenol may be saved.

Properties.—Colourless needles (from hot water) or monoclinic prisms (from alcohol). Sublimes at 200°. Volatile with steam. $FeCl_3$ colours its aqueous solution violet, the colour not being removed by acetic acid. Prevents ppn. of copper sulphate ($\frac{1}{2}$ mol.) by alkalis. With albuminoids it forms compounds containing about 14 p.c. of the acid (Farsky, *C. C.* 1877, 148). Bromine-water yields a pp. of $C_6H_2Br_4O$ in dilute aqueous solutions. Iodine and potash give a red powder $C_6H_3I(OI)CO_2K$ (Messinger a. Vortmann, *B.* 22, 2321). Antiseptic. Anti-rheumatic.

Reactions.—1. Split up into CO_2 and phenol when rapidly heated to 220°; at 250° diphenylene-ketone oxide [174°] is formed (Klepl, *J. pr.* [2] 28, 217). Conc. HClAq at 150° decomposes it in like manner (Graebe, *A.* 139, 143). Potash-fusion also gives phenol.—2. $KMnO_4$ oxidises it to formic acid and CO_2. *Chromic acid mixture* acts in like manner.—3. *Chlorine* forms chloro-oxy-benzoic and di-chloro-oxybenzoic acids.—4. *Iodine* and HIO_3 give mono, di-, and tri-, iodo-oxy-benzoic acids and tri-iodo-phenol.—5. *Nitrous acid* passed into its ethereal solution forms nitro- and diazo-oxy-benzoic acids (Goldberg, *J. pr.* [2] 19, 368).—6. PCl_5 forms $C_6H_4(COCl).O.POCl_2$ (168° at 11 mm.). This compound is partially decomposed on distillation, yielding *o*-chloro-benzoyl chloride. Moist air converts it into $C_6H_4(CO_2H).O.PO(OH)_2$. Further treatment with PCl_5 at 170° forms $C_6H_4(COCl).OPCl_4$ (179° at 11 mm.) converted by water into $C_6H_4(CO_2H).OP(OH)_4$. Excess of PCl_5 forms $C_6H_4Cl.CCl_3$ (Couper, *A.* 109, 370; Anschütz, *A.* 228, 314; 239, 314; Chasanovitch, *B.* 20, 1166).—7. PCl_3 forms $C_7H_4ClPO_3$, which may be $C_6H_4<\begin{matrix}CO.O\\O\end{matrix}>PCl$. It forms crystals [37°] (127° at 11 mm.), and is sol. ether, benzene, and $CHCl_3$, but decomposed by water into salicylic and phosphorous acids (Anschütz a. Emery, *A.* 239, 301). It is converted by PCl_5 or free chlorine into $C_7H_4Cl_3PO_3$ (167° at 11 mm.), S.G. $\frac{20}{4}$ 1·557; whence water forms $C_7H_4(OH)_3PO_3$ [142°]. The chloride $C_7H_4ClPO_3$ takes up bromine forming $C_7H_4ClBr_2PO_3$ (c. 187° at 12 mm.). 8. *Aniline* at 210° produces aniline, phenol, and $C_6H_4(OH).CONPhH$ (Limpricht, *B.* 22, 2906).—9. *Cyanamide* and alcohol at 100° form urea and o-oxy-benzoic ether.—10. *Benzamidine* forms a compound $C_{21}H_{15}N_3O$ (Pinner, *B.* 23, 3824).—11. *Glycerin* and gaseous HCl forms $C_6H_4(OH).CO.OC_3H_5Cl_2$ [44°], S.G. 1·331 (Göttig, *B.* 24, 508), whence sodic salicylate at 180°–200° forms crystalline $C_3H_5(O.CO.C_6H_4OH)_3$ and $CH(OBz)(CH_2.O.COC_6H_4OH)_2$ [95°] (Fritsch, *B.* 24, 779).—12. *Acetochlorhydrose* forms $C_{23}H_{30}O_{15}$ [185°], whence $C_{23}H_{23}(OAc)_7O_5$ [111°] (Michael, *B.* 15, 1922).—13. *Phenol* and $SnCl_4$ at 120° yield *op*-di-oxy-benzophenone [144°] (Michael, *Am.* 5, 83).—14. *Resorcin* at 200° forms tri-oxy-benzophenone.—15. *Orcin* gives '(β)-oxy-methyl-xanthone' $C_6H_4<\begin{matrix}O\\CO\end{matrix}>C_6H_2Me(OH)$ [285°] (Von Kostanecki a. Nessler, *B.* 24, 1895). 16. *Phloroglucin* forms iso-euxanthone $C_6H_4<\begin{matrix}O\\CO\end{matrix}>C_6H_2(OH)_2$ [247°].—17. When taken internally it is excreted as salicyluric acid or salicyl-glycocoll $C_9H_9NO_4$ [c. 160°] (Bertagnini, *Il Nuovo Cimento*, i. 363).—18. With *camphor* it forms a compound $C_7H_6O_32C_{10}H_{16}O$ [60°] $[\alpha]_D = +27°{\cdot}3$ (in dilute alcohol) (Léger, *C. R.* 111, 110).—19. $K_2S_2O_7$ (17 pts.) added to a solution of salicylic acid (10 pts.) and KOH (8 pts.) in water (25 pts.) forms the crystalline compound $C_6H_4(CO_2K).OSO_3K$ (Baumann, *B.* 11, 1914).—20. A solution of salicylic acid and borax in water deposits crystals of $C_{14}H_{10}NaBO_7$, whence the corresponding salts NH_4A', KA', $MgA'_2$10aq and $CaA'_2$10aq (Jahns, *Ar. Ph.* [3] 12, 212).—21. *Chloral* at 140° forms $C_6H_4<\begin{matrix}O\\CO.O\end{matrix}>CH.CCl_3$ [124°] (Wallach, *A.* 193, 1).

Salts.—$C_6H_4(ONa).CO_2Na$. With $POCl_3$ it gives di-phenylene-ketone-oxide $C_{13}H_8O_2$ [174°]. The normal salt $C_6H_4(OH).CO_2Na$ is converted by $POCl_3$ into an isomeric body [91°] (R. Richer, *J. pr.* [2] 23, 349; 28, 303).—$NaHA'_2$. Large crystals, sol. alcohol (E. Hoffmann, *Ar. Ph.* [3] 12, 226).—$KA'\frac{1}{2}$aq. Decomposed at 210° into CO_2, phenol, and disodium *p*-oxy-benzoate (Ost, *J. pr.* [2] 11, 392). In presence of excess of KOH the change does not take place. The Na salt does not give *p*-oxy-benzoic acid when heated alone or with NaOH, but when heated in a current of CO_2 at 300° it yields oxy-isophthalic and oxytrimesic acids.—NH_4A'.—$NH_4A'\frac{1}{2}$aq: monoclinic crystals.—BaA'_2aq. Small needles, sl. sol. cold water.—$BaC_7H_4O_3$2aq. Needles, sl. sol. hot water.—$SrA'_2$2aq.—$CaA'_2$2aq. Octahedra, v. sol. water, sol. alcohol.—$CaC_7H_4O_3$aq. Crystalline powder, nearly insol. water.—$MgA'_2$4aq.—$ZnA'_2$3aq. S. 5 at 20°. Needles, sol. alcohol (Vulpius, *Ar. Ph.* [3] 14, 239).—$ZnA'_2$2aq (Marignac, *J.* 1855, 485).—CdA'_2aq.—$HgC_7H_4O_3$ (Lajoux a. Grandval, *J. Ph.* [5] 20, 5).—HgA'_2.—PbA'_2aq.—$PbC_7H_4O_3$.—Oxysalt: $Pb_5O_3(C_7H_4O_3)_2$.—TlA'.—$Tl_2C_7H_4O_3$.—$BiOA'$. Insoluble powder got by adding sodium salicylate to a solution of bismuth nitrate in glycerin

(Wolff, *Ph.* [3] 14, 508).—AlA'_3 (Van der Velden, *J. pr.* [2] 15, 151).—FeA'_3: brown pp., quickly becoming violet.—$MnA'_2 2aq$.—$CuA'_2 4aq$: bluish-green needles, v. sol. water and alcohol.—$CuC_7H_4O_3aq$. Insoluble.—$CuK_2(C_7H_4O_3)_2 4aq$: green tables, v. sol. water.—$CuBa(C_7H_4O_3)_2 4aq$ (Pellizzari, *G.* 14, 365).—AgA': monoclinic needles.

Methyl ether $C_6H_4(OH).CO_2Me$. Mol. w. 152. (224° cor.). S.G. $\frac{0}{}$ 1·197. S.V. 155·9 (Ramsay); 156·7 (Lossen, *A.* 254, 64). H.F. 129,224 (Stohmann, *J. pr.* [2] 36, 353). Constitutes oil of wintergreen, oil of *Gaultheria punctata* and *leucocarpa*, and oil of birch (Köhler, *B.* 12, 246; Pettigrew, *Ph.* [3] 14, 167). PCl_5 yields $C_6H_4(COCl).O.POCl_2$ (*v. supra*). Phenyl cyanate at 160° forms $C_6H_4(CO_2Me).O.CONHPh$ [238°] (Snape, *C. J.* 47, 775). Hydroxylamine hydrochloride yields $C_6H_4(OH).CO.NH(OH)$ [169°] (Jeaurenaud, *B.* 22, 1273). Benzamide forms, on heating, phenyl benzoate and a compound $C_{22}H_{28}N_4O$ [256° cor.] crystallising from chloroform in yellow needles (Guareschi, *A.* 171, 143). Forms the crystalline salts $C_6H_4(OK).CO_2Me \frac{1}{2}aq$ and BaA'_2aq.

Ethyl ether EtA'. (227°). H.F. 139,252. Oil (Göttig, *B.* 9, 1473). With benzamidine hydrochloride it gives $(C_7H_6O_3)C_7H_7NO$ [120°], benzamidine salicylate $C_{14}H_{14}N_2O_3$ [202°], and a compound $C_{21}H_{15}N_3O$ [246°], whence $C_{21}H_{14}AcN_3O$ [141°] (Pinner, *B.* 23, 2935).

Ethylene ether $C_2H_4A'_2$. [83°].

Propyl ether PrA'. (239°). S.G. $\frac{21}{}$ 1·021. H.F. 147,880.

Isoamyl ether $C_5H_{11}A'$. (270°).

Phenyl ether PhA'. *Salol.* [42°]. Formed by slowly adding $POCl_3$ (28 g.) to a mixture of salicylic acid (60 g.) with phenol (48 g.) at 135° (Seiffert, *J. pr.* [2] 31, 472). Anti-rheumatic. The yield is good (99 g.). Trimetric tablets (from alcohol, $a:b:c = \cdot963:1:\cdot697$ (Léger), insol. water. Its alcoholic solution is coloured violet by $FeCl_3$. Conc. NaOH forms solid $C_6H_4(ONa).CO_2Ph$, but boiling NaOHAq saponifies it. When heated for a long time to boiling it gives CO_2, phenol, and diphenylene ketone oxide. Dissolved in HOAc it is nitrated by HNO_3 to $C_6H_3(NO_2)(OH).CO_2Ph$ [150°] and a di-nitro- compound [183°]. HNO_3 (S.G. 1·53) forms also $C_6H(NO_2)_3(OH).CO_2Ph$ [100°] (Knebel, *J. pr.* [2] 42, 158).

Nitro-phenoxy-ethyl ether $C_6H_4(NO_2)O.C_2H_4A'$. The o- isomeride [106°] yields an acetyl derivative [80°]. The *p*- isomeride crystallises from alcohol in needles [131°] (Wagner, *J. pr.* [2] 27, 215).

Tolyl ethers C_6H_4MeA'. The o-, *m*-, and *p*- compounds [35°], [74°], and [39°] are insol. water, sl. sol. alcohol (Nencki, *C. R.* 108, 254).

Methyl derivative $C_6H_4(OMe).CO_2H$. [98·5°]. S.G. $\frac{99}{4}$ 1·1801. μ_β 1·5521. R_∞ 64·59 (Brühl). S. ·5 at 20°. Formed by saponifying its methyl ether, which is formed from oil of Wintergreen, KOMe, and MeI (Cahours, *A.* 92, 315). Monoclinic tables (from water). Its aqueous solution is not coloured by $FeCl_3$. Yields the salts BaA'_2, PbA'_2aq, and AgA', and the ethers MeA' (228°), EtA' (235°) (Fölsing, *B.* 17, 486), and PhA' [59°] (Seiffert, *J. pr.* [2] 31, 474).

Ethyl derivative $C_6H_4(OEt).CO_2H$. [19·4°]. Forms the salts CaA'_2, BaA'_2, $PbA'_2 2aq$, $Cu_2A'_3(OH)$, and AgA' (Kraut, *A.* 150, 1) and the ethers MeA' (245°) and EtA' (251°).

Isopropyl derivative $C_6H_4(OPr).CO_2H$. Oil, forming the salts $CaA'_2 2aq$, BaA'_2aq, and $AgA' \frac{1}{2}aq$ and the ether MeA' (250°).

Allyl derivative $C_6H_4(OC_3H_5).CO_2H$. [113°]. Forms the salt AgA' and the ether MeA' (245°) (Scichilone, *G.* 12, 449).

Ethylene derivative $C_2H_4(O.C_6H_4.CO_2H)_2$. [152°]. Formed by saponification of its ethyl ether Et_2A'' [97°], which is itself got by heating $C_6H_4(ONa).CO_2Et$ with ethylene bromide at 130°. Silky needles (from water) (Weddige, *J. pr.* [2] 21, 128).

Phenyl derivative $C_6H_4(OPh).CO_2H$. [113°]. (355°). Formed by adding Na to $C_6H_4(OH).CO_2Ph$ at 300° (Graebe, *B.* 21, 502), and also by the action of phenol on o-diazobenzoic acid (Griess, *B.* 21, 982). Plates, v. sl. sol. hot water. Heated with conc. H_2SO_4 it yields diphenylene ketone oxide. Heating with baryta forms diphenyl oxide [25°]. Bromine-water at 150° forms $C_6H_2Br_3O.C_6H_4CO_2H$ [176°], whence AgA' and EtA' [57°] (Arbenz, *A.* 257, 86). HNO_3 at 0° forms a di-nitro- derivative [153°], which gives the salts $BaA'_2 4aq$, $CaA'_2 4aq$, and AgA', and the ethers MeA' [126°], EtA' [76°], and an amide [166°]. The phenyl derivative of salicylic acid forms the salts NH_4A', KA', $CaA'_2 2aq$, BaA'_2aq, and AgA', and the ether, MeA' and EtA', boiling above 360°, and PhA' [109°].

Nitro-phenyl-ethylene derivative $C_6H_4(NO_2).OC_2H_4O.C_6H_4.CO_2H$. The o- acid [142°-148°] forms a crystalline ether EtA' [c. 100°], and the *p*-acid [132°] forms a similar ether EtA' [81°] (Wagner, *J. pr.* [2] 27, 214). The o- acid yields on reduction an amido- acid [110°], forming $C_{15}H_{15}NO_4.HCl$ [177°].

Benzyl derivative $C_6H_5CH_2O.C_6H_4.CO_2H$. [75°]. Tables (Perkin, *A.* 148, 27).—AgA'.

Tolyl derivative. Occurs in natural salicylic acid (J. Williams, *Ph.* [3] 8, 785).

Acetyl derivative $C_6H_4(OAc).CO_2H$. [118°]. Formed from the acid and AcCl (Kraut, *A.* 150, 9). Needles (from water), v. sl. sol. cold water. Hydrolysed by alkalis, but not by boiling water.

Benzoyl derivative $C_6H_4(OBz).CO_2H$. The crystalline methyl ether MeA' is formed from methyl salicylate and BzCl (Gerhardt, *A. Ch.* [3] 45, 104).

Amide $C_6H_4(OH).CONH_2$. [139°]. From the ethers and NH_3Aq (Limpricht, *A.* 98, 258). Formed by the action of AcCl on o-oxy-benzaldoxim (Claisen a. Stock, *B.* 24, 138). Plates and tables. Gives saligenin on reduction with sodium amalgam (Hutchinson, *C. J.* 57, 957). With bromine-water it yields $C_6H_2Br_2(OH).CONH_2$ [183°] (Spilker, *B.* 22, 2769). When heated in a current of HCl it forms $(C_6H_4(OH).CO)_2NH$ [199°], which yields $(C_7H_5O_2)_2NAg$ and $(C_{14}H_{11}NO_4)_2HCl$.—AgA': flocculent pp.

Benzoyl derivative of the amide $C_6H_4(OBz).CONH_2$. [200°]. Needles, sl. sol. alcohol.

Cuminyl derivative of amide [200°].

Methyl derivative of the amide $C_6H_4(OMe).CONH_2$. [129°]. Prisms (from ether) (Grimaux, *Bl.* [2] 13, 26). The homologous ethyl derivative [110°] (Limpricht, *A.*

98, 264) and isopropyl derivative are crystalline.

Anilide $C_6H_4(OH).CONHPh$. [134°]. Prisms (from dilute alcohol) (Wanstrat, *B.* 6, 336; Kupferberg, *J. pr.* [2] 16, 442; Hübner a. Meusching, *A.* 210, 341). $FeCl_3$ colours its alcoholic solution violet. On heating with sulphur it forms $C_6H_4<{}^{N}_{S}>C.C_6H_4OH$ [129°] (Hofmann, *B.* 13, 1237). Yields on nitration $C_6H_3(NO_2)(OH).CONHPh$ [224°]. Forms the salts $KC_{13}H_{10}NO_2\,2\frac{1}{2}aq$ and $TlC_{13}H_{10}NO_2$.

Nitro-anilide $C_6H_4(OH).CO.NHC_6H_4NO_2$. The o-, *m*-, and *p*- varieties melt at 154°, 218°, and 230° respectively.

p-Toluide $C_7H_5O_2.NHC_7H_7$. [156°].

Piperidide $C_6H_4(OH).CO.NC_5H_{10}$. [142°]. Yellowish tables (Schotten, *B.* 21, 2252).

Hydroxylamide $C_6H_4(OH).CO.NH(OH)$. [169°]. Needles. Yields $Pb(C_7H_6NO_3)_2 4aq$ (Jeanrenaud, *B.* 22, 1270).

Anhydride $O(C_6H_4.CO_2H)_2$. *Disalicylic acid.* Formed, together with salicylide, by the action of $POCl_3$ on dry sodium salicylate (Gerhardt, *A. Ch.* [3] 37, 322). Amorphous mass, v. sol. alcohol and ether. Gives no colour with $FeCl_3$. Dissolves unchanged in aqueous Na_2CO_3. Boiling KOHAq converts it into salicylic acid. An anhydride $C_{56}H_{34}O_{17}$ is formed by heating sodium salicylate (3 pts.) with $POCl_3$ (1 pt.) at 150° (Kraut, *A.* 150, 13). It is insol. cold alcohol. A third anhydride $C_{28}H_{18}O_9$ is got by heating $C_6H_4(OAc).CO_2H$ at 200°–240° (Kraut). It is sol. alcohol, and softens at 70°.

Internal anhydride $C_7H_4O_2$ or $C_{14}H_8O_4$ *i.e.* $C_6H_4<{}^{O\,.CO}_{CO.O}>C_6H_4$. *Salicylide.* [195°–200°]. Formed as above. Nodular groups of plates (from alcohol) (Schiff, *A.* 163, 220). Insol. water, sl. sol. alcohol. Not attacked by AcCl. Reconverted by potash into salicylic acid. A resinous anhydride $C_{28}H_{18}O_9$ accompanying salicylide is still less soluble in alcohol.

Nitrile $C_6H_4(OH).CN$. o-*Cyano-phenol.* [98°]. Formed by the action of P_2O_5 or P_2S_5 on the amide, and also from $C_6H_4(OH).CH{:}NOH$ and Ac_2O (Miller, *B.* 22, 2771, 2797; Tiemann, *B.* 20, 3082; Meyer, *B.* 20, 3289; *cf.* Grimaux, *Bl.* [2] 13, 26; Ahrens, *B.* 20, 2953). Formed also from diazophenol chloride by Sandmeyer's reaction. In most of these preparations it is accompanied by a small quantity of a substance melting at 195°. Needles, v. sol. alcohol, m. sol. cold water. Coloured violet by $FeCl_3$. Gives a white crystalline pp. with bromine water. Gives a *methyl derivative* $C_6H_4(OMe).CN$ (256°), and an *ethyl derivative* $C_6H_4(OEt).CN$ (258°) which may be got from $C_6H_4(OEt)NH_2$ (Pinner, *B.* 23, 2952). The *acetyl derivative* $C_6H_4(OAc).CN$ is an oil (253°) (Lach, *B.* 17, 1572) while the *benzoyl derivative* $C_6H_4(OBz).CN$ [149°] is crystalline (Limpricht, *A.* 99, 250; Henry, *B.* 2, 491).

Polynitrile $(C_6H_4(OH).CN)_x$. [296°–299°]. Obtained by heating the amide to 270° (L.) and as a by-product in preparing the nitrile (Miller, *B.* 22, 2798). Yellow needles, insol. alcohol, sl. sol. ether. Decomposed by HCl at 200° into CO_2, phenol, and NH_3.

m-Oxy-benzoic acid $C_6H_4(OH).CO_2H$. [200°]. S. ·37 at 0° (Ost); ·9 at 18° (Fittica, *B.* 11, 1208). H.F. 111,000 (Von Rechenberg); 136,000 (Stohmann, *J. pr.* [2] 40, 129). H.C. 729,000.

Formation.—1. By the action of nitrous acid on amido-benzoic acid (Gerland, *A.* 91, 185; Graebe a. Schultzen, *A.* 142, 350).—2. By fusing sulpho-benzoic acid with potash (Barth, *A.* 148, 30).—3. By potash-fusion from *m*-chloro-benzoic acid (Dembey, *A.* 148, 222), *m*-cresol, and even benzoic acid (Barth, *A.* 154, 361; *M.* 3, 802).

Properties.—Nodular groups of needles (from water). May be distilled. V. sol. boiling water and alcohol. Volatile with steam. Blackens when quickly heated to 300°, but gives no phenol. When the acid (2 mols.) is heated with baryta (3 mols.) at 350° it forms no phenol unless the baryta is used in large excess (7 mols.) (Klepl, *J. pr.* [2] 27, 159). It tastes sweet. Its solutions are not coloured by $FeCl_3$. Iodine and KOHAq, followed by an acid, give a coffee-brown pp. (Messinger, *B.* 22, 2321). It is not acted upon by hydroxylamine.

Reactions.—1. *Bromine* (3 mols.) forms tribromo-*m*-oxy-benzoic acid, soluble in water (Werner, *Bl.* [2] 46, 276).—2. *Sodium-amalgam* reduces it, in acid solution, to *m*-oxy-benzyl alcohol.—3. Conc. H_2SO_4 forms, on heating, several di-oxy-anthraquinones (*q. v.*). When benzoic acid is also present, the two oxy-anthraquinones are also formed.—4. Heated with cinnamic acid and H_2SO_4 it yields anthracoumarin $C_{16}H_8O_3$ [260°] (*v.* CINNAMIC ACID, *Reaction* 14).—5. By nitration with dilute nitric acid, which takes place extremely readily, it yields a mixture of three nitro-oxy-benzoic acids $C_6H_3(NO_2)(OH)CO_2H$[4:3:1], [2:3:1], and [5:3:1] (Griess, *B.* 20, 403).—6. PCl_5 forms the chloride $C_6H_4(COCl).OPOCl_2$ of *m*-carboxy-phenyl-phosphoric acid (*q. v.*).—7. The K salt heated with $K_2S_2O_7$ forms $SO_3K.O.C_6H_4.CO_2K$ [220°–225°] (Baumann, *B.* 11, 1915).—8. When taken internally, it appears in the urine as oxybenzuric acid $C_6H_4(OH).CO.NH.CH_2.CO_2H$, crystallising in needles (Baumann a. Herter, *H.* 1, 260).

Salts.—NH_4A': needles, v. sol. cold water. —$CaA'_2\,3aq$: m. sol. water.—BaA'_2: gummy.—TlA'.—$Tl_2C_7H_4O_3$.—PbA'_2.—CdA'_2.—$CuA'_2\,aq$: green needles.

Acetyl derivative $C_6H_4(OAc).CO_2H$. [127°].

Ethyl ether EtA'. [72°]. (282°). Tables (from water), nearly insol. cold water. Conc. NaOHAq forms crystalline $C_6H_4(ONa).CO_2Et$.

Methyl derivative $C_6H_4(OMe).CO_2H$. [107°]. Formed from its methyl ether, and also by oxidising $CH_3.C_6H_4(OMe)$ with $KMnO_4$ (Oppenheim a. Pfaff, *B.* 8, 887). Formed also by the action of CO_2 and Na on $C_6H_4Br(OMe)$ (Körner, *Bull. Acad. Belg.* [2] 24, 155) and by boiling the sulphate of *m*-diazobenzoic acid with MeOH (Griess, *B.* 21, 979). White needles, v. sl. sol. cold water. It forms the salts $CaA'_2\,aq$ and AgA' and the ether $C_6H_4(OMe)CO_2Me$ which is formed by heating *m*-oxybenzoic acid with KOH and MeI at 140°.

Ethyl derivative $C_6H_4(OEt).CO_2H$. [137°]. Formed from its ethyl ether $C_6H_4(OEt).CO_2Et$ (263°) (Heintz, *A.* 153, 331) or by boiling the sulphate of diazo-benzoic acid with alcohol (Fittica, *B.* 11, 1209; Griess, *B.* 21, 979). Needles. Yields $CaA'_2\,2aq$, $BaA'_2\,2aq$, and AgA'.

Allyl derivative $C_6H_4(OC_3H_5).CO_2H$. [148°]. Colourless laminæ. Its ethyl ether is a thick pungent oil (284°) (Scichilone, *G.* 12, 449).

Phenyl derivative $C_6H_4(OPh).CO_2H$. [145°]. Formed by the action of phenol on the sulphate of *m*-diazo-benzoic acid (Griess, *B.* 21, 980). Needles, almost insol. hot water. Yields BaA'_2 3½aq.

Amide $C_6H_4(OH).CONH_2$. [167°]. Formed from the ether and conc. NH_3Aq (Schulerud, *J. pr.* [2] 22, 290). Thin plates (from water), sol. alcohol and ether, insol. chloroform.

Anilide $C_6H_4(OH).CONHPh$. [155°]. Needles, insol. water (Kupferberg, *J. pr.* [2] 16, 442).

Nitrile $C_6H_4(OH).CN$. [82°]. Formed by the diazo- reaction from $C_6H_4(NH_2).CN$ by displacing NH_2 by OH (Griess, *B.* 8, 859) or from $C_6H_4(NH_2).OH$ by displacing amidogen by Cy (Ahrens, *B.* 20, 2953). Plates (from water) with intensely sweet taste. Its acetyl derivative $C_6H_4(OAc).CN$ [60°] is got by boiling *m*-oxy-benzaldoxim with Ac_2O (Clemm, *B.* 24, 827).

Anhydride $C_{14}H_{10}O_5$. Formed, together with an anhydride $C_{56}H_{34}O_{17}$ [165°] by the action of $POCl_3$ at 45° on *m*-oxy-benzoic acid (Schiff, *B.* 15, 2588). Minute crystals, sol. boiling alcohol.

Tetra-hydride $CH_2{<}{\begin{smallmatrix}CO\,.\,CH_2\\CH_2.CH_2\end{smallmatrix}}{>}CH.CO_2H$. Formed by warming the tetrahydride of oxy-terephthalic acid with water (Baeyer a. Lutein, *B.* 22, 2183). Mixes with water. Forms the hygroscopic salt NaA′ crystallising in slender needles. Yields an oxim $C_7H_{11}NO_3$ [170°] and a phenyl-hydrazide $C_{17}H_{16}N_2O_2$ [125°].

***p*-Oxy-benzoic acid** $C_6H_4(OH).CO_2H$. [213°]. S. ·173 at 0° (Ost, *J. pr.* [2] 17, 230); ·8 at 15° (Saytzeff). H.F. 113,000 (Von Rechenberg); 139,100 (Stohmann, *J. pr.* [2] 40, 130). H.C. 725,900.

Formation.—1. By heating anisic acid with conc. HIAq at 130° for 12 hours (Saytzeff, *A.* 127, 129).—2. By the action of nitrous acid on *p*-amido-benzoic acid (G. Fischer, *A.* 127, 145). 3. By potash-fusion from *p*-sulpho-benzoic acid (Remsen, *Z.* [2] 7, 81; *A.* 178, 281), anethol (Ladenburg, *A. Suppl.* 8, 87), anisic acid (Barth, *Sitz. W.* 54 [2] 633), gum benzoïn, acaroid resin (Hlasiwetz a. Barth, *A.* 134, 265; 138, 61), tyrosine (Barth, *A.* 136, 110; Ost, *J. pr.* [2] 12, 159), carthamin (Malin, *A.* 136, 115), phloretic acid, *p*-cresol, and even benzoic acid (Barth, *A.* 152, 96; 154, 359; 164, 141; *M.* 3, 802).—3. By passing CO_2 through C_6H_5OK dissolved in boiling phenol, or, better, by heating C_6H_5OK in a current of CO_2 at 170°–210° (Kolbe, *J. pr.* [2] 8, 336; 10, 89, 451; 11, 24; Ost, *J. pr.* [2] 11, 385; Hartmann, *J. pr.* [2] 16, 35). At 130°–150° the product is salicylic acid.—4. The basic salt $C_6H_4(OK).CO_2K$ is formed, together with CO_2 and phenol, by heating potassium (but not sodium) salicylate at 220°. A mixture of salicylic acid (1 mol.) and excess of KOH (3 mols.) is not affected at 250°, but at 300° yields only K_2CO_3 and C_6H_5OK.—5. Together with a smaller quantity of salicylic acid by heating phenol with alcoholic potash (or soda) and CCl_4. The reaction takes place less quickly in aqueous solution (Tiemann a. Reimer, *B.* 9, 1285; Hasse, *B.* 10, 2186).

Properties.—Monoclinic crystals (containing aq); $a:b:c = 1{\cdot}370:1:1{\cdot}102$; $\beta = 105°\ 26'$. V. sol. hot water, alcohol, and ether, sl. sol. chloroform (unlike salicylic acid) and CS_2 (unlike benzoic acid). Split up at 220° into CO_2 and phenol. With iodine and potash it gives a pale-red pp., which becomes yellow on acidifying (Messinger a. Vortmann, *B.* 22, 2321). Not attacked by hydroxylamine. With $FeCl_3$ it gives a yellow amorphous pp. Excess of bromine-water gives CO_2 and tri-bromo-phenol.

Reactions.—1. *p*-Oxy-benzoic acid (1 mol.) is converted by PCl_5 (1 mol.) into $C_7H_4Cl_3PO_3$ *i.e.* $C_6H_4(COCl)OPOCl_2$ (176° at 14 mm.). S.G. $\frac{20}{4}$ 1·542. This chloride shows the following reactions: (*a*) Water forms *p*-carboxy-phenyl-phosphoric acid $C_6H_4(CO_2H)OPO(OH)_2$ which forms plates [200°], v. sol. water, alcohol, and ether. It is not decomposed by boiling aqueous KOH, but water at 160° forms phosphoric acid and *p*-oxy-benzoic acid. (*b*) Distillation under atmospheric pressure somewhat decomposes it. (*c*) The chloride (1 mol.) heated with PCl_5 (1 mol.) at 160° forms *p*-chloro-benzoyl chloride, $C_6H_4Cl.COCl$ (Anschütz a. Moore, *A.* 239, 342). 2. On distillation half of it splits up into phenol and CO_2, the rest yields several anhydrides.—3. The K salt when distilled yields diphenylene oxide, di-phenylene-ketone oxide, and phenol (Goldschmiedt, *M.* 4, 127).—4. Yields 50 or 60 p.c. of the theoretical amount of phenol on fusion with NaOH (Barth a. Schreder, *B.* 12, 1257).—5. The Na salt heated in a current of CO_2 at 290° yields salicylic acid (Kupferberg, *J. pr.* [2] 16, 424).—6. The Ca salt on dry distillation yields phenol, CO_2, salicylic acid, oxy-isophthalic acid, diphenylene oxide, and di-phenylene-ketone oxide.—7. H_2SO_4 at 100° forms $C_6H_3(OH)(SO_3H).CO_2H$ (Klepl, *J. pr.* [2] 28, 196).—8. The K salt heated with $K_2S_2O_7$ forms $C_6H_4(CO_2K).O.SO_3K$ (Baumann, *B.* 11, 1916).—9. Taken internally it appears in the urine as *p*-oxy-benzuric acid $C_9H_9NO_4$ [c. 228°].

Salts.—NaA'_2 5aq: very soluble efflorescent plates.—$Na_2C_7H_4O_3$.—KA′ 3aq.—NH_4A'aq: long efflorescent prisms.—CaA'_2 4aq: slender needles.—BaA'_2 aq: flat needles.—BaA'_2 2aq: rhombohedra.—$BaC_7H_4O_3$: sandy powder.—TlA′.—CdA'_2 4aq.—CdA'_2 6aq.—ZnA'_2 8aq.—PbA'_2 2aq. CuA'_2 6aq.—AgA′ 2aq.

Acetyl derivative $C_6H_4(OAc).CO_2H$. [185°]. By heating the acid with Ac_2O. Silvery plates (from $CHCl_3$).

Methyl ether MeA′. [117°]. (283°). H.F. 138,800. Formed from the acid, KOH, and MeI (Ladenburg a. Fitz, *A.* 141, 250). Large tables (from ether), v. sl. sol. hot water.

Ethyl ether EtA′. [112·5°] (G.); [116°] (Hartmann). (298°). H.F. 147,690. Formed from the acid, alcohol, and HCl (Graebe, *A.* 139, 134). Crystalline. Yields solid $C_6H_4(ONa).CO_2Et$.

Phenyl ether PhA′. [176°]. Present in the volatile product of the destructive distillation of *p*-oxy-benzoic acid (Klepl, *J. pr.* [2] 28, 214). Trimetric tablets (from chloroform). Saponified by cold NaOHAq. With alcohol and HCl it yields phenol and *p*-oxy-benzoic acid. The acetyl derivative $C_6H_4(OAc).CO_2Ph$ crystallises in long plates [84°].

Methyl derivative $C_6H_4(OMe).CO_2H$. *Anisic acid.* Mol. w. 152. [184°]. (275°–280°).

S. ·04 at 18°. H.C.p. 895,200. H.F. 132,800 (Stohmann, *J. pr.* [2] 40, 131). Formed by oxidation of anise-camphor, and of oils of anise, fennel, and tarragon, being derived from the anethol contained therein (Cahours, *A. Ch.* [3] 2, 287; 14, 483; 23, 351; 25, 21; 27, 439; Laurent, *Rev. scient.* 10, 6, 362; Gerhardt, *A. Ch.* [3] 7, 292; Ladenburg, *A.* 141, 241). Obtained also from its methyl ether, which is formed by heating *p*-oxy-benzoic acid (1 mol.) with KOH (2 mols.) and MeI (2 mols.) at 120° (Ladenburg). It is a product of the oxidation of chica (Erdmann, *J. pr.* 71, 198). It is also produced by oxidising $C_6H_4Me(OMe)$ (Körner, *Bl.* [2] 10, 468) and by boiling the sulphate of *p*-diazobenzoic acid with MeOH (Griess, *B.* 21, 979). Prepared by mixing basic potassic *p*-oxybenzoate (got by heating potassic salicylate at 220°, or by adding KOH to a solution of *p*-oxybenzoic acid) with a solution of $KMeSO_4$ and evaporating to dryness. The residue is treated with HCl, and the anisic acid separated from undecomposed *p*-oxybenzoic acid by solution in chloroform (E. v. Meyer a. P. Richter, *J. pr.* [2] 32, 429). Monoclinic prisms, m. sol. hot water. Yields, on nitration, $C_6H_3(NO_2)(OMe)CO_2H$, $C_6H_3(NO_2)_2OMe$, and $C_6H_2(NO_2)_3OMe$. HIAq converts it into MeI and *p*-oxy-benzoic acid (Graebe, *A.* 139, 148). When taken internally it passes into the urine as anisuric acid (*q. v.*). $POCl_3$ forms the anhydride $C_{16}H_{14}O_5$ [99°] (Pisani, *A.* 102, 284). PCl_5 forms crystalline $C_6H_4(OMe).COCl$. Forms the salts NH_4A', KA', NaA' ½aq, NaA' 5aq, BaA'_2, SrA'_2 aq, CaA'_2 aq, MgA'_2 4aq, PbA'_2 aq, ZnA'_2 3aq, CdA'_2 3aq, Pb(OH)A', $Cr_2A'_3(OH)_3$, MnA'_2 3aq, CoA'_2 3aq, NiA'_2 3aq, CuA'_2 3aq, CuA'(OH), and AgA' (Borrella, *G.* 15, 303). Its ethers are MeA' [47°], (255°) and EtA' (c. 253°). Its amide $C_6H_4(OMe).CONH_2$ [163°] is formed by the action of NH_3 on $C_6H_4(OMe).COCl$. It is also formed by passing cyanic acid vapour and dry HCl through C_6H_5OMe containing $AlCl_3$, and by the action of $ClCONH_2$ and $AlCl_3$ on C_6H_5OMe dissolved in CS_2 (Gattermann, *A.* 244, 62; *B.* 23, 1197). It crystallises from water in needles or plates. The anilide $C_6H_4(OMe).CONPhH$ [169°] is formed by the action of phenyl cyanate on anisole containing $AlCl_3$ (Leuchart a. Schmidt, *B.* 18, 2338). The nitrile $C_6H_4(OMe).CN$, [62°], (254°), is formed by heating the amide alone or with PCl_5 (Henry, *Z.* [2] 6, 209; *B.* 2, 667), and by heating $C_6H_4(OMe).CH{:}NOH$ with AcCl at 115° (Miller, *B.* 22, 2791). It crystallises in needles, v. sol. alcohol and ether. Hydroxylamine converts it into $C_6H_4(OMe)C(NH_2)NOH$ [123°].

Ethyl derivative $C_6H_4(OEt).CO_2H$. [195°]. Formed from its ether EtA' (275°) which is got from *p*-oxy-benzoic acid, KOH, and EtI (L. a. F.). Got also by oxidising the ethyl derivative of phloretic acid with chromic acid mixture (Körner a. Corbetta, *B.* 7, 1731); and by boiling the sulphate of *p*-diazo-benzoic acid with alcohol (Griess, *B.* 21, 980). Needles. Yields AgA' crystallising in needles. The amide $C_6H_4(OEt).CONH_2$ [202°] (G.), [206°] (P.), is formed by the action of cyanic acid or $ClCONH_2$ on C_6H_4OEt in presence of $AlCl_3$ (Gattermann, *A.* 244, 63; *B.* 23, 1197), and by adding NaOHAq to *p*-ethoxy-benzamidine hydrochloride (Pinner, *B.* 23, 2954). The anilide $C_6H_4(OEt).CONHPh$ [170°] is formed by the action of phenyl cyanate on phenetole in presence of $AlCl_3$ (L. a. S.). The nitrile $C_6H_4(OEt).CN$ [69°], (258°), is got from $C_6H_4(OEt).NH_2$ by Sandmeyer's reaction (Pinner, *B.* 23, 2953). It is volatile with steam.

Ethylene derivative. The amide $C_2H_4(OC_6H_4.CONH_2)_2$ [280°] is formed by the action of $ClCONH_2$ on $C_2H_4(OPh)_2$ in CS_2, in presence of $AlCl_3$ (Gattermann, *A.* 244, 69).

Allyl derivative $C_3H_5O.C_6H_4.CO_2H$. [123°]. Formed from its ether EtA' [109°] (260°) which is got by heating *p*-oxy-benzoic ether with KOH and allyl iodide at 120° (Scichilone, *G.* 12, 451).

Phenyl derivative $C_6H_4(OPh).CO_2H$. [160°]. Obtained by the action of phenol on the sulphate of *p*-diazo-benzoic acid (Griess, *B.* 21, 980), and also by the action of boiling alcoholic potash upon $C_6H_4(OPh).CO_2Ph$, a white sublimate [73°–78°] got by strongly heating *p*-oxybenzide in a current of hot CO_2 (Klepl, *J. pr.* [2] 28, 200).

Phenoxy-ethyl derivative $C_2H_4(OPh).O.C_6H_4.CO_2H$. [196°]. Satiny needles (from alcohol) (Wagner, *J. pr.* [2] 27, 227). Its ether EtA' [81°] is crystalline.

Nitro-phenoxy-ethyl derivative $C_6H_4(NO_2).O.C_2H_4.O.C_6H_4CO_2H$. The *o*-compound [207°] forms an ether EtA' [103°] crystallising from alcohol in plates, and may be reduced to $C_6H_4(NH_2).O.C_2H_4O.C_6H_4.CO_2H$ [185°]. The *p*- isomeride [218°] forms a salt NaA'3aq and an ether EtA' [131°] crystallising in minute needles.

Amide $C_6H_4(OH).CONH_2$. [162°]. Needles (containing aq). Forms the sodium compounds $C_6H_4(ONa).CONH_2$ and $C_6H_4(ONa).CONH_3Cl$ [206°]. Yields *p*-oxy-benzyl alcohol on reduction with sodium-amalgam (Hutchinson, *B.* 24, 175).

Anilide $C_6H_4(OH).CONPhH$. [197°]. Yellow plates, v. sol. alcohol.

Piperidide $C_6H_4(OH).CONC_5H_{10}$. [210°]. Prisms (from dilute alcohol) (Schotten, *B.* 21, 2254).

Nitrile $C_6H_4(OH).CN$. *p-Cyanophenol.* [113°]. Formed by distilling ammonium *p*-oxybenzoate with P_2O_5 (Hartmann). Formed also from *p*-amido-phenol by Sandmeyer's reaction (Ahrens, *B.* 20, 2954), and by the action of NH_3 on *p*-oxy-benzide. Thin trimetric laminæ; $a{:}b{:}c = \cdot855{:}1{:}2\cdot308$. M. sol. hot water. Forms an acetyl derivative $C_6H_4(OAc).CN$, [57°], (266°), crystallising in white needles.

Anhydride $C_7H_4O_2$. *p-Oxybenzide.* Left in the retort after distilling *p*-oxy-benzoic acid below 350° (Klepl, *J. pr.* [2] 25, 525; 28, 194). White amorphous powder, blackening at 350° without melting. Insol. alcohol. Reconverted into *p*-oxy-benzoic acid by boiling KOHAq; not attacked by NH_3 or Na_2CO_3Aq. Heated in sealed tubes with PCl_5 it yields $C_6H_4Cl.CCl_3$.

Anhydride $C_{14}H_{10}O_5$ *i.e.* $CO_2H.C_6H_4.O.CO.C_6H_4.OH$. [261°]. A product of the action of heat on *p*-oxy-benzoic acid. Minute needles, v. sol. alcohol. Quickly converted by alkalis into *p*-oxy-benzoic acid. Yields NaA', BaA'_2, and $C_{14}H_9AcO_5$ [217°].

Anhydride $C_{21}H_{14}O_7$ *i.e.* $CO_2H.C_6H_4.O.CO.C_6H_4.O.CO.C_6H_4.OH$. [280°]. S. (alcohol) ·45 in the cold, 1·3 at 78°. Accompanies *p*-oxybenzide. Crystalline powder. Con-

verted by potash into *p*-oxy-benzoic acid. Gives NaA' and $C_{21}H_{13}AcO_7$ [230°].

Anhydride $C_{28}H_{18}O_9$. Formed from the acid and $POCl_3$ (Schiff, *B.* 15, 2588). Insoluble powder.

Di-oxy-benzoic acid $C_7H_6O_4$ *i.e.* $C_6H_3(OH)_2CO_2H$ [3:2:1]. *Pyrocatechin carboxylic acid.* Mol. w. 154. [204°]. Formed in small quantity, together with protocatechuic acid by heating pyrocatechin (1 pt.) with ammonium carbonate (4 pts.) and water (5 pts.) at 140° (A. Miller, *C. J.* 41, 398; *A.* 220, 116). Formed also by heating iodosalicylic acid with KOH. Needles (containing 2aq), m. sol. water, v. sol. alcohol and ether. $FeCl_3$ gives a blue colour not destroyed by excess, but changed to violet-red by Na_2CO_3. Gives a flocculent pp. with $Pb(OAc)_2$.—BaA'_2 5aq: prisms. (S. of BaA'_2) 1 at 18°.

Isomeride *v.* PROTOCATECHUIC ACID.

s-**Di-oxy-benzoic acid** $C_6H_3(OH)_2CO_2H$ [5:3:1]. (α)-*Resorcylic acid.* [222°] (B. a. S.); [233°] (B.). Formed by fusing *s*-di-sulpho-benzoic acid with potash (Barth a. Senhofer, *A.* 159, 222). Formed also from bromo-sulpho-benzoic acid by potash-fusion (Böttinger, *B.* 8, 374). Prisms or needles (containing $1\frac{1}{2}$ aq), m. sol. cold water. Gives no colour with $FeCl_3$. Conc. H_2SO_4 at 140° forms a red solution whence water ppts. green flakes of anthrachrysone $C_{14}H_8O_6$. Yields resorcin on fusion with potash.

Salts.—NaA'aq.—$BaA'_2$4aq.—$CuA'_2$$6\frac{1}{2}$aq.—$CdA'_2$$4\frac{1}{2}$aq.—$AgA'$aq: crystalline pp.

Ethyl ether EtA'. [below 100°]. Prisms.

Methyl ether of the methyl derivative $C_6H_3(OH)(OMe)CO_2Me$. (315°). Formed, together with $C_6H_3(OMe)_2CO_2Me$ from *s*-di-oxy-benzoic acid, MeI, and KOH (Meyer, *M.* 8, 430). Oil.

Di-methyl derivative $C_6H_3(OMe)_2CO_2H$. [176°]. Formed by methylation and also by oxidation of the di-methyl ether of orcin (Tiemann a. Streng, *B.* 14, 2002). White needles, sol. hot water.—AgA': crystalline pp.

Methyl ether of the di-methyl derivative $C_6H_3(OMe)_2CO_2Me$. [81°]. (298°). Four-sided prisms (M.).

Di-ethyl derivative $C_6H_3(OEt)_2CO_2H$. [88°]. Prisms. Forms oily $C_6H_3(OEt)_2CO_2Et$.

Di-oxy-benzoic acid $C_6H_3(OH)_2CO_2H$ [4:2:1]. (β)-*Resorcylic acid.* [205°]. S. ·26 at 17°. H.F. 188,100. H.C.p. 676,900 (Stohmann, *J. pr.* [2] 40, 132).

Formation.—1. From $C_6H_3Me(OH)(SO_3H)$ [1:2:4] by heating with KOH (Ascher, *A.* 161, 11). 2. From toluene disulphonic acid by oxidation and potash-fusion (Blomstrand, *B.* 5, 1088; Fahlberg, *Am.* 2, 196).—3. By oxidation of its aldehyde or of umbelliferone (Tiemann a. Reimer, *B.* 12, 997; 13, 2358).—4. By heating resorcin with ammonium carbonate and water at 125° (Brunner a. Senhofer, *B.* 13, 2356).—5. By oxidising morin with HNO_3 (Benedikt a. Hazura, *M.* 5, 170).—6. By warming $C_6H_3(OH)_2CS_2H$ with acid (Lippmann, *M.* 9, 306; 10, 620).

Preparation.—20 pts. of resorcin are heated for an hour and a half with a solution of 100 pts. of potassium or sodium hydric carbonate in 200 grms. of water; the yield is 80 p.c. of the resorcin (Bistrzycki a. Kostanecki, *B.* 18, 1984).

Properties. — Crystallises from ether in needles (containing 3aq) and from water in prisms (containing $\frac{1}{2}$aq, $1\frac{1}{2}$aq, or $2\frac{1}{2}$aq). Decomposes at its melting-point into CO_2 and resorcin. $FeCl_3$ colours its solution dark rose-red. Bleaching-powder gives a violet tint, changing to brown. By treating the acid with $C_6H_3(OH)_2CO_2H$ [5:2:1] and Ac_2O and distilling the product there is formed euxanthone $\left[\begin{smallmatrix}4 & 1\\ & 2\end{smallmatrix}\right]C_6H_3(OH)<\begin{smallmatrix}CO\\O\end{smallmatrix}>C_6H_3(OH)\left[\begin{smallmatrix}1 & \\ 2 & 5\end{smallmatrix}\right]$ (Graebe, *B.* 22, 1405).

Salts.—KA'aq.—$BaA'_2$4aq.—$BaA'_2$7aq.—$CuA'_2$8aq.—AgA'.

o-Methyl derivative $C_6H_3(OH)(OMe)CO_2H$ [4:2:1]. Formed by oxidising $C_6H_3(OAc)(OMe)CHO$ (Tiemann a. Parrisius, *B.* 13, 2354). Crystalline. Sol. water. Gives no colour with $FeCl_3$.

p-Methyl derivative $C_6H_3(OMe)(OH)CO_2H$ [4:2:1]. [154°]. S. ·7 at 20°. Got by partial methylation of the acid (T. a. P.), and also by the action of CO_2 on $C_6H_4(ONa)(OMe)$ at 215° (Körner a. Bertoni, *Rendiconti d. R. Istit. Lombardo*, 13, 741; *B.* 14, 847). Needles, sol. hot water. Gives a reddish-violet colour with $FeCl_3$.—NaA'aq.—KA'.—$BaA'_2$4aq.—PbA'_2aq.

Di-methyl derivative $C_6H_3(OMe)_2CO_2H$. [108°]. Got by methylation (T. a. P.) and by oxidation of the di-methyl derivative of (β)-methyl-umbellic acid (Pechmann, *B.* 16, 2126; 17, 2133). Needles, sl. sol. cold water.—CuA'_2.—PbA'_2.—AgA': white pp.

Di-ethyl derivative $C_6H_3(OEt)_2CO_2H$. [99°]. Got from the aldehyde (Tiemann a. Lewy, *B.* 10, 2215).

Di-oxy-benzoic acid $C_6H_3(OH)_2CO_2H$ [6:2:1]. [c. 147°]. Formed, together with the (4, 2, 1)-isomeride, by heating resorcin with ammonium carbonate and water (B. a. S.). Obtained also from the methyl derivative of the nitrile (Lobry de Bruyn, *R. T. C.* 2, 205). Needles. Decomposes on fusion into CO_2 and resorcin. $FeCl_3$ gives a violet colour, changed to blue by excess. Bromine-water gives tri-bromo-resorcin.—BaA'_2aq.—$CuA'_2$8aq.—AgA': crystalline pp.

Di-methyl derivative $C_6H_3(OMe)_2CO_2H$. [179°]. Tables (from alcohol).

Nitrile of the di-methyl derivative $C_6H_3(OMe)_2CN$. [118°]. (310°). Formed from $C_6H_3(OMe)(NO_2)CN$ by boiling with MeOH and KOH. Crystals. Gives with nitric acid a nitro- compound $C_9H_8N_2O_4$ [111°]. The corresponding nitriles $C_6H_3(OMe)(OEt)CN$ [66°] and $C_6H_3(OEt)_2CN$ [122°] crystallise from alcohol, the former in trimetric crystals, $a:b:c$ = ·796:1:1·65, and the latter in di-metric crystals $a:c$ = 1: ·565 (Lobry de Bruyn, *R. T. C.* 3, 383).

Di-oxy-benzoic acid $C_6H_3(OH)_2CO_2H$ [5:2:1]. *Gentisic acid. Hydroquinone carboxylic acid.* [197°].

Formation.—1. By fusing iodo-salicylic acid [196°] or bromo-salicylic acid with KOH (Lautemann, *A.* 120, 299; Bakowsky a. Leppert, *B.* 8, 789; Miller, *A.* 220, 124; P. F. Frankland, *C. J.* 37, 750).—2. From oxy-amido-benzoic acid (Goldberg, *J. pr.* [2] 19, 371).—3. By fusing gentisin with potash (Hlasiwetz a. Habermann, *A.* 175, 66; Tiemann a. Miller, *B.* 14, 1988).—4. By digesting $KHCO_3$ (4 pts.) with hydroquinone (1 pt.) and water (4 pts.) (Senhofer a. Sarlay, *M.* 2, 448).

Properties.—Needles or prisms, v. sol. water, alcohol, and ether. $FeCl_3$ colours its solution blue. Reduces Fehling's solution on heating. Split up on distillation into CO_2 and hydroquinone. Benzamidine forms a compound [266°] (Pinner, *B.* 23, 2939).

Salts.—$NaA'_2 5\frac{1}{2}aq$. Deliquescent prisms. —$KA'aq$.—$CaA'_2 7aq$.—BaA'_2. S. 40 at 18°.— $PbA'_2 2aq$.—$CuA'_2 4\frac{1}{2}aq$.

Ethyl ether EtA'. [75°]. Crystals.

m-Methyl derivative $C_6H_3(OH)(OMe)CO_2H$ [2:5:1]. [142°]. S. ·17 at 10°; 9 at 100°. Formed by oxidising the acetyl-methyl derivative of gentisic aldehyde $C_6H_3(OAc)(OMe)CHO$ with $KMnO_4$, and saponifying the product (Tiemann a. Miller, *B.* 14, 1997). Formed also by the action of CO_2 at 225° on $C_6H_4(ONa)(OMe)$ (Körner a. Bertoni). Needles. Its solution is coloured blue by $FeCl_3$.

Di-methyl derivative $C_6H_3(OMe)_2CO_2H$. [76°]. Formed by oxidising $C_6H_3(OMe)_2CHO$. Needles.—AgA': small white needles.

Tri-oxy-benzoic acid *v.* Gallic acid.

Tri-oxy-benzoic acid $C_6H_2(OH)_3CO_2H$.

Tri-methyl derivative $C_6H_2(OMe)_3CO_2H$. [109°]. Formed by oxidising the tri-methyl derivative of æsculetic acid (Will, *B.* 16, 2113).

Tri-ethyl derivative $C_6H_2(OEt)_3CO_2H$. [134°]. Formed by oxidation of the tri-ethyl derivative of (α)- or (β)- æsculetic acid with $KMnO_4$ (W.). Slender needles.

Tri-oxy-benzoic acid $C_6H_2(OH)_3CO_2H$ [4:3:2:1]. Mol. w. 170. [206°–220°]. S. ·13 at 12·5°. H.F. 231,300. H.C.p. 633,700 (Stohmann). Formed, together with pyrogallol dicarboxylic acid, by heating pyrogallol with ammonium carbonate (Senhofer a. Brunner, *M.* 1, 474; Kostanecki, *B.* 18, 3202; Schiff, *A.* 245, 35). Needles (containing $\frac{1}{3}aq$), sol. alcohol. $FeCl_3$ colours its dilute solution violet. Bleaching-powder and nitric acid do the same. Lime and baryta-water gives a bluish pp. Reduces ammoniacal $AgNO_3$ in the cold. H_2SO_4 does not form rufigallic acid (difference from gallic acid). $POCl_3$ forms an acid $C_{14}H_{10}O_9$ greatly resembling tannin. It is an astringent yellow powder and gives $Ba(C_{14}H_9O_9)_2$ and $C_{14}H_5Ac_5O_9$.

Salts.—$KA'aq$.—$NaA' 2aq$.—$BaA'_2 5aq$.— $CaA'_2 4aq$.—$Pb_2C_7H_2O_5 1\frac{1}{2}aq$: white flocculent pp.

Methyl ether $C_6H_2(OH)_3CO_2Me$. [152°]. Needles (containing $2\frac{1}{2}aq$).

Tri-methyl derivative $C_6H_2(OMe)_3CO_2H$. [99°]. Crystals (Will, *B.* 21, 2020).

Methyl ether of the tri-methyl derivative $C_6H_2(OMe)_3CO_2Me$. (281°). Oil.

Ethyl ether EtA'. [102°]. Colourless crystals (containing aq) melting at 86° when hydrated. $FeCl_3$ gives a greenish-brown colour (Will a. Albrecht, *B.* 17, 2100; Schiff, *A.* 245, 40).

Tri-ethyl derivative $C_6H_2(OEt)_3CO_2H$. [100°]. Formed by oxidation of the tri-ethyl derivative of daphnetic acid with $KMnO_4$ (Will, *B.* 17, 1088, 2099). Silky needles, sl. sol. cold water.—BaA'_2.—AgA'. Gives $C_6H_3(OEt)_3$ when heated.

Ethyl ether of the tri-ethyl derivative $C_6H_2(OEt)_3CO_2Et$. Oil. Formed by ethylating the acid.

Tri-oxy-benzoic acid $C_6H_2(OH)_3CO_2H$. *Phloroglucin carboxylic acid.* Formed by boiling phloroglucin (1 pt.) with $KHCO_3$ (4 pts.) and water (4 pts.) (Will a. Albrecht, *B.* 17, 2103; 18, 1323). Colourless crystals (containing aq), sol. alcohol and ether. Split up by boiling water into CO_2 and phloroglucin. $FeCl_3$ gives a transient blue colour. Alcohol and HCl yields CO_2 and the diethyl ether of phloroglucin. On heating with $POCl_3$ it gives an isomeride of tannin, which is, however, not very astringent and gives no colour with $FeCl_3$ (Schiff).

Tri-methyl derivative? $C_6H_2(OMe)_3CO_2H$. *Asaronic acid.* [144°]. (300°). Formed by oxidising asarone with boiling aqueous $KMnO_4$ (Butlerow a. Rizza, *J. R.* 19, 3). Needles. On distillation with lime it yields $C_6H_3(OMe)_3$ (246°).

References.—Bromo-, Bromo-nitro-, Chloro-, Chloro-iodo-, Chloro-nitro-, Iodo-, and Iodo-nitro-oxy-benzoic acids.

o-OXY-BENZOIC ALDEHYDE $C_7H_6O_2$ *i.e.* $C_6H_4(OH).CHO$. *Salicylic aldehyde.* Mol. w. 122. [c. −20°]. (196·5°). S.G. $\frac{20}{4}$ 1·1671 (Brühl). μ_β 1·5960. R_∞ 54·53. Occurs in the blossom of the meadow-sweet (*Spiræa ulmaria*) (Ettling, *A.* 35, 247) and in *Crepis fœtida* (Wicke, *A.* 91, 374).

Formation.—1. By oxidation of saligenin or salicin (Piria, *A.* 30, 153).—2. In the products of the dry distillation of quinic acid (Wöhler, *A.* 51, 146).—3. By mixing chloroform (15 pts.), phenol (10 pts.), NaOH (20 pts.), and water (35 pts.), at 50°, boiling with inverted condenser, distilling off excess of chloroform, acidifying and distilling with steam (Tiemann a. Reimer, *B.* 9, 423, 824).

Properties.—Liquid, with pleasant odour, v. sl. sol. water, miscible with alcohol and ether. Turns red in air. Added to 'Vermouth' and other liqueurs. Produces epileptic convulsions in dogs (Laborde a. Magnan, *J. Ph.* [5] 16, 448). $FeCl_3$ colours its aqueous solution violet. Does not reduce Fehling's solution. Combines with $KHSO_3$ forming $C_7H_6O(OH)SO_3K$ crystallising in needles (Bertagnini, *A.* 85, 193).

Reactions.—1. Yields o-oxy-benzoic acid on *oxidation.*—2. *Sodium-amalgam* reduces it to saligenin (Beilstein a. Reinecke, *A.* 128, 179).— 3. Heated with $ZnCl_2$ and HOAc it forms red amorphous $C_{14}H_{10}O_3$, insol. water, which dissolves in alkalis with violet-red colour but is insol. acids. It yields amorphous $C_{14}H_9AcO_3$ (Bourquin, *B.* 17, 502).—4. Ac_2O (2 mols.) at 180° forms $C_6H_4(OAc).CH(OAc)_2$ [100°] which splits up on distillation into Ac_2O and $C_6H_4(OAc).CHO$ (255°). On treatment with soda the compound $C_6H_4(OAc).CH(OAc)_2$ yields $C_6H_4(OH).CH(OAc)_2$ [104°] (Barbier, *C. R.* 90, 37).—5. *Acetyl chloride* yields 'disalicyl aldehyde' $C_{14}H_{10}O_3$ [130°]. The same body is formed by the action of BzCl, succinyl chloride, and PCl_3 (Cahours, *A.* 78, 228; Perkin, *A.* 145, 299; Zwenger, *A. Suppl.* 8, 42). It crystallises from alcohol in long needles, and is converted by Br in HOAc to $C_{14}H_8Br_2O_3$ [166°], together with $C_6H_3Br(OH).CHO$ [105°] and $C_6H_2Br_2(OH).CHO$ [83°] (Bradley, *B.* 22, 1134). 6. *Zinc-dust* and HOAc form $C_{14}H_{10}O_2$ crystallising in needles [82°] (Tiemann, *B.* 19, 357).—7. *Bromine* forms $C_6H_2Br_2(OH).CHO$ and $C_6H_2Br_4O$ (Werner, *Bl.* [2] 46, 277).—8. *Cyanogen*

bromide forms crystalline $C_8H_5NO_2$ (Cahours, *A.* 108, 322).—9. *Ammonium cyanide* and alcohol form $C_{22}H_{18}N_2O_4$ [143°] and $C_{29}H_{21}N_3O_3$ [168°] (Haarmann, *B.* 6, 341).—10. *Sodium succinate* and acetic anhydride form, on heating, dicoumarin $C_6H_4\!<\!\begin{matrix}O & .\dot{C}O & \dot{C}O.O & \\ CH{:}\dot{C} & — & \dot{C} & {:}CH\end{matrix}\!>\!C_6H_4$ (Fittig, *B.* 18, 2523).—11. *Thioglycollic acid* and zinc chloride form $C_6H_4(OH).CH(SCH_2.CO_2H)_2$ [148°] (Bongartz, *B.* 21, 480).—12. Gaseous or alcoholic *ammonia* gives rise to 'hydrosalicylamide' $C_6H_4(OH).CH:N.CH(C_6H_4.OH).N:CH.C_6H_4.OH$ which forms yellow crystals [145°] (Ettling, *A.* 35, 249; Herzfeld, *B.* 10, 1270). It is insol. water, sl. sol. cold alcohol, and is decomposed by boiling acids and alkalis into NH_3 and o-oxy-benzoic aldehyde. It is converted by alcoholic ammonium sulphide into crystalline $C_{21}H_{18}N_2SO_2$, and by HCy and HCl into two isomeric crystalline 'hydrocyansalides' $C_{22}H_{16}N_2O_3$ (Beilstein, *A.* 136, 170). Hydrosalicylamide forms the salts $FeC_{21}H_{15}N_2O_3NH_3$ and $Cu_3(C_{21}H_{15}N_2O_3)_22NH_3$.—13. *Methylamine* gas forms $C_6H_4(OH).CH:NMe$ an oil (229°), resolved by acids and alkalis into NH_2Me and salicylic aldehyde (Dennstedt a. Zimmermann, *B.* 21, 1553).—14. *Ethylamine* forms the homologous $C_9H_{11}NO$ (237°).—15. *Aniline* forms $C_6H_4(OH).CH:NPh$ [50·5°] (Schischkoff, *C. R.* 45, 272; Emmerich, *A.* 241, 344). It forms a crystalline compound with HCy. *p-Nitro-aniline* forms the compound $C_6H_4(NO_2).N:CH.C_6H_4OH$ [115°].—16. *Di-methyl-p-phenylene diamine* forms in like manner $C_6H_4(OH).CH:N.C_6H_4NMe_2$ [134°] (Nuth, *B.* 18, 573). Di-methyl-aniline and $ZnCl_2$ form $C_6H_4(OH).CH(C_6H_4NMe_2)_2$.—17. *Benzidine* in weak alcoholic solution forms the compound $C_{12}H_8[N:CH.C_6H_4.OH]_2$ crystallising from benzene in colourless needles [260°]. Di-amido-ditolyl forms the homologous $C_{14}H_{12}[N:CH.C_6H_4.OH]_2$ [202°] (Schiff a. Vanni, *A.* 258, 374).—18. *Ethylene-diamine* forms $C_2H_4(N:CH.C_6H_4OH)_2$ [126°] (Mason, *B.* 20, 271).—19. *Ethylene-aniline* forms $C_2H_4:(NPh)_2:CH.C_6H_4OH$ [116°] (Moos, *B.* 20, 733).—20. *p-Toluidine* gives rise to $C_6H_4Me.N:CH.C_6H_4.OH$ [100°] (Jaillard, *Z.* 1865, 440).—21. *Phenylene-m-diamine hydrochloride* yields $C_6H_4(N:CH.C_6H_4OH)_2$ forming crystalline $B'_2H_2PtCl_6$ (Schiff, *A.* 253, 329). Tolylene-*m*-diamine yields homologous $C_7H_6(N:CH.C_6H_4OH)_2$ [109°].—22. *Tolylene-o-diamine* forms a compound $C_{28}H_{22}N_2O_3$ [106°–110°] and azurine $C_{35}H_{32}N_4O_3$ [250·5°] which exhibits blue fluorescence in alkaline solution (Ladenburg, *B.* 11, 596).—23. (β)-*Naphthylamine* reacts forming $C_{10}H_7N:CH.C_6H_4OH$ [121°] (Emmerich, *A.* 241, 351).—24. *Urea* in aqueous solution gives crystalline $(NH_2.CO.NH)_2CH.C_6H_4OH$ whence $Cu(C_9H_{11}N_4O_3)_2$ (Schiff, *A.* 151, 199).—25. *m-Amido-benzoic acid* forms the compound $CO_2H.C_6H_4.N:CH.C_6H_4OH$ [190°] which forms an amide [186°] (Schiff, *A.* 210, 114).

Salts.—$KC_7H_5O_2$ aq: yellow tables. S. (alcohol) 5 (Michael, *Am.* 1, 309).—$NaHA'_2\frac{1}{2}$aq.—$BaA'_2$2aq.—$Pb(OH)A'$.—CuA'_2: brownish-green crystals.

Acetyl derivative $C_6H_4(OAc).CHO$. [37°]. (253°). Formed from $C_6H_4(ONa).CHO$ in ether by adding Ac_2O (Perkin, *A.* 148, 203; 150, 82).

Butyryl derivative $C_{11}H_{12}O_3$. (260°–270°). Oil.

Benzoyl derivative $C_6H_4(OBz).CHO$. Oil.

Glucoside v. Helicin.

Methyl derivative $C_6H_4(OMe).CHO$. [35°]. (238°). Formed from $C_6H_4(ONa).CHO$, MeI, and MeOH (Perkin, *A.* 145, 302; *C. J.* 55, 550; Voswinckel, *B.* 15, 2024). Thick prisms, nearly insol. water, m. sol. alcohol, v. sol. ether. Alcoholic HCl and H_2S form the (β)-thioaldehyde $C_{24}H_{24}S_3O_3$ [224°]. While at −10° the (α)-isomeride $C_{24}H_{24}S_3O_3$ [157°] is formed (Baumann a. Fromm, *B.* 24, 1446). Alcohol and colourless ammonium sulphide yield $C_{48}H_{48}S_5O_6$ [85°–88°]. When KCy followed by HCl is added to the ethereal solution of $C_6H_4(OMe).CHO$ there is formed $C_6H_4(OMe).CH(OH).CN$ [71°] whence alcoholic NH_3 at 70° yields $(C_6H_4(OMe).CHCy)_2NH$ [123°], and alcoholic aniline at 100° gives $C_6H_4(OMe).CH(NHPh).CN$ [61°] (V.). Ethylene-diamine at 120° forms crystalline $C_2H_4(N:CH.C_6H_4.OMe)_2$.

Ethyl derivative $C_6H_4(OEt).CHO$. [7°]. (249°) (Göttig, *B.* 10, 8; Perkin, *A.* 145, 306; *C. J.* 55, 551). With alcoholic NH_3 it yields crystalline $N_2(CH.C_6H_4.OEt)_3$, which is converted by heating at 165° into an amorphous isomeride yielding crystalline $B'_2H_2PtCl_6$ (Perkin, *A.* 145, 308). Forms with aniline oily $C_6H_4(OEt).CH:NPh$ (Schiff, *A.* 150, 195), and with ethyl-aniline oily $C_6H_4(OEt).CH(NEtPh)_2$. Aqueous urea forms crystalline $C_{11}H_{16}N_4O_3$ aq.

Isobutyl derivative $C_6H_4(OC_4H_9).CHO$. (265°). Oil (Baumann a. Fromm, *B.* 24, 1448). Alcoholic HCl and H_2S form the (α) [142°] and (β) [163°] isomerides $C_{33}H_{42}S_3O_3$. Ammonium sulphide yields $C_{44}H_{56}S_5O_4$ [52°–56°].

Benzyl derivative $C_6H_4(OC_7H_7).CHO$. [46°].

Derivatives of o-oxy-benzoic orth-aldehyde

$C_6H_4(OH).CH(OAc)_2$ [104°]. Formed from the aldehyde and Ac_2O at 150° (Perkin, *A.* 146, 371). Tables (from alcohol).

$C_6H_4(OAc).CH(OAc)_2$. [101°]. Needles (from alcohol).

$C_6H_4(OMe).CH(OAc)_2$. [75°]. Prisms.

$C_6H_4(OEt).CH(OAc)_2$. [89°]. Prisms, insol. Aq.

Oxim $C_6H_4(OH).CH:NOH$. [57°]. White crystals, resolved by warm HClAq into its components (Lach, *B.* 16, 1782; 17, 1572). Ac_2O converts it into acetyl-o-oxy-benzonitrile. The compound $NHPh.CO.O.C_6H_4.CH:NO.CO.NHPh$ [115°] is formed by phenyl cyanate (Goldschmidt a. Schulthess, *B.* 22, 3102).—$B'HCl$.—$C_6H_4(ONa).CH:NONa$ 3aq: small pearly scales.

Derivatives of the oxim

$C_6H_4(OMe).CH:NOH$. [92°]. With phenyl cyanate it yields $C_6H_4(OMe).CH:NO.CO.NHPh$ [105°] (Goldschmidt, *B.* 23, 2741).

$C_6H_4(OMe).CH:NOMe$. Oil.

$C_6H_4(OEt).CH:NOEt$. Oil.

$C_6H_4(OH).CH:NOC_7H_7$. The (α)-isomeride [63°] is formed from *o*-oxy-benzoic aldehyde and (α)-benzyl-hydroxylamine, while the (β)-isomeride [100°] is obtained by using (β)-benzyl-hydroxylamine (Beckmann, *B.* 23, 3319).

Phenyl hydrazide $C_6H_4(OH).CH:N.NHPh$. [143°]. Colourless needles (from alcohol) (Fischer, *B.* 17, 575; Rossing, *B.* 17, 3003). Yields $C_6H_4(OAc).CH:N.NAcPh$ [133°], which forms a crystalline dibromide converted by boiling alcohol into $C_6H_2Br_2(OAc).CH:N_2HPh$ [188°], which

yields $C_6H_2Br_2(OAc).CH:N_2AcPh$ [158°] and $C_6H_2Br_2(OH).CH:N_2HPh$ [148°].

m-**Oxy-benzoic aldehyde** $C_6H_4(OH).CHO$ [3:1]. [104°]. (240°). Formed by reduction of *m*-oxy-benzoic acid in acid solution by sodium-amalgam (Sandmann, *B.* 14, 969). Obtained also by oxidation and diazotisation from *m*-amido-cinnamic acid (Luff, *B.* 22, 294). Prepared from *m*-nitro-benzoic aldehyde by reduction and treatment of the amido- compound with nitrous acid (Tiemann a. Ludwig, *B.* 15, 2043). Needles (from water). Excess of Ac_2O forms $C_6H_4(OAc).CH(OAc)_2$ crystallising in plates [76°].

Acetyl derivative $C_6H_4(OAc).CHO$.(263°). Formed from the K salt and Ac_2O. Oil.

Methyl derivative $C_6H_4(OMe).CHO$.(230°).

Oxim $C_6H_4(OH).CH:NOH$. [87·5°]. Soft silky needles (Clemm, *B.* 24, 826).

Phenyl hydrazide $C_6H_4(OH).CH:N_2HPh$. [131°]. Prisms, v. sol. alcohol (Rudulph, *A.* 248, 102).

p-**Oxy-benzoic aldehyde** $C_6H_4(OH).CHO$ [4:1]. [115°]. Formed by heating its methyl derivative with HClAq at 200° (Bücking, *B.* 9, 527). Prepared, together with the o- isomeride, by the action of chloroform and alkalis on phenol (Tiemann a. Reimer, *B.* 9, 824; 10, 63).

Properties.—Needles (from water), v. sol. alcohol and ether. Not volatile with steam. $FeCl_3$ gives a slight violet tint to its aqueous solution. Reduces ammoniacal $AgNO_3$. With $NaHSO_3$ it forms the crystalline compound $C_6H_4(OH).CH(OH)SO_3Na$ [112°].

Reactions.—1. *Potash-fusion* forms *p*-oxy-benzoic acid.—2. *Sodium-amalgam* and water reduce it to $C_6H_4(OH).CH(OH).CH(OH).C_6H_4(OH)$ [222°] and the isomeric di-oxy-isohydrobenzoïn [198°] which forms the crystalline derivative $C_2H_2(OH)_2(C_6H_4OAc)_2$ [192°] (Herzfeld, *B.* 10, 1268; Tiemann, *B.* 19, 354).—3. *Bromine* ppts. $C_6H_2Br_2(OH).CHO$ [181°] and, when in excess, forms $C_6H_2Br_4O$ (Werner, *Bl.* [2] 46, 278).—4. Boiling Ac_2O (3 pts.) forms $C_6H_4(OAc).CH(OAc)_2$ [94°] (Tiemann a. Herzfeld, *B.* 10, 64; Barbier, *C. R.* 90, 37).—5. Heating with HOAc and $ZnCl_2$ forms red amorphous $C_{14}H_{10}O_3$, which gives a violet solution in alkalis (Bourquin, *B.* 17, 503).—6. *Ammonia* forms an oily compound.—7. *Aniline* in ethereal solution forms $C_6H_4(OH).CH:NPh$ [191°].—8. *p-Toluidine* yields the compound $C_6H_4(OH).CH:NC_7H_7$ [213°]. — 9. *Di-methyl-phenylene-diamine* gives rise to crystalline $C_6H_4(OH).CH:NC_6H_4NMe_2$ decomposing at 240° (Nuth, *B.* 18, 574). — 10. (β)-*Naphthylamine* forms $C_6H_4(OH).CH:NC_{10}H_7$ [220°] (Emmerich, *A.* 241, 356).

Acetyl derivative $C_6H_4(OAc).CHO$. (260°) (Barbier, *Bl.* [2] 33, 52; *C. R.* 90, 37); (265°) (T. a. H.). Formed from $C_6H_4(OK).CHO$ and Ac_2O. Oil.

Methyl derivative $C_6H_4(OMe).CHO$. *Anisic aldehyde.* Mol. w. 136. (248°). S.G. $\frac{18}{}$ 1·228. Formed, together with anisic acid, by oxidation of anethol or oil of aniseed (Cahours, *A. Ch.* [3] 14, 484; 23, 354; Rossel, *A.* 151, 25). Formed also by distilling calcium anisate with calcium formate (Piria, *A.* 100, 105) and by methylation of *p*-oxy-benzoic aldehyde (T. a. H.). Oil, forming with H_2SO_4 a crimson solution, turned violet on heating. With $NaHSO_3$ it forms crystalline $C_8H_7NaSO_4$ aq (Bertagnini, *A.* 85, 268). *Reactions.*—1. *Alcoholic potash* forms the corresponding alcohol and acid.—2. Alcoholic HCl and H_2S form $C_{24}H_{24}S_3O_3$ [183°] and, at -10°, an isomeride [127°] (Baumann a. Fromm, *B.* 24, 1442). Alcoholic H_2S forms the thio-aldehyde [75°-77°], while alcoholic ammonium sulphide forms a polymeric thioanisic aldehyde [92°] and the disulphide $(C_6H_4(OMe).CH_2)_2S_2$ (B. a. F.).—3. *Sodium-amalgam* forms two 'hydranisoïns' $C_6H_4(OMe).CH(OH).CH(OH).C_6H_4OMe$, melting at 172° and 125° (Samosadsky, *Z.* 1867, 678; 1868, 643). Boiling dilute H_2SO_4 converts the isomeride [172°] into $C_{16}H_{16}O_3$ [95°] (Rossel, *A.* 151, 36). *Zinc* and hydrochloric acid form $C_6H_4(OMe).CH_2OH$ and crystalline $C_{16}H_{16}O_3$ [215°]. — 4. Aqueous HCy (28 p.c.) forms $C_6H_4(OMe).CH(OH)CN$ [63°], which yields $C_6H_4(OMe).CH(OH).CO_2H$ on saponification (Tiemann a. Friedländer, *B.* 14, 1976).—5. Alcoholic KCy yields anisoïn.—6. *Succinic acid* yields $C_6H_4(OMe).CH:CH.CH_2.CO_2H$ and $C_6H_4(OMe).CH:CH.C(CO_2H):CH.C_6H_4OMe$ (Fittig, *B.* 18, 2523).—7. *Di-thio-glycol* gives rise to $C_6H_4(OMe).CH:S_2:C_2H_4$ [65°] (Fasbender, *B.* 21, 1476).—8. Aqueous *ammonia* produces 'anis-hydramide' $N_2(CH.C_6H_4OMe)_3$ [120°] converted at 170° into crystalline 'anisine' $C_{24}H_{24}N_2O_3$, which forms the salts B'HCl aq and $B'_2H_2PtCl_6$ (Bertagnini, *A.* 88, 128).—9. *Ethylene-diamine* forms $C_2H_4(N:CH.C_6H_4OMe)_2$ [111°] (Mason, *B.* 20, 272).—10. *Aniline* gives rise to crystalline $C_6H_4(OMe).CH:NPh$. — 11. *Ethylene-aniline* forms $C_6H_4(OMe).CH:(NPh)_2:C_2H_4$ [164°] (Moos, *B.* 20, 733).—12. *o-Toluidine* reacts, forming $C_6H_4(OMe).CH:NC_6H_4Me$ [32°]. The *p*-isomeride [92°] is also crystalline (Steinhart, *A.* 241, 340).—13. *Phenylene-di-methyl-p-diamine* forms $C_6H_4(OMe).CH:N.C_6H_4NMe_2$ [148°] (S.; *cf.* Nuth, *B.* 18, 574). — 14. *Tolylene-o-diamine* hydrochloride forms $C_{23}H_{22}N_2O_2$ [152°-156°] (Ladenburg, *B.* 11, 1660). — 15. (β)-*Naphthylamine* yields $C_6H_4(OMe).CH:NC_{10}H_7$ [98°].—16. *Acetamide* at 120°-180° forms $C_6H_4(OMe).CH(NHAc)_2$ [180°] (Schuster, *A.* 154, 80).—17. *Benzamide* gives $C_6H_4(OMe).CH(NHBz)_2$ [192°].—18. *Urea* forms crystalline $C_6H_4(OMe).CH(NH.CO.NH_2)_2$ and $C_{19}H_{24}N_6O_5$.—19. *Carbamic ether* and HCl give $C_6H_4(OMe).CH(NH.CO_2Et)_2$ (172°].

Oxim $C_6H_4(OH).CH:NOH$. [65°]. Formed from the aldehyde and hydroxylamine (Lach, *B.* 16, 1785). White needles. Converted by Ac_2O and by AcCl into $C_6H_4(OH).CN$. Yields $C_6H_4(ONa).CH:NONa$ 3aq.

Methyl derivative of the oxim $C_6H_4(OMe).CH:NOH$. (α)-Isomeride [62°]. Formed from anisic aldehyde and hydroxylamine (Westenberger, *B.* 16, 2993; Goldschmidt a. Polonowska, *B.* 20, 2407; 22, 3102; 23, 2163; Beckmann, *B.* 21, 768; 23, 1687; Miller, *B.* 22, 2790). White plates, m. sol. hot water. Tastes sweet. Heated with Ac_2O and HCl it gives $C_6H_4(OMe).CN$ [61°]. NaOEt and benzyl chloride yield the (α)-benzyl ether [46·5°]. Ac_2O forms $C_6H_4(OMe).CH:NOAc$ [48°] (Hantzsch, *B.* 24, 41), crystallising in prisms. Phenyl cyanate forms $C_6H_4(OMe).CH:NO.CO.NHPh$ [82°]. NaOMe and MeI form $C_6H_4(OMe).CH:NOMe$ [43°] (246°).—(β)-Isomeride [130°]. Ppd. as hydrochloride by passing HCl into an ethereal solution of the (α)-isomeride. Slender needles. Has no taste. With NaOEt and benzyl chloride it yields the

(β)-benzyl ether [107°]. The acetyl derivative $C_6H_4(OMe).CH:NOAc$ [64°] is converted by Na_2CO_3Aq into the nitrile [60°].

Phenyl-hydrazide $C_6H_4(OH).CH:N_2HPh$ [178°]. Tufts of needles (Rudolph, *A.* 248, 102).

Phenyl-hydrazide of the methyl derivative $C_6H_4(OMe).CH:N_2HPh$. [121°].

c-**Di-oxy-benzoic aldehyde.** *m-Methyl derivative* $C_6H_3(OMe)(OH).CHO$ [3:2:1]. (264°–268). Formed, together with vanillin, by the action of chloroform on a solution of guaiacol in dilute NaOH (Tiemann a. Koppe, *B.* 14, 2020). Liquid, volatile with steam; sol. alcohol, ether, and benzene, nearly insol. water. $FeCl_3$ colours its alcoholic solution violet.

Di-oxy-benzoic aldehyde $C_6H_3(OH)_2CHO$ [4:2:1]. (β)-*Resorcylic aldehyde.* [135°]. Formed by the action of chloroform and NaOHAq on resorcin (Tiemann a. Lewy, *B.* 10, 2212). Needles (from water), v. sol. water, alcohol, and ether. $FeCl_3$ colours the aqueous solution reddish-brown. Readily resinified.

o-*Methyl derivative* $C_6H_3(OH)(OMe)CHO$ [4:2:1]. [153°]. Formed, together with the *p*-methyl derivative, by the action of chloroform and NaOH on $C_6H_4(OH)(OMe)$ [1:3] (Tiemann a. Parrisius, *B.* 13, 2365). Colourless plates, sl. sol. water. Gives white crystalline pps. with ammoniacal $AgNO_3$, and with $Pb(OAc)_2$. Yields an acetyl derivative $C_6H_4(OAc)(OMe)CHO$ [86°].

p-Methyl derivative $C_6H_3(OMe)(OH)CHO$ [4:2:1]. [63°]. Formed by partial methylation of the aldehyde. White plates, nearly insol. water. $FeCl_3$ colours its alcoholic solution reddish-violet. Gives pps. with ammoniacal $AgNO_3$ and lead acetate.

Di-methyl derivative $C_6H_3(OMe)_2CHO$. [68°]. Obtained by methylation, and also by oxidation of the di-methyl derivatives of (α) and (β) umbellic acid with $KMnO_4$ (Will, *B.* 16, 2117). Needles (from dilute alcohol).

Di-ethyl derivative. [72°].

Phenyl hydrazide $C_6H_3(OH)_2CH:N_2HPh$. [c. 158°]. Needles (Rudolph, *A.* 248, 104).

Di-oxy-benzoic aldehyde $C_6H_3(OH)_2.CHO$ [5:2:1]. *Gentisic aldehyde.* [99°]. Formed by boiling hydroquinone with chloroform and aqueous (18 p.c.) NaOH (Tiemann a. Müller, *B.* 14, 1986). Flat yellow needles, v. sol. water. Gives a transient blue colour with $FeCl_3$. Yields gentisic acid on fusion with potash. Alcoholic aniline forms the anilide $C_6H_3(OH)_2CH:NPh$, crystallising in red needles.

m-Methyl derivative $C_6H_3(OMe)(OH)CHO$ [5:2:1]. [4°]. (248°). V.D. (H=1) 75·7 (obs.). Formed from methyl hydroquinone $C_6H_4(OH)(OMe)$ [1:4], chloroform, and NaOHAq. Liquid, volatile with steam, sl. sol. water. Gives a bluish-green colour with $FeCl_3$. Aniline yields $C_6H_3(OMe)(OH)CH:NPh$ [59°], crystallising in red needles. The acetyl derivative $C_6H_3(OMe)(OAc)CHO$ [63°] crystallises in needles, and is converted by boiling Ac_2O into $C_6H_3(OMe)(OAc).CH(OAc)_2$.

Di-methyl derivative $C_6H_3(OMe)_2CHO$. [51°]. Volatile with steam. Not coloured by $FeCl_3$.

m-Ethyl derivative $C_6H_3(OEt)(OH)CHO$ [5:2:1]. [52°]. (230°). Yellow prisms, nearly insol. water. Coloured violet by $FeCl_3$. Yields $C_6H_3(OEt)(OAc)CHO$ [69°], (c. 285°).

Di-ethyl derivative $C_6H_3(OEt)_2CHO$. [60°]. (c. 283°). Needles (T. a. M.; Hantzsch, *J. pr.* [2] 22, 468).

Di-oxy-benzoic aldehyde $C_6H_3(OH)_2CHO$ [4:3:1] *v.* PROTOCATECHUIC ALDEHYDE.

Tri-oxy-benzoic aldehyde. *Tri-ethyl derivative* $C_6H_2(OEt)_3CHO$ [4:3:2:1]. [70°]. Formed by oxidising the tri-ethyl derivative of daphnetic acid with $KMnO_4$ (Will a. Jung, *B.* 17, 1088).

Tri-oxy-benzoic aldehyde. *Tri-ethyl derivative* $C_6H_2(OEt)_3CHO$. [95°]. Formed by oxidation of the tri-ethyl derivative of (α)- or (β)-æsculetic acid with alkaline $KMnO_4$ (Will, *B.* 16, 2112). Large crystals, insol. water.

Tri-oxy-benzoic aldehyde. *Tri-methyl derivative* $C_6H_2(OMe)_3CHO$. [114°]. Formed by oxidation of asarone (Butlerow a. Rizza, *J. R.* 19, 3). Needles, v. sol. hot water.

References.—BROMO-, CHLORO-, and IODO-OXY-BENZOIC ALDEHYDE.

m-**OXY-BENZOPHENONE** $C_6H_5.CO.C_6H_4(OH)$ [116°]. Formed by the action of nitrous acid upon *m*-amido-benzophenone (Geigy a. Koenigs, *B.* 18, 2402). Needles.

p-**Oxy-benzophenone** $C_6H_5.CO.C_6H_4.OH$ [1:4]. *p-Benzoyl phenol.* Formed by heating phenol with BzCl and $ZnCl_2$ (Grucarevitch a. Merz, *B.* 6, 1245). Obtained also from *p*-amido-benzophenone by the diazo- reaction (Doebner a. Weiss, *B.* 14, 1840; *A.* 210, 275). Needles or plates.

Acetyl derivative [81°]. Needles (from alcohol) (Doebner a. Stackmann, *B.* 10, 1970).

Benzoyl derivative [113°].

Methyl derivative $C_6H_5.CO.C_6H_4OMe$. [62°]. Four-sided prisms (Rennie, *C. J.* 41, 227). Possesses two oxims $C_6H_5.C(NOH).C_6H_4OMe$, a stable oxim [116°] yielding B′HCl, an acetyl derivative [53°], and a benzyl ether [74°], and an unstable oxim [140°], which yields B′HCl [124°], an acetyl derivative [135°], and a benzyl ether [60·5°] (Schäfer, *A.* 264, 158; Hantzsch, *B.* 24, 53).

Ethyl derivative $C_6H_5.CO.C_6H_4OEt$. [39°]. (above 300°). Formed from C_6H_5OEt, benzoyl chloride, and $AlCl_3$ (Gattermann, Ehrhardt, a. Marsch, *B.* 23, 1206).

Di-o-oxy-benzophenone $CO(C_6H_4.OH)_2$. [60°]. (c. 335°). Formed by heating diphenylene ketone oxide with alcoholic potash at 180° (Richter, *J. pr.* [2] 28, 273; Graebe a. Feer, *B.* 19, 2607). Prisms or plates (from ligroïn).—KHA″: yellow crystals (from alcohol).—K_2A'': crystals, v. e. sol. water.

Acetyl derivative $C_{13}H_8Ac_2O_3$. [96°] (G. a. F.); [83°] (R.). Prisms (from alcohol).

Benzoyl derivative $C_{13}H_8Bz_2O_3$ [104°].

Methyl derivative $C_{13}H_9MeO_3$ [69°].

Di-methyl derivative $C_{13}H_8Me_2O_3$. [98°] (R.); [104°] (G. a. F.). Prisms. Forms the oxim $C(NOH)(C_6H_4.OMe)_2$ [188°].

Di-ethyl ether $C_{13}H_8Et_2O_3$. [109°]. Needles (from dilute alcohol). Yields the phenyl-hydrazide $C(N_2HPh)(C_6H_4OEt)_2$ [114°].

Oxim $C(NOH)(C_6H_4OH)_2$. [99°].

Phenyl-hydrazide $C(N_2HPh)(C_6H_4OH)_2$. [152°].

op-**Di-oxy-benzophenone** [2:1] $C_6H_4(OH).CO.C_6H_4(OH)$ [1:4]. [144°]. Formed by heating salicylic acid with phenol

and $SnCl_4$ at 120° (Michael, *B.* 14, 656; *Am.* 5, 83). Large yellow plates, sl. sol. water.—Ag_2A''aq.

Acetyl derivative $C_{13}H_8Ac_2O_3$. [88°].

Di-*p*-oxy-benzophenone $CO(C_6H_4OH)_2$. [210°].

Formation.—1. From $CH_2(C_6H_4OBz)_2$ by oxidation and saponification (Gail, *A.* 194, 334). 2. By fusing phenol-phthaleïn with potash (Baeyer a. Burkhardt, *B.* 11, 1299; *A.* 202, 126). 3. By heating aurin with water at 240° (Caro a. Graebe, *B.* 11, 1348), or rosaniline with water at 270° (Liebermann, *B.* 6, 951; 11, 1435).—4. By the action of HNO_2 on di-*p*-amido-benzophenone (Staedel a. Sauer, *B.* 11, 1747).

Properties.—Long needles, m. sol. hot water. On treatment with PCl_3 followed by phenol and H_2SO_4 it yields aurin. Bromine forms $C_{13}H_6Br_4O_3$ [214°].

Acetyl derivative $C_{13}H_8Ac_2O_3$. [148°].

Benzoyl derivative $C_{13}H_8Bz_2O_3$. [182°].

Methyl derivative $C_{13}H_8Me_2O_3$. [144°]. Needles (Bösler, *B.* 14, 328). Yields $C_{15}H_{12}Br_2O_3$ [181°] and an oxim [133°].

Ethyl derivative $C_{13}H_9EtO_3$. [147°].

Di-ethyl derivative $C_{13}H_8Et_2O_3$. [147°]. (Gail); [131°] (Gattermann, *B.* 22, 1131).

(β)-Di-oxy-benzophenone $C_{13}H_{10}O_3$. [162°]. Formed from di-nitro-benzophenone [149°] by reduction and application of the diazo- reaction (Staedel a. Sauer, *B.* 13, 836). Needles.

Acetyl derivative $C_{13}H_8Ac_2O_3$. [90°].

Benzoyl derivative $C_{13}H_8Bz_2O_3$. [102°].

Di-oxy-benzophenone $C_6H_5.CO.C_6H_3(OH)_2$. [145°]. Formed from di-benzoyl-pyrocatechin, BzCl, and $ZnCl_2$ (Doebner, *A.* 210, 261). Needles (containing ½aq).

Benzoyl derivative $C_{13}H_8Bz_2O_3$. [95°].

Di-oxy-benzophenone $C_6H_5.CO.C_6H_3(OH)_2$. *Benzoresorcin.* [144°]. Formed from resorcin, BzCl, and ZnCl at 120° (Doebner a. Stachmann, *B.* 11, 2270). Needles, sol. hot water.

Benzoyl derivative $C_{13}H_8Bz_2O_3$. [141°].

Tri-oxy-benzophenone $C_6H_4(OH).CO.C_6H_3(OH)_2$ [1:2:4]. [133°]. Formed by heating salicylic acid with resorcin at 200° (Michael, *B.* 14, 658), or by heating oxy-di-phenylene ketone oxide with NaOH at 270° (Graebe, *A.* 254, 291). Plates, sl. sol. water.

Tetra-oxy-benzophenone $CO(C_6H_4(OH)_2$ [1:2:5]$)_2$. [202°] is Euxanthonic acid (*q. v.*).

Hexa-oxy-benzophenone $CO(C_6H_4(OH)_3)_2$. *Anhydride* $C_{13}H_8O_6$. *Anhydropyrogalloketone.* Formed by fusing galleïn with alkalis (Buchka, *A.* 209, 270). Brown powder.

Acetyl derivative $C_{13}H_4Ac_4O_6$. [237°].

***p*-OXY-BENZOPHENONE *o*-CARBOXYLIC ACID.** *Methyl derivative* $C_{15}H_{12}O_4$ *i.e.* $C_6H_4(OMe).CO.C_6H_4.CO_2H$. *Anisole-phthaloic acid.* [143°]. Formed by the action of phthalic anhydride (50 g.) on anisole (150 g.) in presence of $AlCl_3$ (80 g.) (Nourisson, *B.* 19, 2103). Colourless crystals (from toluene). Split up by potash-fusion into benzoic and *p*-oxy-benzoic acids. Yields a bromo- derivative [196°]. Conc. H_2SO_4 forms *m*-oxy-anthraquinone. Distillation with zinc-dust gives anthracene.—NaA'.—KHA'_2.—CaA'_2 2aq.—BaA'_2 4aq: white needles.—AgA'.

Di-oxy-benzophenone carboxylic acid $C_6H_3(OH)_2.CO.C_6H_4.CO_2H$. [200°]. Got by fusing fluoresceïn with NaOHAq (Baeyer, *A.* 183, 23). Crystals (containing aq).

DI-OXY-BENZOPHENONE SULPHONIC ACID $C_6H_3(OH)_2.CO.C_6H_4SO_3H$. Formed by heating $C_6H_4(SO_3NH_4)CO_2H$ with resorcin (Remsen, *Am.* 9, 5, 372; 11, 73). Small plates (containing 2aq).—BaA''.—NH_4HA''.

OXY-BENZOYL ACETIC ACID $C_9H_8O_4$ *i.e.* $C_6H_5.CO.CH(OH).CO_2H$. [125°]. Formed from nitroso-benzoyl-acetic ether Bz.C(NOH).CO_2Et and NaOHAq (Baeyer a. Perkin, *B.* 16, 2133; *C. J.* 47, 245). Small prisms (from water).—AgA'.

OXY-BENZOYL BROMIDE. *Methyl derivative* $C_6H_4(OMe).COBr$. Formed from anisic aldehyde by cautious treatment with bromine (Cahours, *A. Ch.* [3] 14, 486). Silky crystals, resolved by KOHAq into potassium anisate and potassium bromide.

***p*-OXY-BENZOYL CHLORIDE.** *Methyl derivative* $C_6H_4(OMe).COCl$. (262°). S.G. $\frac{15}{}$ 1·261. Formed from anisic acid and PCl_5 (Cahours, *A. Ch.* [3] 23, 351). Oil, converted by water into anisic acid.

***p*-OXY-BENZURIC ACID** $C_9H_9NO_4$ *i.e.* $C_6H_4(OH).CO.NH.CH_2.CO_2H$. [c. 228°]. Occurs in the urine of dogs to which *p*-oxy-benzoic acid or hydro-*p*-coumaric acid has been administered (Baumann a. Herter, *H.* 1, 260; Schotten, *H.* 7, 26). Prisms, m. sol. water.

OXY-DIBENZYL *v.* Oxy-di-phenyl-ethane.

***o*-OXY-BENZYL ALCOHOL** $C_7H_8O_2$ *i.e.* $C_6H_4(OH).CH_2OH$. *Saligenin.* Mol. w. 124. [82°]. S. 7 at 22°. S. (benzene) 1·9 at 18°. Formed by the hydrolysis of salicin (Piria, *A.* 56, 37), by reducing *o*-oxy-benzoic aldehyde with sodium-amalgam (Beilstein, *A.* 128, 179), and by heating phenol with CH_2Cl_2 and aqueous NAOH at 100° (Greene, *Am.* 2, 19). Tables, v. e. sol. hot water. $FeCl_3$ gives a blue colour. Dilute H_2SO_4 forms saliretin $C_{14}H_{14}O_3$ or $C_{28}H_{26}O_5$, a yellowish powder, insol. water (Gerhardt, *A. Ch.* [3] 7, 215; Beilstein, *A.* 117, 84; Kraut, *A.* 156, 124). On heating with glycerin at 100° it forms saliretone $C_{14}H_{12}O_3$ [121·5°] crystallising from water (Giacosa, *J. pr.* [2] 21, 221).

Methyl derivative $C_6H_4(OMe).CH_2OH$. (248°). S.G. $\frac{23}{}$ 1·120 (Cannizzaro a. Körner, *B.* 5, 436).

Ethyl derivative $C_6H_4(OEt).CH_2OH$. (265°). Solidifies at 0° (Bötsch, *M.* 1, 621).

***m*-Oxy-benzyl alcohol** [3:1]$C_6H_4(OH).CH_2OH$. [67°]. (c. 300°). A product of the action of sodium-amalgam on *m*-oxy-benzoic acid in acid solution (Van der Velden, *J. pr.* [2] 15, 163). White mass, v. sol. hot water. $FeCl_3$ gives a violet colour.

Acetyl derivative $C_6H_4(OH).CH_2OAc$. [55°]. (295°–302°). Crystalline, v. sl. sol. water.

Di-acetyl derivative $C_6H_4(OAc).CH_2OAc$. (c. 290°). Oil, sol. alcohol and ether.

***p*-Oxy-benzyl alcohol** $C_6H_4(OH).CH_2.OH$. [110°]. Prepared by slowly adding 40 pts. of 3 p.c. sodium-amalgam to a solution of 1 pt. para-oxy-benzaldehyde in 10 pts. water and 5 pts. alcohol, kept slightly acid with H_2SO_4 (Biedermann, *B.* 19, 2373). Thin white needles. V. sol. water, alcohol, and ether, sl. sol. benzene and chloroform, nearly insol. ligroïn. Dissolves in conc. H_2SO_4 with a splendid violet colour.

Mono-acetyl derivative $C_6H_4(OH).CH_2.OAc$: [84°]; small yellowish needles; v. sol. alcohol and ether, sl. sol. water.

Di-acetyl derivative $C_6H_4(OAc).CH_2.OAc$: [75°]; small needles; v. sol. alcohol and ether, nearly insol. water.

Methyl derivative $C_6H_4(OMe).CH_2OH$. *Anisic alcohol.* Mol. w. 138. [45°]. Formed, together with anisic acid, by mixing anisic aldehyde with alcoholic potash (Cannizzaro a. Bertagnini, *A.* 98, 188; 137, 246; *G.* 2, 61). Obtained also by methylation (Biedermann, *B.* 19, 2376). White needles. HClAq forms oily $C_6H_4(OMe)CH_2Cl$ whence NaOMe forms the compound $C_6H_4(OMe).CH_2OMe$ (226°).

Di-oxy-benzyl alcohol. *Ethyl derivative* $C_6H_3(OEt)(OH).CH_2OH$ [5:2:1]. [84°]. Formed by adding 5 p.c. sodium-amalgam to the corresponding aldehyde suspended in water. The product is acidified and shaken with ether (Hantzsch, *J. pr.* [2] 22, 475). Large thick tablets, changing at 100° into a brown amorphous mass. Acids also resinify it.

Di-oxy-benzyl alcohol $C_6H_3(OH)_2.CH_2OH$ [4:3:1]. *Methyl derivative* $C_8H_{10}O_3$ *i.e.* $C_6H_3(OH)(OMe).CH_2OH$ [4:3:1]. *Vanillyl alcohol.* [115°]. Formed by the action of sodium-amalgam on vanillin (Tiemann, *B.* 8, 1125; 9, 415). Formed also by the action of emulsin on the glucoside $C_6H_3(OC_6H_{11}O_5)(OMe)CH_2OH$ [120°], a crystalline body (containing aq) prepared by reduction of glucosyl-vanillin (Tiemann *B.* 18, 1595). Prisms, v. sol. alcohol.

Methylene derivative $C_6H_3(O_2CH_2).CH_2OH$. *Piperonyl alcohol.* [51°]. Got by reducing piperonal $C_6H_3(O_2CH_2).CHO$ with sodium-amalgam and hot-water (Fittig a. Remsen, *A.* 159, 138). Long crystals, m. sol. hot water.

Reference.—Chloro-oxy-benzyl alcohol.

o-OXY-BENZYL-AMINE $C_6H_4(OH).CH_2NH_2$. [125°]. Formed by heating its methyl derivative with HClAq at 150° (Goldschmidt a. Ernst, *B.* 23, 2744) and by the action of dilute H_2SO_4 and zinc-dust on $C_6H_4(OH).CH:N.NH.C_6H_4CO_2H$ (Tiemann, *B.* 23, 3017). Groups of white needles (from ether). Readily sublimes. Ferric chloride colours its solution deep violet-blue.—B'HCl.—$B'_2H_2PtCl_6$ 2aq. [197°]. Golden needles.

Acetyl derivative $C_6H_4(OH).CH_2.NHAc$. [140°]. Colourless needles, sol. alkalis.

Methyl derivative $C_6H_4(OMe).CH_2.NH_2$. (224° at 724 mm.). Formed by reducing the oxim $C_6H_4(OMe).CH:NOH$ in alcoholic solution with sodium-amalgam and HOAc (Goldschmidt a. Ernst, *B.* 23, 2742). Liquid, v. sol. water. Yields $C_6H_4(OMe).CH_2.NHAc$. [97°].—B'HCl. [150°].—$B'_2H_2PtCl_6$ 2aq. [187°]. Golden plates.

p-Oxy-benzylamine $C_6H_4(OH).CH_2.NH_2$ aq [95°]. Formed from *p*-amido-benzylamine, $NaNO_2$, and HCl (Salkowski, *B.* 22, 2143). Plates.—B'HCl.—$B'_2H_2PtCl_6$ 2aq: flat needles.

Methyl derivative $C_6H_4(OMe).CH_2NH_2$. (222°) (S.); (235°) (G. a. P.). Formed by reducing hydroanisamide in alcoholic solution with sodium amalgam (Steinhart, *A.* 241, 335). Obtained also by reduction from the oxim $C_6H_4(OMe).CH:NOH$ (Goldschmidt a. Polonowska, *B.* 20, 2407). Liquid, sol. water, volatile with steam.—B'HCl. [230°].—$B'HHgCl_3$ aq. [200°]. Scales.—$B'_2H_2PtCl_6$. [210°]. Bright yellow needles. Absorbs CO_2 from the air, forming a compound crystallising in needles [110°] (*cf.* Cannizzaro, *A.* 117, 240).

Acetyl derivative $C_6H_4(OMe).CH_2.NHAc$. [96°].

Di-*o*-oxy-di-benzyl-amine $NH(CH_2.C_6H_4OH)_2$. [170°]. Formed by reducing hydrosalicylamide in alcoholic solution with sodium-amalgam (Emmerich, *A.* 241, 349). Needles, v. sl. sol. water. Gives an oily nitrosamine.—$B'_2H_2PtCl_6$.

Di-*p*-oxy-di-benzyl-amine. *Di-methyl derivative* $(C_6H_4(OMe).CH_2)_2NH$. [34°]. Formed by the action of $C_6H_4(OMe).CH_2Cl$ on alcoholic ammonia, and also by reducing $(C_6H_4(OMe).CH)_3N_2$. White needles. Yields a nitrosamine [80°].—B'HCl. [243°]. Flat prisms.—$B'_2H_2PtCl_6$ 2aq.

o-OXY-BENZYL-ANILINE $C_6H_4(OH).CH_2.NPhH$. *Phenyl-ω-amido-cresol.* [106°]. Formed by reducing o-oxybenzylidene-aniline with sodium-amalgam (Emmerich, *A.* 241, 344). Needles or plates, sl. sol. water. Its nitrosamine is oily.—B'HCl. [131°].—$B'_2H_2PtCl_6$. [184°]. M. sol. water.

p-Oxy-benzyl-aniline. [208°]. Formed in like manner (E.). White needles.—$B'_2H_2PtCl_6$.

Methyl derivative $C_6H_4(OMe).CH_2NHPh$. [65°]. Formed by reducing $C_6H_4(OMe).CH:NPh$ (Steinhart, *A.* 241, 337). Prisms. Gives a nitrosamine [104°].—B'HCl. [163°].—$B'_2H_2PtCl_6$.

DI-OXY-DI-BENZYL-BENZENE $C_6H_4(CHPh.OH)_2$. [171°]. Formed by reducing $C_6H_4(COPh)_2$ with sodium-amalgam (Wehnen, *B.* 9, 310). Satiny needles (from dilute alcohol). Yields $C_{20}H_{19}AcO_2$ [97°] and $C_{20}H_{18}Ac_2O_2$ [144°].

OXY-o-BENZYL-BENZOIC ACID $C_{14}H_{12}O_3$ *i.e.* $C_6H_5.CH(OH).C_6H_4.CO_2H$. *Benzhydryl carboxylic acid.*—KA': amorphous.—BaA'_2. From the anhydride and baryta.

Anhydride $C_6H_5.CH\left\langle\begin{matrix}C_6H_4\\O\end{matrix}\right\rangle CO$. [115°].

Formed by reducing o-benzoyl-benzoic acid with zinc and HCl (Rotering, *J.* 1875, 596). White insoluble powder.

Exo-Oxy-*m*-benzyl-benzoic acid. [121°]. Formed by reducing *m*-benzoyl-benzoic acid with sodium-amalgam (Senff, *A.* 220, 242). Satiny needles in hemispherical groups (from hot water). Reduced by HIAq (127°) at 170° to *m*-benzyl-benzoic acid.—NaA' 4aq.—CaA'_2 5aq.—AgA' aq.

Oxy-*p*-benzyl-benzoic acid. [165°]. Formed by reducing *p*-benzoyl-benzoic acid (Zincke, *A.* 161, 102). Needles (from hot water).—NH_4A'.—NaA'.—KA'.—CaA'_2 5aq.—BaA'_2.—AgA': pp.

Methyl ether MeA'. [110°]. Prisms.

Ethyl ether EtA'. Oil.

Oxy-benzyl-benzoic acid $C_6H_5.CH_2.C_6H_3(OH).CO_2H$. [140°]. Formed from benzyl-phenol, sodium, and CO_2 (Paterno a. Fileti, *G.* 3, 237). Needles (from water), sl. sol. hot water.—AgA': curdy pp., sl. sol. hot water.

DI-OXY-BENZYL ETHYL KETONE CARBOXYLIC ACID. *Methylene derivative* $C_6H_3(O_2CH_2).CH_2.CO.C_6H_4CO_2H$. *Piperoketonic acid.* [84°]. Formed by heating di-bromo-piperhydronic acid with aqueous Na_2CO_3 (Weinstein, *A.* 227, 33). Silky needles (from CS_2).—CaA'_2.—AgA': flocculent pp.

OXY-BENZYLIDENE-ACETONAMINE *v.* Acetonamine.

o-**OXY-BENZYLIDENE-*m*-AMIDO-BENZOIC ACID** $C_6H_4(OH).CH:N.C_6H_4CO_2H$. [190°]. Formed from salicylic aldehyde and aqueous *m*-amido-benzoic acid (Schiff, *A*. 210, 114). Yellowish needles, v. e. sol. alcohol.

Amide $C_{14}H_{12}N_2O_2$. [186°]. Converted by boiling benzoic aldehyde into crystalline $C_{35}H_{28}N_4O_3$ whence Ac_2O yields $C_{35}H_{26}Ac_2N_4O_4$ [220°]. The glucosyl derivative of the amide $C_6H_{11}O_5O.C_6H_4.CH:N.C_6H_4.CONH_2$ [113°] is formed by the action of helicin on *m*-amido-benzamide.

Di-oxy-benzylidene-o-amido-benzoic acid $C_6H_4(OH).CH:N.C_6H_3(OH)CO_2H$ [5:2:1]. [245°]. Formed from oxy-amido-benzoic acid and salicylic aldehyde. Needles, v. e. sol. alcohol.

DI-OXY-BENZYLIDENE-DI-AMIDO-DIPHENYL $C_{12}H_8[N:CH.C_6H_4OH]_2$. [145°]. Formed from di-o-amido-diphenyl and salicylic aldehyde (Reuland, *B*. 22, 3012). Yellow plates.

o-**OXY-BENZYLIDENE-ANILINE** $C_6H_4(OH).CH:NPh$. [51°]. *V.* OXY-BENZOIC ALDEHYDE. The *p*- isomeride melts at 191°.

OXY-BENZYLIDENE-ANTHRONE. *Ethyl ether* $C_6H_4{<}{\scriptstyle C(CPh.OEt) \atop \scriptstyle CO}{>}C_6H_4$. [173°].

Formed from bromo-benzylidene-anthrone and NaOEt (Bach, *B*. 23, 2529). Yellow plates, v. sol. ether.

OXY-BENZYLIDENE-DICARBAMIC ETHER. *Methyl derivative* $C_{14}H_{20}N_2O_5$ *i.e.* $C_6H_4(OMe).CH(NH.CO_2Et)_2$. [172°]. Formed from anisic aldehyde and carbamic ether (Bischoff, *B*. 7, 1078). Needles (from dil. alcohol).

DI-*o*-OXY-BENZYLIDENE-ETHYLENE-DIAMINE $C_{16}H_{16}N_2O_2$ *i.e.* $C_2H_4(N:CH.C_6H_4OH)_2$. [126]. Formed from ethylene-diamine and o-oxy-benzoic aldehyde (Mason, *B*. 20, 271). The di-methyl derivative [c. 113°] and its *p*- isomeride $C_2H_4(N:CH.C_6H_4.OMe[1:4])_2$ [111°] are both crystalline.

o-**OXY-BENZYLIDENE-MALONIC ACID.** *Methyl derivative* $C_6H_4(OMe)CH:C(CO_2H)_2$. [178°]. Formed by heating a mixture of malonic acid, $C_6H_4(OMe).CHO$, and HOAc at 100° (Stuart, *C. J.* 53, 142).

OXY-BENZYLIDENE-NAPHTHYLAMINE $C_6H_4(OH).CH:NC_{10}H_7$. The o- [121°] and *p*- [220°] compounds are formed from (β)-naphthylamine and the corresponding oxy-benzoic aldehydes (Emmerich, *A*. 241, 350).

o-**OXY-BENZYLIDENE-DITHIOGLYCOLLIC ACID** $C_6H_4(OH).CH(S.CH_2.CO_2H)_2$. [148°]. Formed from o-oxy-benzoic aldehyde, thioglycollic acid, and $ZnCl_2$ (Bongartz, *B*. 21, 478).

o-**OXY-BENZYLIDENE-*p*-TOLUIDINE** $C_6H_4(OH).CH:NC_7H_7$. [100°] (Jaillard, *J*. 1865, 428; *v*. OXY-BENZOIC ALDEHYDE).

OXY-BENZYLIDENE-DI-UREA $C_6H_4(OH).CH(NH.CO.NH_2)_2$ *v*. o-OXY-BENZOIC ALDEHYDE.

OXY-BENZYL-MALONIC ACID. *Ethyl derivative* $C_6H_5.CH(OEt).CH(CO_2H)_2$. [c. 120°]. Formed from benzylidene-malonic acid and cold alcoholic KOH (Claisen a. Crismer, *A*. 218, 141). Crystalline. Split up at 120° into alcohol and benzylidene-malonic acid [192°].—K_2A''. Ag_2A''.

Isomeride *v*. BENZYL-TARTRONIC ACID.

OXY-BENZYL-METHYL-ETHYL-PYRIMIDINE $CH_2Ph.C{<}{\scriptstyle N.CMe \atop \scriptstyle N:C(OH)}{>}CEt$. [193·5°]. Formed from phenyl-acetamidine hydrochloride, ethyl-acetoacetic ether, dilute (10 p.c.) NaOH, and alcohol (Pinner, *B*. 22, 1623). Needles, m. sol. water, v. e. sol. alcohol.

Di-oxy-benzyl-methyl-ethyl-pyrimidine

$CH(OH)Ph.C{<}{\scriptstyle N.CMe \atop \scriptstyle N:C(OH)}{>}CEt$. [148°–152°].

Formed from oxy-phenyl-acetamidine, aceto-acetic ether, and NaOHAq (Pinner, *B*. 23, 2951).

OXY-BENZYL-METHYL-PYRIMIDINE

$CH_2Ph.C{<}{\scriptstyle N.CMe \atop \scriptstyle N:C(OH)}{>}CH$. [175°]. Formed from phenyl-acetamidine, acetoacetic ether, alcohol, and dilute (10 p.c.) NaOH (Pinner, *B*. 22, 1622). Prisms, m. sol. hot water.

Oxy-benzyl-di-methyl-pyrimidine

$CH_2Ph.C{<}{\scriptstyle N.CMe \atop \scriptstyle N:C(OH)}{>}CMe$. [181°]. Formed from phenyl-acetamidine, methyl-acetoacetic ether, and NaOHAq (P.). M. sol. water.

Oxy-di-benzyl-methyl-pyrimidine

$CH_2Ph.C{<}{\scriptstyle N.CMe \atop \scriptstyle N:C(OH)}{>}C.CH_2Ph$. [192°]. Formed from phenyl-acetamidine, benzyl-acetoacetic ether, and NaOHAq (P.). Needles, insol. water.

Di-oxy-benzyl-methyl-pyrimidine $C_{12}H_{12}N_2O_2$ *i.e.* $CH(OH)Ph.C{<}{\scriptstyle N.CMe \atop \scriptstyle N:C(OH)}{>}CH$. [216°]. Formed from oxy-phenyl-acetamidine, NaOHAq and aceto-acetic ether in the cold (Pinner, *B*. 23, 2949). Long needles, v. sl. sol. water, sl. sol. alcohol, sol. acids and alkalis. — B'HCl. [217°]. Needles.—$B'C_6H_2(NO_2)_3OH$. [175°]. $AgC_{12}H_{11}N_2O_2$: white pp.

Acetyl derivative

$CH(OAc)Ph.C{<}{\scriptstyle N.CMe \atop \scriptstyle N:C(OH)}{>}CH$. [170°]. Formed by boiling with Ac_2O. Yields $AgC_{14}H_{13}N_2O_3$, B'HCl [188°], and $B'C_6H_2(NO_2)_3OH$ [160°].

Benzoyl derivative $C_{12}H_{11}BzN_2O_2$. [205°–208°].—B'HCl. [240°]. From the base and BzCl.

Di-oxy-benzyl-methyl-pyrimidine. [233°]. Got from potassium methyl-uracil and benzyl chloride (Hagen, *A*. 244, 1).

Di-oxy-benzyl-di-methyl-pyrimidine

$CH(OH)Ph.C{<}{\scriptstyle N.CMe \atop \scriptstyle N:C(OH)}{>}CMe$. [155°]. Formed from oxy-phenyl-acetamidine, NaOHAq, and methyl-acetoacetic ether (Pinner, *B*. 23, 2951).—B'HOAc: needles.—$AgC_{13}H_{13}N_2O_2$: white pp.

OXY-BENZYL-(β)-NAPHTHYLAMINE. The following compounds have been prepared by reducing the products of the action of (β)-naphthylamine on the corresponding aldehydes (Steinhart, *A*. 241, 341; Emmerich, *A*. 241, 352):—

[1:2] $C_6H_4(OH).CH_2.NHC_{10}H_7$. [147°].—B'HCl. [188°].
[1:2] $C_6H_4(OH).CH_2.N(NO)C_{10}H_7$. [165°].
[1:2] $C_6H_4(OMe).CH_2.NH.C_{10}H_7$. [92°]. (223°).
[1:4] $C_6H_4(OH).CH_2.NHC_{10}H_7$. [117°].
[1:4] $C_6H_4(OH).CH_2.N(NO).C_{10}H_7$. [142°].
[1:4] $C_6H_4(OMe).CH_2.NHC_{10}H_7$. [101°].—B'HCl. [195°].—$B'_2H_2PtCl_6$.—*Nitrosamine* $C_6H_4(OMe).CH_2.N(NO).C_{10}H_7$. [133°].

OXY-BENZYL-ISOPHTHALIC ACID. *Benzhydryl-isophthalic acid. Anhydride*

$C_6H_5.CH<\begin{smallmatrix}C_6H_3(CO_2H)\\O.CO\end{smallmatrix}>$. [207°]. Formed by the action of zinc and HClAq on benzoyl-isophthalic acid (Zincke, *B.* 9, 1763). Needles (from dilute alcohol).—BaA'_2 $2\frac{1}{2}$aq.—AgA': pulverulent pp.—EtA'. [115°]. An isomeric acid, obtained by reduction of benzoyl-terephthalic acid, forms $Ca(C_{15}H_9O_4)_2$ 3aq (Weber, *J.* 1878, 403).

p-**OXY-BENZYL-PHTHALIMIDINE**

$C_6H_4<\begin{smallmatrix}CH_2\\CO\end{smallmatrix}>N.C_7H_6OH$ or

$C_6H_4<\begin{smallmatrix}CH_2\\C(NC_7H_6OH)\end{smallmatrix}>O$. [187°–198°].

Formed from the amido- compound by the diazo-reaction (Hafner, *B.* 23, 344). Red needles. Converted by conc. HClAq at 150° into a base $C_8H_9NO_2$.

OXY-BENZYL-PYRIDINE TETRAHYDRIDE

$C_7H_7.CH<\begin{smallmatrix}CO.NH\\CH_2.CH_2\end{smallmatrix}>CH_2$. (β)-*Benzyl-piperidone.* [118°]. Formed by distilling δ-amido-α-benzyl-valeric acid (Aschan, *B.* 23, 3696). Pearly plates (from hot water). $B'C_6H_2(NO_2)_3OH$. [97°]. Crystals, sl. sol. water.

Nitrosamine $C_{12}H_{14}(NO)NO$. [62·5°].

OXY-BENZYL-PYRIMIDINE CARBOXYLIC ACID $CH_2Ph.C<\begin{smallmatrix}N.C(CO_2H)\\N:C(OH)\end{smallmatrix}>CH$. [230°]. Formed from phenyl-acetamidine, oxalacetic ether, and (10 p.c.) NaOHAq (Pinner, *B.* 22, 1627). Prisms, v. sl. sol. water.

OXY-BENZYL-PYROTARTARIC ACID

$C_6H_5.CH(OH).CH(CO_2H).CHMe.CO_2H$. *Phenyl-homoitamalic acid.* Formed from benzoic aldehyde, sodium pyrotartrate, and Ac_2O at 125° (Penfield, *A.* 216, 119; Fittig a. Liebmann, *A.* 255, 257). The acid splits up, at the moment of liberation, into water and anhydride.—$CaC_{12}H_{12}O_5$ 3aq.—BaA'' 2aq.—Ag_2A''.

Anhydride $C_{12}H_{12}O_4$. *Phenylhomoparaconic acid.* [177°]. Plates (from water).—$AgC_{12}H_{11}O_4$: crystals, m. sol. water.—BaA'' aq.—CaA''.

Isomeride

$C_6H_5.CH(OH).CMe(CO_2H).CH_2.CO_2H$. Formed together with the preceding acid. Its salt $BaC_{12}H_{12}O_5$ is got by heating the anhydride with baryta-water.—CaA'' aq.—Ag_2A'': bulky flocculent pp.

Anhydride $CHPh<\begin{smallmatrix}CMe(CO_2H)\\O.CO.CH_2\end{smallmatrix}>$. (124·5°). Yields $Ba(C_{12}H_{11}O_4)_2$, CaA'_2 2aq, and AgA'.

DI-OXY-BENZYL-QUINOLINE CARBOXYLIC ACID. *Ethyl derivative*

$C_6H_4<\begin{smallmatrix}CO.C(C_7H_7)(CO_2H)\\N\ :C(OEt)\end{smallmatrix}$. [147°]. Formed by reducing benzyl-o-nitro-benzoyl-malonic ether (Bischoff, *B.* 22, 386).

OXY-BENZYL-SUCCINIC ACID $C_{11}H_{12}O_5$ *i.e.* $PhCH(OH).CH(CO_2H).CH_2.CO_2H$. Its salts are formed by warming the anhydride with bases.—$CaC_{11}H_{10}O_5$.—BaA'' 2aq.—Ag_2A''.

Ethyl ether

$CHPh(OH).CH(CO_2Et).CH_2CO_2H$. Oil.

Anhydride $C_6H_5.CH<\begin{smallmatrix}CH(CO_2H)\\O.CO\end{smallmatrix}>CH_2$. *Phenyl-paraconic acid.* [99°]. Formed by heating sodium succinate with benzoic aldehyde and Ac_2O (Fittig a. Jayne, *A.* 216, 108; 256, 63). Needles (from water); converted by NaOEt into phenylitaconic acid. Yields $Ca(C_{11}H_9O_4)_2$ 2aq, BaA'_2 3aq, and AgA', and the ether EtA' (252° at 25 mm.).

p-**OXY-BENZYL-THIOCARBIMIDE**

$C_6H_4(OH).CH_2NCS$. From *p*-oxy-benzylamine, CS_2, and $HgCl_2$ (Salkowski, *B.* 22, 2144). Liquid, sol. alkalis.

p-**OXY-BENZYL-THIO-UREA.** *Methyl derivative* $C_6H_4(OMe).CH_2.NH.CS.NH_2$. [95°]. (Goldschmidt a. Polonowska, *B.* 20, 2409).

Di-oxy-di-benzyl-thio-urea. *Di-methyl derivative* $(C_6H_4(OMe).CH_2.NH)_2CS$. [150°].

o-**OXY-BENZYL-*p*-TOLUIDINE** $C_{14}H_{15}NO$ *i.e.* $C_6H_4(OH).CH_2.NH.C_6H_4Me$. [116°]. Formed by reducing *o*-oxy-benzylidine-*p*-toluidine in alcoholic solution with sodium-amalgam (Emmerich, *A.* 241, 346). Crystals. Yields the methyl derivative $C_6H_4(OMe).CH_2.NHC_6H_4Me$ [110°] and a tetra-nitro- derivative [168°].—B'HCl. [147°].—$B'_2H_2PtCl_6$: reddish-yellow needles.

p-**Oxy-benzyl-*p*-toluidine** [186°]. Yields $B'_2H_2PtCl_6$ and $C_6H_4(OMe).CH_2.NHC_6H_4Me$ [68°], whence B'HCl [160°], $B'_2H_2PtCl_6$ and the nitrosamine $C_6H_4(OMe).CH_2.N(NO).C_6H_4Me$ [108°].

p-**Oxy-benzyl-o-toluidine.** *Methyl derivative.* [55°]. Triangular plates (Steinhart, *A.* 241, 340). Yields an oily nitrosamine.

o-**OXY-BENZYL-UREA** $C_8H_{10}N_2O_2$ *i.e.* $C_6H_4(OH).CH_2.NH.CO.NH_2$. [170°]. Formed by warming *o*-oxy-benzylamine hydrochloride with potassium cyanate (Goldschmidt a. Ernst, *B.* 23, 2745). Prisms, v. sol. hot water.

Methyl derivative

$C_6H_4(OMe).CH_2.NH.CO.NH_2$. [127°].

p-**Oxy-benzyl-urea.** *Methyl derivative* [167°]. Needles (Goldschmidt a. Polonowska, *B.* 20, 2409).

δ-**OXY-α-BENZYL-VALERIC ACID**

$CH_2(OH).CH_2.CH_2.CH(CH_2Ph).CO_2H$. Formed from nitroso-oxy-benzyl-pyridine tetrahydride and NaOHAq (Aschan, *B.* 23, 3697). Liquid, m. sol. hot water.

γ-**Oxy-β-benzyl-valeric acid**

$CH_3.CH(OH).CH(CH_2Ph).CH_2.CO_2H$. [76°]. Formed by carefully adding dilute HCl to its Ca salt obtained from the lactone (Erdmann, *A.* 254, 217). Prisms (containing aq). Melts at 56° when hydrated. HClAq converts it into the lactone.—$Ca(C_{12}H_{15}O_3)_2$ 4aq.—CaA'_2 6aq.

Lactone $CH_3.CH<\begin{smallmatrix}CH(CH_2Ph)\\O.CO.CH_2\end{smallmatrix}>$. [86°]. Got by reducing benzyl-acetyl-propionic acid [99°] with sodium-amalgam, and boiling the product with dilute H_2SO_4. Large crystals.

DI-OXY-BUTANE $CH_2(OH).CHEt(OH)$. *n-Butylene glycol.* Mol. w. 90. (192°). S.G. $\frac{0}{0}$ 1·0189. Obtained from ωα-di-bromo-*n*-butane by boiling with baryta-water (Grabowsky a. Saytzeff, *A.* 179, 325). Liquid, v. sol. water. Yields glycollic and glyoxylic acids on oxidation.

Di-oxy-butane $C_4H_{10}O_2$ *i.e.* $CH_2(OH).CMe_2OH$. *Isobutylene glycol.* (178°). S.G. $\frac{0}{}$ 1·129. Formed from the bromide and K_2CO_3Aq (Nevolé, *C. R.* 83, 65, 146) and by the action of HClAq on isobutyl alcohol (Lwoff, *Bl.* [2] 43, 112). Formed also in the alcoholic fermentation of sugar (Henninger a. Sanson, *C. R.* 95, 94; 106, 208). Does not form an acetal with aldehyde (Lochert, *A. Ch.* [6] 16, 58).

Di-oxy-butane $CHMe(OH).CHMe(OH)$. (184°). Formed by heating *s*-butylene oxide with water at 100° (Eltekoff, *J. R.* 14, 372). Liquid.

Di-oxy-butane $CHMe(OH).CH_2.CH_2OH$. (β)-*Butylene glycol.* (207°). S.G. $\frac{0}{}$ 1·0259. Formed by reduction of a dilute, slightly acid, solution of aldol by sodium-amalgam (Kekulé, *B.* 5, 56; *A.* 162, 310; Wurtz, *C. R.* 97, 473). Thick liquid, miscible with water. Ac_2O at 100° forms $C_4H_8(OAc)_2$ (207°). S.G. $\frac{0}{}$ 1·055. HIAq yields $C_4H_8I_2$ S.G. $\frac{0}{}$ 2·291.

Di-oxy-butane $C_4H_8(OH)_2$. (184°). S.G. $\frac{0}{}$ 1·048. Obtained, *viâ* $C_4H_8(OAc)_2$ (c. 200°), from the crude $C_4H_8Br_2$ got from fusel oil (Wurtz, *A. Ch.* [3] 55, 452). Liquid, miscible with water.

Di-oxy-butane $CH_2(OH).CH_2.CH_2.CH_2(OH)$. *Tetramethylene glycol.* (204°). S.G. 1·011. Formed by the action of dilute H_2SO_4 on tetramethylene dinitramine $C_4H_8(NH.NO_2)_2$ (Dekkers, *R. T. C.* 9, 101).

Tri-oxy-butane $CH_3.CH(OH).CH(OH).CH_2(OH)$. *Butenylglycerin.* (173° at 27 mm.). Formed from crotonic aldehyde by reduction, addition of bromine, and boiling the resulting $CH_3.CHBr.CHBr.CH_2OH$ with water (Lieben a. Zeisel, *M.* 1, 832). Thick liquid with sweet taste. Ac_2O yields $C_4H_7(OAc)_3$ (262°). Yields $C_4H_7(OH)_2Cl$, $C_4H_7(OH)Cl_2$, and C_4H_7OCl (Zikes, *M.* 6, 348).

Tri-oxy-butane $C_4H_{10}O_3$. (240° at 18 mm.). Formed from isobutyl iodide by chlorinating and heating the resulting tri-chloro-butane with water at 170° (Prunier, *Bl.* [2] 42, 261; *C. R.* 99, 193). Yields nearly solid $C_4H_7(OAc)_3$.

Tetra-oxy-butane *v.* Erythrite.

OXY-BUTANE TRICARBOXYLIC ACID $CMe(OH)(CO_2H).CH(CO_2H).CH_2CO_2H$.

Lactone $C_7H_8O_6$. Formed by heating acetosuccinic ether with *K*Cy and HCl (Rach, *A.* 234, 35). At 180° it yields pyrocinchonic anhydride. — BaA″. — CaA″. — $Ca_3(C_7H_7O_7)_2$. — $Ba_3(C_7H_7O_7)_2$.

Di-oxy-butane tetra-carboxylic ether $CH(CO_2Et)_2.CH(OH).CH(OH).CH(CO_2Et)_2$. Formed by the action of malonic ether on glyoxal in presence of conc. $ZnCl_2$ Aq (Polonowsky, *A.* 246, 2). Oil, not volatile with steam.

Tetra-oxy-butane tri-carboxylic acid $CO_2H.CH(OH).CH(OH).CH(OH).C(OH)(CO_2H)_2$. [147°]. Formed by oxidation of levulose carboxylic acid by dilute HNO_3 (Düll, *B.* 24, 348).—K_2HA'''. Large prisms.—$Ca_3A'''_2$ 6aq.

OXY-BUTANE-PHOSPHONIC ACID $C_3H_7.CH(OH).PO(OH)_2$. [168°]. Formed from isobutyric aldehyde by successive treatment with PCl_3 and water (Fossek, *M.* 5, 640). Trimetric crystals; $a:b:c$ = ·97:1:3·94.

OXY-ISOBUTANE SULPHONIC ACID $CMe_2(OH).CH_2SO_3H$. Formed from ammonium sulphite solution and isobutylene bromide or $CH_2Br.CMe_2OH$ (Guareschi a. Garzino, *Ann. chim. farm.* [4] 6, 110; 9, 96).—BaA'_2 1½aq.—NaA′: plates (from alcohol).

DI-OXY-BUTYL-BENZENE $C_{10}H_{14}O_2$ *i.e.* $C_6H_5.CH(OH).C_2H_4.CH_2OH$. (200°). Formed by the action of sodium-amalgam on an alcoholic solution of $C_6H_5.CO_2.C_2H_4.CHO$ which is got from phenyl propyl ketone by successive treatment with CrO_2Cl_2 and water (Burcker, *C. R.* 94, 220). Syrup. Forms oily $C_{10}H_{12}(OAc)_2$.

ISOBUTYL-*o*-OXY-BENZOIC ACID $C_6H_3(C_4H_9)(OH)CO_2H$ [4:2:1]. Formed from $C_6H_4(C_4H_9)ONa$ and CO_2 at 140° (Dobrzycki, *J. pr.* [2] 36, 391). Needles.—CaA'_2 6aq.—BaA'_2 2aq: needles, v. sol. water.

Ethers MeA′. [54°]. (266°).—EtA′. (276°). Oil.—C_6H_5A'. [68°]. Formed from the acid, phenol, and $POCl_3$. Converted by long boiling into $C_{17}H_{16}O_2$ [158°].

DI-OXY-BUTYLENE $C_4H_6(OH)_2$. *Crotonylene glycol.* (197°). S.G. $\frac{0}{}$ 1·0616; $\frac{20}{}$ 1·0465. Obtained by the action of boiling baryta on its formyl derivative which is formed when erythrite is distilled with formic acid (Henninger, *B.* 5, 1060; *A. Ch.* [6] 7, 215). Liquid, sol. water. Yields $C_4H_6(OAc)_2$ (203°).

DI-OXY-DI-BUTYL-DIKETONE.

Anhydride $\begin{matrix} CH_2 & .CH_2 \\ CHMe.O & \end{matrix} > C < \begin{matrix} CH_2.CH_2 \\ O\ \ .CHMe \end{matrix}$.

Di-methyl-oxetone. (169·5° i.V.). S.G. $\frac{0}{}$ ·978. Formed, together with CO_2, by heating its carboxylic acid $\begin{matrix} CH_2.CH(CO_2H) \\ CHMe\text{———}O \end{matrix} > C < \begin{matrix} CH_2.CH_2 \\ O\ \ .CHMe \end{matrix}$ (divalonic acid) [130°] which is got by the action of NaOHAq at 90° on 'divalolactone,' the product of the action of NaOHAq on valerolactone (Fittig, 256, 128). Liquid. Volatile with steam.

OXY-BUTYL-MALEIC ACID. *Lactone* $CHPr < \begin{matrix} C(CO_2H) \\ O.CO \end{matrix} > CH$. *Propaconic acid.* [124°]. Formed by distilling the bromide of propyl-itaconic acid with steam; the acid remains behind and is extracted with ether (Fittig, *A.* 256, 108).—Needles.—BaA'_2.

OXY-ISOBUTYL-MALONIC ACID $C_7H_{12}O_5$ *i.e.* $C_4H_9.C(OH)(CO_2H)_2$. [110°–114°]. Obtained from $C_4H_9CCl(CO_2Et)_2$ and KOHAq (Conrad a. Bischoff, *B.* 13, 600; 14, 617; Guthzeit, *A.* 209, 237). Deliquescent mass, v. e. sol. water.

DI-OXY-ISOBUTYL-METAPYRAZOLE $C_7H_{12}N_2O_2$ *i.e.* $\begin{matrix} C_4H_9.CH\text{ —}N \\ | \\ C(OH):N \end{matrix} > C(OH)$. [210°]. Obtained by boiling with dilute HCl the product $(C_4H_9.CH(CN).NH.CO.NH_2)$ of the action of urea upon valeric-aldehyde-cyanhydrin. Small white needles. M. sol. alcohol and hot water, sl. sol. cold water. Dissolves readily in alkalis (Pinner a. Lifschutz, *B.* 20, 2356).

OXY-BUTYL SUCCINIC ACID. The salts are got by the action of bases on the anhydride. $Ca(C_8H_{12}O_5)$ 5aq.—BaA″ 2aq.—Ag_2A''. *Anhydride* $CHPr < \begin{matrix} CH(CO_2H) \\ O\text{ —— }CO \end{matrix} > CH_2$. *Propyl-paraconic acid* [73·5°]. Formed by heating butyric aldehyde with sodium succinate and Ac_2O (Schmidt, *A.* 255, 68). Needles (from ligroïn). Yields heptenoic acid and oxy-heptoic lactone on distillation. — $Ca(C_8H_{11}O_4)_2$ 2aq.—BaA'_2.—AgA′.

Ethyl ether EtA′. (c. 214° at 96 mm.).

Oxy-isobutyl-succinic acid. *Salts.* — $Ba(C_8H_{12}O_5)_2$ 2aq.—Ag_2A''.

Anhydride. Formed, like the preceding isomeride, using isobutyric aldehyde (Zanner, *A.* 255, 86).—$Ba(C_8H_{11}O_4)_2$ 3aq.—CaA'_2 2aq.—AgA′.

OXY-BUTYRAMIDINE $C_4H_{10}N_2O$ *i.e.* $CMe_2(OH).C(NH).NH_2$. The crystalline hydrochloride is formed from oxy-butyrimido-ethyl ether and NH_3 (Pinner, *B.* 17, 2009). It is v. e. sol. water.

α-OXY-*n*-BUTYRIC ACID $C_4H_8O_3$ *i.e.* $CHEt(OH).CO_2H$. Mol. w. 104. [43°]. Formed by the action of moist Ag_2O upon bromo-*n*-butyric acid (Naumann, *A.* 119, 115; Friedel a. Machuca, *A.* 120, 279), and by the action of HCy and HCl on propionic aldehyde (Prschibiteck, *B.* 9, 1312). Formed also by reduction of ethyl-glyoxylic acid. Deliquescent crystals. Yields propionic acid on oxidation (Markownikoff, *A.* 176, 309; Ley a. Popoff, *A.* 174, 61).—$Ca'A_2$ 6aq. ZnA'_2 2aq. S. 2·35 at 18°.—AgA': prisms.

Ethyl ether EtA'. (167° i. V.). S.G. $\underline{0}$ 1·004; $\underline{19}$ ·995 (Schreiner, *B.* 12, 177; *A.* 197, 21). Yields ethyl-glyoxylic ether on oxidation (Aristoff a. Demjanoff, *C. C.* 1887, 1157). Acetyl derivative $CHEt(OAc).CO_2Et$ (198°) (Gal, *A.* 142, 373). Butyryl derivative (215°).

Methyl derivative $CHEt(OMe).CO_2H$. Formed from its Me and Et ethers which are made by the action of NaOMe on bromo-butyric ether (Duvillier, *C. R.* 86, 47, 1026; 87, 931; 88, 598; *A. Ch.* [5] 17, 528). Liquid, sol. water. —AgA'.—MeA'. (150°–155° i.V.).—EtA'. (160°) (D.); (148° i. V.) (Schreiner, *A.* 197, 16).

Ethyl derivative $CHEt(OEt).CO_2H$. Formed from its ether, which is made from bromo-butyric ether and NaOEt. Liquid, v. sol. water.—KA'.—BaA'_2.—AgA'.—MeA'. (157°).—EtA'. (168°–174°) (D.); (169° i.V.) (S.).

Methyl derivative of the amide $CHEt(OMe).CONH_2$ [78°]. Formed from $CHEt(OMe).CO_2Me$ and alcoholic NH_3 (D.). Slender needles, v. sol. water.

Ethyl derivative of the amide $CHEt(OEt)CONH_2$. [69°]. Laminæ, sol. water.

β-Oxy-*n*-butyric acid $CH_3.CH(OH).CH_2.CO_2H$. Occurs in urine and blood of diabetic patients (Külz, *Zeit. Biol.* 20, 165; 23, 329; Minkowski, *Fr.* 24, 153; Stadelmann, *Zeit. Biol.* 32, 456; Wolpe, *C. C.* 1887, 277; Hugounenq, *Bl.* [2] 47, 545; Deichmüller, Szymanski, a. Tollens, *A.* 228, 92). Formed by reducing acetoacetic acid with sodium-amalgam (Wislicenus, *A.* 149, 205), and from propylene chlorhydrin by successive treatment with KCy and KOH (Markownikoff, *A.* 153, 237). Obtained also by oxidising aldol with moist Ag_2O (Wurtz, *C. R.* 76, 1165). Thick syrup, volatile with steam. Decomposes at 130° into water and (α)-crotonic acid. When prepared from urine it is lævorotatory; $[\alpha]_D = -23·4$.—NaA': very deliquescent needles.—ZnA'_2.—CuA'.—AgA'.

Ethyl derivative $CH_3.CH(OEt).CH_2.CO_2H$. (c. 215°). Formed by the action of HCl on the nitrile, which is formed by combining allyl cyanide with alcohol (Pinner, *B.* 12, 2057).

Amide $CH_3.CH(OEt).CH_2.CONH_2$. [71°].

γ-Oxy-*n*-butyric acid $CH_2(OH).CH_2.CH_2.CO_2H$. Obtained by the action of boiling lime- or baryta-water upon its lactone, which is formed by treating succinyl chloride, dissolved in HOAc and ether, with sodium-amalgam (Saytzeff, *B.* 6, 1255; *A.* 171, 270; *J. pr.* [2] 25, 66; *Bl.* [2] 37, 540). Formed also from $CH_2Br.CH_2.CH_2OH$ by successive treatment with alcoholic KCy and potash (Frühling, *M.* 3, 700), and by boiling oxy-ethyl-acetoacetic ether with conc. baryta-water (Chanlaroff, *A.* 226, 325). Liquid, which volatilises in the cold. Volatile with steam. Sol. water. Forms the lactone slowly in the cold, more quickly on heating. Chromic acid mixture oxidises it to succinic acid.—KA': deliquescent tufts.—NaA'. —ZnA'_2 (dried at 100°).—BaA'_2 (dried at 110°): dendritic mass (from alcohol).

Lactone $CH_2{<}^{CH_2.CO}_{CH_2\text{——}}{>}O$. (206°). S.G. $\frac{0}{0}$ 1·1441; $\frac{16}{0}$ 1·1286. C.E. (0° to 16°) ·00086. *Butyrolactone.* Formed as above. Formed also by heating the lactonic acid of γ-oxy-ethyl-malonic acid at 120° (Röder, *A.* 227, 22), and by heating γ-chloro-butyric acid at 200° (Henry, *C. R.* 101, 1158). Mobile liquid, miscible with water, but separated therefrom by K_2CO_3. May be converted into *n*-butyric acid by successive treatment with HI and sodium-amalgam.

α-Oxy-isobutyric acid $(CH_3)_2C(OH).CO_2H$. *Acetonic acid. Butylactic acid.* [79°]. (212°).

Formation.—1. From acetone, HCy, and HClAq (Städeler, *A.* 111, 320).—2. From bromo-isobutyric acid and moist Ag_2O or Na_2CO_3Aq (Markownikoff, *A.* 146, 339; 153, 228, 251; Fittig, *A.* 200, 70).—3. From dimethyl oxalate by treatment with $ZnMe_2$ followed by water (Frankland a. Duppa, *A.* 133, 80; 135, 25).—4. By oxidising isobutyric acid with alkaline $KMnO_4$ (R. Meyer, *A.* 219, 240).—5. By oxidising di-oxy-pentane (amylene glycol) with diluted HNO_3 (Wurtz, *A.* 107, 197).—6. By heating acetone-chloroform with water at 180° (Willgerodt, *B.* 15, 2307; *Bl.* [2] 39, 157). Hygroscopic needles, v. e. sol. water, alcohol, and ether. Volatile with steam. Sublimes at 50°. Yields acetone and acetic acid on oxidation. Phenyl-hydrazine at 160° forms a ψ-phenyl-hydrazide [152°] converted by nitrous acid into a nitrosamine [98°] (Reissert a. Kayser, *B.* 22, 2926).

Salts.—BaA'_2.—$ZnA'_2$2aq: hexagonal plates, sl. sol. water. S. ·6 at 15°.—AgA': stellate groups of nacreous scales. S. 7.

Ethyl ether EtA'. (151°).

Ethyl derivative $(CH_3)_2C(OEt).CO_2H$. (180°). S.G. $\frac{0}{0}$ 1·0211; $\frac{16}{16}$ 1·0101. Formed from $CMe_2Br.CO_2H$ and KOEt (Hell a. Waldbauer, *B.* 10, 449).—BaA'_2aq.—PbA'_2aq.—ZnA'_2.—AgA': plates: m. sol. water.—EtA'. (155°).

Isopropylidene derivative $C_{11}H_{20}O_6$ *i.e.* $CMe_2(O.CMe_2.CO_2H)_2$. (197° uncor.). V.D. 120·3 (calc. 124). Formed by the action of KOH (8 mols.) on acetone-chloroform (2 mols.) and acetone (1 mol.), or upon a mixture of chloroform (1 mol.) and acetone (2 mols.) (Willgerodt, *B.* 20, 2445; Engel, *C. R.* 104, 688). Liquid, converted into oxy-isobutyric acid by heating with water. — CaA'' $1\frac{1}{2}$aq.—BaA'' $\frac{1}{2}$aq.—PbA'' (W.); PbA'' 2aq (E.).—ZnA''aq: small scales (W.); ZnA'' 2aq (E.).

Nitrile *v.* ACETONE CYANHYDRIN, vol. i. p. 31.

Anhydride $C_8H_{14}O_5$ *i.e.* $O(CMe_2.CO_2H)_2$. *Dibutylactic acid.* A product of the action of alcoholic potash on chloro-isobutyric acid (Balbiano, *J.* 1878, 704; 1880, 789). Amorphous, v. sol. water.—Na_2A'': deliquescent.

αβ-Di-oxy-butyric acid $CH_3.CH(OH).CH(OH).CO_2H$. [80°]. Formed by boiling bromo-oxy-butyric acid with water (C. Kolbe, *J. pr.* [2] 25, 390), and by heating β-methyl-glycidic acid with water at 100° in sealed tubes (Melikoff, *J. R.* 16, 526; *B.* 21, 2055). Mass of slender needles, v. e. sol. water, not volatile with

steam.—AgA′: needles. Gives a silver mirror when boiled with water.

Ethyl ether EtA′. (c. 228°). Liquid.

Anhydride v. METHYL-GLYCIDIC ACID.

βγ-Di-oxy-butyric acid $CH_2(OH).CH(OH).CH_2.CO_2H$. *Butylglyceric acid.* Formed from $CH_2(OH).CH(OH).CH_2Cl$ by successive treatment with KCy and dilute HNO_3 (Hanriot, *A. Ch.* [5] 17, 106). Formed also by warming its anhydride with water (Melikoff, *B.* 15, 2587). Thick liquid, v. sol. water, alcohol, and ether.—BaA'_2: amorphous.

Anhydride $CH_2<\begin{matrix}CH.CH_2.CO_2H\\O\end{matrix}$. *Butylglycidic acid.* Formed from (β)-crotonic acid by successive treatment with HOCl and alcoholic potash. Mobile liquid. Unites with HCl, forming chloro-oxy-butyric acid [99°]. The ether $C_4H_5EtO_3$ (145°–150°), S.G. $\frac{21.5}{}$ ·9931 is formed by the action of sodium-amalgam on a mixture of epichlorhydrin and chloroformic acid (Kelly, *B.* 11, 2225).

Di-oxy-isobutyric acid $CH_2(OH).CMe(OH).CO_2H$. [100°]. Formed from α-methyl-glycidic acid (*q. v.*) by warming with water at 100° (Melikoff, *J. R.* 16, 535). Prisms, v. sol. water.—KA′ $\frac{1}{2}$aq: small prisms.

Tri-oxy-isobutyric acid $(CH_2(OH))_2C(OH).CO_2H$. [116°]. Formed from glycerose by successive treatment with HCy and HCl (Fischer a. Tafel, *B.* 22, 106). Prisms (from alcohol), insol. benzene. HIAq followed by zinc-dust yields isobutyric acid.—CaA'_2 4aq. —PbA'_2 aq: needles, sl. sol. hot water.

A **tri-oxy-butyric acid** is also formed in the oxidation of gallic acid and tannin by dilute HNO_3 (Böttinger, *A.* 257, 248).

References.—BROMO- and CHLORO-OXYBUTYRIC ACIDS.

β-OXY-*n*-BUTYRIC ALDEHYDE *v.* ALDOL.

α-OXY-ISOBUTYRIC ALDEHYDE $CMe_2(OH).CHO$. (c. 90°). Obtained by boiling with HOAc the compound $C_{12}H_{26}O_3$ formed by the action of $NaOC_4H_9$ on iodoform (Gorboff, *J. pr.* [2] 41, 243). Mobile liquid, oxidised by Ag_2O to oxy-isobutyric acid [79°]. Forms with water a hydrate [c. 70°]. Polymerises on standing, forming prisms [c. 65°] v. sol. water.

Di-isobutyl derivative of oxyisobutyric orthaldehyde $CMe_2(OC_4H_9).CH(OH)(OC_4H_9)$. (125°). S.G. $\frac{0}{}$ ·9041. One of the products of the action of iodoform (or iodine) on $NaOC_4H_9$. Oil, with bitter taste. Converted by HOAc into isobutyl acetate and oxyisobutyric aldehyde.

OXY-BUTYRIC IMIDO-ETHYL ETHER $CMe_2(OH).C(NH)OEt$. The hydrochloride $C_6H_{13}NO_2HCl$ is formed from acetone, HCy, alcohol, and HCl (Pinner, *B.* 17, 2009). It is crystalline.

OXYBUTYROCYAMINE *v.* GUANIDO-BUTYRIC ACID.

OXY-CAFFEÏNE *v.* CAFFEÏNE.

OXY-CAMPHOR *v.* CAMPHOR and CAMPHOLENIC ACID.

OXY-CAMPHORAMIC ACID *v.* CAMPHORIC ACID.

OXY-CAMPHORIC ACID *v.* CAMPHORIC ACID.

OXY-CAMPHORIC ANHYDRIDE *v.* CAMPHANIC ACID.

OXY-CAMPHORONIC ACID *v.* CAMPHORONIC ACID.

OXY-CAPROIC ACID *v.* OXY-HEXOIC ACID.

OXYTRICARBALLYLIC ACID. *Methyl derivative* $C_3H_4(OMe)(CO_2H)_3$. Formed by heating $(C_3H_5)_2C(OMe).CO_2H$ with dilute HNO_3 (Schatzky, *J. R.* 17, 85). Syrup.—$CaH_4A'''_2$ $\frac{1}{2}$aq. —$BaH_4A'''_2$ 2aq.

OXY-CARBOSTYRIL *v.* DI-OXY-QUINOLINE.

OXY-CARBOXYLIC ACID *v.* BENZENE-TRI-QUINONE.

OXY-*o*-CARBOXY-PHENYL-ACETIC ACID $CO_2H.C_6H_4.CH(OH).CO_2H$. Formed from $CO_2H.C_6H_4.CO.CO_2H$ and sodium-amalgam (Scherks, *B.* 18, 381). Quickly changes, when set free, to the anhydride (phthalide carboxylic acid) [149·5°].

Oxy-carboxy-di-phenyl-acetic acid $C_6H_4(CO_2H).CPh(OH).CO_2H$. [c. 80°]. Formed by warming benzil *o*-carboxylic acid with alkalis (Graebe, *B.* 21, 2003).—K_2A'' 2aq.

Di-oxy-di-carboxy-phenyl-acetic acid. *Tri-ethyl-ether* $C_6H(OH)_2(CO_2Et)_2.CH_2.CO_2Et$. [98°]. Formed from acetone dicarboxylic ether and sodium (Cornelius a. Pechmann, *B.* 19, 1448). Needles (from alcohol), insol. water.

γ-OXY-*o*-CARBOXY-PHENYL-BUTYRIC ACID. *Lactone* $C_{11}H_{10}O_4$. [121°]. Formed by reducing the anhydride of carboxy-benzoyl-propionic acid with sodium-amalgam (Roser, *B.* 17, 2773).—$AgC_{11}H_9O_4$.—$Ag_2C_{11}H_{10}O_5$.

An **isomeric lactone** [140°] is obtained by reducing phthalyl-propionic acid (Gabriel a. Michael, *B.* 11, 1681). — $BaC_{11}H_{10}O_5$. — $Ba(C_{11}H_9O_4)_2$.—$AgC_{11}H_9O_4$.

OXY-CARBOXY-PHENYL-PROPIONIC ACID. *Lactone* $C_{10}H_8O_4$ *i.e.* $C_6H_4<\begin{matrix}CH—CH_2.CO_2H\\ \quad >O \\ CO\end{matrix}$. Formed by reducing phthalyl-acetic acid with sodium-amalgam, and acidifying (Gabriel a. Michael, *B.* 10, 1558, 2200). Needles (containing aq). Yields $AgC_{10}H_7O_4$, $Ag_2C_{10}H_8O_5$, and $BaC_{10}H_8O_5$ 2aq.

Tri-oxy-carboxy-phenyl-propionic acid. *Lactone* $[4:3:\frac{1}{2}]C_6H_2(OH)_2<\begin{matrix}CH—CH_2.CO_2H\\ \quad >O \\ CO\end{matrix}$. [228°]. Formed by reducing its di-methyl derivative (meconic-acetic acid) with HI and P (Liebermann a. Kleemann, *B.* 19, 2293). Tables. Gives a blue colour with $FeCl_3$.

Ethyl ether EtA′. [c. 131°]. Crystalline.

OXYCHRYSOQUINONE *v.* CHRYSOQUINONE.

OXYCINCHENE *v.* CINCHENE.

OXYCINCHONIDINE *v.* CINCHONIDINE.

OXY-CINNAMIC ACID *v.* COUMARIC ACID.

α-Oxy-cinnamic acid. $C_6H_5.CH:C(OH).CO_2H$. Formed in small quantity in the preparation of the isomeric phenyl-glycidic acid by the action of alcoholic potash on $C_6H_5.CHBr.CH(OH).CO_2H$ (Plöchl, *B.* 16, 2821). Readily decomposes, yielding phenyl-acetic aldehyde and di-oxy-phenyl-propionic acid.

Phenyl derivative $C_6H_5CH:C(OPh).CO_2H$. [180°]. Formed by heating sodium phenoxy-acetate with benzoic aldehyde and Ac_2O (Oglialoro, *C. J.* 40, 276). Prisms.—AgA′: prisms (from water).

(3, 2, 1)-Di-oxy-cinnamic acid $[3:2:1]C_6H_3(OH)_2CH:CH.CO_2H$.

Anhydride $C_6H_3(OH)<\begin{matrix}CH:CH\\O—CO\end{matrix}$. *m-Oxy-*

coumarin. [280°-285°]. Formed by heating pyrocatechin with malic acid and H_2SO_4 (Bezzari, *G.* 15, 34). Needles, sl. sol. cold water. Reduces salts of Au, Cu, and Ag.

(4, 3, 1)-**Di-oxy-cinnamic acid** *v.* CAFFEIC ACID.

(5, 2, 1)-**Di-oxy-cinnamic acid** [5:2:1]$C_6H_3(OH)_2CH:CH.CO_2H$.

Anhydride $\left[5\ \begin{smallmatrix}1\\2\end{smallmatrix}\right]C_6H_3(OH)\langle\begin{smallmatrix}CH:CH\\O.CO\end{smallmatrix}$. [250°]. Formed by heating a mixture of hydroquinone, malic acid, and H_2SO_4 (Pechmann a. Welsh, *B.* 17, 1648). Needles, v. sol. alcohol. Yields an acetyl derivative [147°] crystallising in needles. The methyl derivative [103°] is got from [5:2:1] $C_6H_3(OMe)(OH)CHO$ by boiling with Ac_2O and NaOAc (Tiemann a. Müller, 14, 1996).

o-Methyl derivative [5:2:1]$C_6H_3(OH)(OMe)CH:CH.CO_2H$. [180°]. Obtained from $C_6H_3(NH_2)(OMe)CH:CH.CO_2H$ by the diazo- reaction (Schnell, *B.* 17, 1387). Crystals.

Di-methyl derivative $C_6H_3(OMe)_2CH:CH.CO_2H$. [143°]. Obtained by methylating the *o*-methyl derivative. Needles. Yields di-methyl-gentisic aldehyde on oxidation with $KMnO_4$.

(4, 2, 1)-**Di-oxy-cinnamic acid** *v.* UMBELLIC ACID.

αp-**di-oxy-cinnamic acid.** *Phenyl-methyl derivative* $C_6H_4(OMe).CH:C(OPh).CO_2H$. [200°]. A product of the action of anisic aldehyde and Ac_2O on sodium phenoxy-acetate (Valentini, *G.* 14, 147). Rectangular tablets, sol. hot alcohol.—MeA′. [100°]. Laminæ.

Anhydride of the phenyl derivative $C_{15}H_{10}O_3$. [113°]. Formed from salicylic aldehyde, Ac_2O, and sodium phenoxy-acetate (Oglialoro, *C. C.* 1887, 1164). Yellow prisms, v. sl. sol. hot water.

Tri-oxy-cinnamic acid *v.* ÆSCULETIC ACID and DAPHNETIN.

Tetra-oxy-cinnamic acid. *Di-methyl methylene ether* $C_6H(O_2CH_2)(OMe)_2CH:CH.CO_2H$. [196°]. Formed from apiolic aldehyde, Ac_2O, and NaOAc (Ciamician a. Silber, *B.* 22, 2485). Small yellow needles (from hot alcohol), sl. sol. ether and hot water.

OXY-CINNAMIC ALDEHYDE *v.* COUMARIC ALDEHYDE.

Di-oxy-cinnamic aldehyde. *Methyl derivative v.* FERULIC ALDEHYDE.

OXY-CINNOLINE $C_8H_6N_2O$ *i.e.* $C_6H_4\langle\begin{smallmatrix}C(OH):CH\\N=\!=\!=N\end{smallmatrix}$. [225°]. Formed by heating its carboxylic acid at 260° (Richter, *B.* 16, 681). Small prisms, v. sol. alcohol and ether, sl. sol. water. May be sublimed. Sol. Na_2CO_3Aq.—$B'_2H_2PtCl_6$: small prisms.

Oxy-cinnoline carboxylic acid $C_6H_4\langle\begin{smallmatrix}C(OH):C.CO_2H\\N=\!=\!=N\end{smallmatrix}$. [c. 265°]. Formed from *o*-diazo-phenyl-propiolic acid by heating with water at 70°. Colourless needles or scales, sol. HClAq, sl. sol. alcohol, nearly insol. water.

OXY-CITRACONIC ACID $C_5H_6O_5$ *i.e.* $O\langle\begin{smallmatrix}CMe.CO_2H\\CH\ .CO_2H\end{smallmatrix}$. [162°]. Formed from citraconic acid by successive treatment with HOCl and alkalis (Morawski, *J. pr.* [2] 10, 69; 11, 430; Scherko, *A.* 227, 233; Michael, *J. pr.* [2] 40, 171; Melikoff a. Feldmann, *A.* 253, 89). Prisms (containing aq). Hot water converts it into propionic aldehyde and CO_2. With HBr it forms $C_5H_7BrO_5$ [156°]. HCl yields, in like manner, $CO_2H.CClMe.CH(OH).CO_2H$ [162°].

Salts.—$(NH_4)_2A''$.—$(NH_4)HA''$.—KHA″.—BaA″ 4aq.—SrA″ 4aq.—PbA″ 4½aq.

Ethyl ether Et_2A''. (255°). S.G. $\frac{0}{0}$ 1·1376; $\frac{22}{22}$ 1·1167. C.E. (0°-22°) ·0008507.

OXY-CITRIC ACID $C_6H_8O_8$ *i.e.* $C_3H_3(OH)_2(CO_2H)_3$. Occurs in beetroot (Lippmann, *B.* 16, 1078). Formed from aconitic acid by successive treatment with HOCl and lime-water (Pawolleck, *A.* 178, 150). Deliquescent mass, v. e. sol. water.—Salts: $Ba_3A'''_2$ 5aq.—$Ca_3A'''_2$ 9aq.—$Ca_3A'''_2$ 10aq.—$Cd_4(C_6H_4O_8)_2$6aq.—$Cu_4(C_6H_4O_8)_2x$aq.—Et_3A''': oil with bitter taste.

OXYCOBALTAMINES *v.* vol. ii. p. 224.

OXYCOMENIC ACID *v.* COMENIC ACID.

OXY-CONICEÏNE *v.* CONIINE.

OXY-COPAIVIC ACID *v.* COPAIVIC ACID.

OXY-COUMARIC ACID *v.* DI-OXY-CINNAMIC ACID.

OXY-COUMARILIC ACID *v.* COUMARILIC ACID.

OXY-COUMARIN *v. Anhydride of* DI-OXY-CINNAMIC ACID and UMBELLIFERONE.

Di-oxy-coumarin *v.* DAPHNETIN.

OXY-COUMARONE *v.* COUMARONE.

β-OXY-CROTONIC ACID. *Methyl derivative* $CH_3.C(OMe):CH.CO_2H$. [128·5°]. Formed from β-chloro-crotonic acid and NaOMe (Friedrich, *A.* 219, 327, 334). Crystals, insol. water.

Ethyl derivative $CH_3.C(OEt):CH.CO_2H$. [137·5°]. Formed from $CH_3.CCl:CH.CO_2Et$ and alcoholic potash. Prisms, v. sol. alcohol and ether.—KA′: plates.—KA′ 3aq: needles.—EtA′. [30°]. Decomposed by dilute H_2SO_4 into acetone, CO_2, and alcohol.

Phenyl derivative $CH_3.C(OPh):CH.CO_2H$. [150°]. Formed by heating sodium β-chloro-crotonate or β-chloro-isocrotonate with NaOPh (Autenrieth, *A.* 254, 240). Crystals, v. sl. sol. hot water. Yields $CH_3.C(OPh):CH_2$ (162°) on heating.

The above compounds may be viewed as derivatives of acetoacetic acid (*q. v.*).

β-Oxy-isocrotonic acid. This acid is not known in free state, for, like the preceding isomeride, it would at once change to aceto-acetic acid.

Methyl ether of the methyl derivative $CH_2:C(OMe).CH_2.CO_2Me$. (175°). S.G. $\frac{15}{}$ 1·0235. Formed from $CH_2:CCl.CH_2.CO_2Me$ and NaOMe (Enke, *A.* 256, 205).

Methyl ether of the ethyl derivative $CH_2:C(OEt).CH_2.CO_2Me$. [12°]. (195°). S.G. $\frac{15}{}$ ·999.

Ethyl ether of the ethyl derivative $CH_2:C(OEt).CH_2.CO_2Et$. [29°]. (195° cor.). Formed from β-chloro-isocrotonic ether and NaOEt (Koll, *A.* 249, 324). Plates.

Propyl derivative of the methyl ether $CH_2:C(OPr).CH_2.CO_2Me$. (230°). S.G. ·961.

Isobutyl derivative of the methyl ether $CH_2:C(OC_4H_9).CH_2.CO_2Me$. (253°). S.G. ·930.

α-Oxy-isocrotonic acid. *Nitrile* $CH_2:CH.CH(OH).CN$. Formed from acroleïn,

KCy, and HOAc (Lobry de Bruyn, *R. T. C.* 4, 223). Oil.

Isomerides *v.* OXY-METHACRYLIC ACID and ACETOACETIC ACID.

OXYCUMENE *v.* CUMENOL.

Di-oxy-cumene. *Di-methyl derivative* $C_6H_3C_3H_7(OMe)_2$. (246°). Formed by the action of sodium on an alcoholic solution of $C_6H_3(C_3H_5)(OMe)_2$ (263°), which is got by boiling the isomeric methyl ether of eugenol with alcoholic potash (Ciamician a. Silber, *B.* 23, 1164). Colourless oil.

***m*-Di-ω-oxy-ψ-cumene** $C_6H_3(CH_3)(CH_2.OH)_2$ [4:3:1]. [77°]. Formed by boiling *m*-di-ω-bromo-ψ-cumene with aqueous Na_2CO_3. V. sol. water and alcohol, sl. sol. ether (Hjelt a. Gadd, *B.* 19, 867).

Isomeride *v.* HYDRO-ψ-CUMOQUINONE.

Tri-oxy-cumene. *Di-methyl derivative* $C_6H_2(C_3H_7)(OMe)_2(OH)$. (278°). Formed by reduction of iso-apiol (Ciamician a. Silber, *B.* 23, 2285). Thick liquid, sol. KOHAq.

Isomeride *v.* PROPYL-PYROGALLOL.

OXY-CUMIDINE *v.* AMIDO-CUMENOL.

OXY-*n*-CUMINIC ACID $C_6H_3Pr(OH).CO_2H$ [3:2:1]. [94°]. Formed from o-propyl-phenol, Na, and CO_2 (Spica, *J.* 1878, 585).—BaA'_2 $2\frac{1}{2}$aq.—PbA'_2 $2\frac{1}{2}$aq.—AgA': pp.

Oxy-*n*-cuminic acid $C_6H_3Pr(OH).CO_2H$ [5:2:1]. [98°]. Formed from *p*-propyl-phenol, Na, and CO_2 (Spica). Coloured violet by $FeCl_3$. —BaA'_2 3aq.— PbA'_2 2aq.—AgA'.

Oxy-cuminic acid $C_6H_3Pr(OH).CO_2H$ [4:2:1]. [93°]. *Formation.*—1. By fusing carvacrol with potash (Jacobsen, *B.* 11, 1063).—2. By fusing isocymene sulphonic acid with potash (Jacobsen, *B.* 12, 432).—3. From amido-cuminic acid by the diazo- reaction (Widman, *B.* 19, 270).

Properties.—Flat needles or leaflets. Converted by HCl at 190° into *m*-propyl-phenol [26°] (228° i.V.). $FeCl_3$ gives a reddish-violet colour. Yields CaA'_2 and BaA'_2.

Oxy-cuminic acid $C_6H_3Pr(OH)CO_2H$ [4:3:1]. [141°]. *Formation.*—1. From amido-cuminic acid (Cahours, *A. Ch.* [3] 53, 338; Lippmann a. Lange, *B.* 13, 1662).—2. Among the products got from thymol by potash-fusion (Barth, *B.* 11, 1571).—3. By oxidation of potassium cumyl-sulphate $C_6H_3MePr.O.SO_3K$ [1:4:3] or cumyl-phosphate $C_6H_3MePr.O.PO_3K_2$ [1:4:3] with alkaline $KMnO_4$, and saponification of the resulting sulphate or phosphate (Heymann a. Königs, *B.* 19, 3306).

Properties.—Slender needles, sl. sol. cold water. Not attacked by conc. HClAq at 200°.

Salts. — NaA' 2aq. — $Na_2C_{10}H_{10}O_3$ $1\frac{1}{2}$aq. — BaA'_2 aq.—CdA'_2 aq.—AgA': white pp.

Ethyl ether EtA'. [75°]. Prisms.

Ethyl derivative $C_6H_3Pr(OEt).CO_2H$. [140°]. Crystalline powder.—CdA'_2.—AgA'.

Oxy-o-cuminic acid $C_6H_3Pr(OH)CO_2H$ [3:2:1]. [72°]. Formed, together with $C_6H_2Pr(OH)(CO_2H)_2$ [295°], from isopropyl-phenol, Na, and CO_2 (Fileti, *G.* 16, 126). Colourless needles. $FeCl_3$ colours it violet.

Oxy-o-cuminic acid $C_6H_3Pr(OH)CO_2H$ [5:2:1]. [121°]. Obtained from *p*-isopropyl-phenol, sodium, and CO_2 (Paterno, *J.* 1878, 806). Formed also by fusing *m*-isocymenol with KOH (Jesurun, *B.* 19, 1415). Flat needles. $FeCl_3$ colours its solution deep bluish-violet.—CaA'_2.—BaA'_2.—AgA'.

An isomeride [166°–170°] is got by fusing β-isocymene sulphonic acid with potash (Jacobsen, *B.* 12, 433).

Oxy-ψ-cuminic acid $C_6HMe_3(OH)CO_2H$ [6:5:3:2:1]. [181°]. Formed from sodium ψ-cumenol and CO_2 (Krohn, *B.* 21, 884). Needles, v. sol. ether.

Oxy-ψ-cuminic acid $C_6HMe_3(OH)CO_2H$ [1:3:4:5:6]. [148°]. Formed by fusing durenol with potash (Jacobsen a. Schnapauff, *B.* 18, 2844). Small needles, nearly insol. cold water. HClAq at 200° yields ψ-cumenol [93°].—CaA'_2 2aq: prisms, sl. sol. cold Aq.

Di-oxy-ψ-cuminic acid $C_6Me_3(OH)_2CO_2H$ [6:4:3:5:2:1]. [210°]. Formed by reducing ψ-cumoquinone carboxylic acid with zinc-dust and aqueous NaOH (Nef, *B.* 18, 3498; *A.* 237, 13; *C. J.* 53, 428). Needles, m. sol. hot water. Reduces ammoniacal $AgNO_3$. Its alkaline solution turns violet in air.

Ethyl ether EtA'. [109°]. Needles.

OXY-ψ-CUMINIC ALDEHYDE $C_{10}H_{12}O_2$ *i.e.* $C_6HMe_3(OH)CHO$ [6:5:3:2:1]. [106°]. A product of the action of chloroform and NaOHAq upon ψ-cumenol (Auwers, *B.* 17, 2976). Needles.

DI-OXY-DI-ψ-CUMYL $C_{18}H_{22}O_2$ *i.e.* $C_6HMe_3(OH).C_6HMe_3(OH)$. [173°]. Formed in the preparation of ψ-cumenol from ψ-cumidine by the diazo- reaction, and also by oxidation of ψ-cumenol with dilute HNO_3 (Auwers, *B.* 17, 2982; 18, 2659). Crystals. Yields a di-bromo-derivative [187°] and a di-methyl derivative [126°].

α-OXY-CUMYL-ACETIC ACID $C_{11}H_{14}O_3$ *i.e.* $C_6H_4Pr.CH(OH).CO_2H$. [158°]. Formed from cuminic aldehyde, HCy, and HCl (Raab, *B.* 8, 1148). Needles.—BaA'_2 4aq.—PbA'_2.

Oxy-di-cumyl-acetic acid $(C_3H_7.C_6H_4)_2C(OH).CO_2H$. [120°]. Formed from $C_3H_7.C_6H_4.CO.CO.C_6H_4C_3H_7$ by potash-fusion (Boesler, *B.* 14, 326). Needles.—BaA'_2.

OXY-CUMYL-ACRYLIC ACID $C_{12}H_{14}O_3$ *i.e.* $C_6H_3(C_3H_7)(OH).CH:CH.CO_2H$. The (4, 2, 1)-acid [176°] and the (4, 3, 1)-isomeride [206°] are formed by the diazo- reaction from the corresponding amido- acids. Both are crystalline (Widman, *B.* 19, 268, 417).

DI-OXY-DI-CUMYL-PYRAZINE DICARBOXYLIC ACID

[1:4:3] $CO_2H.C_6H_3Pr.N\!\left<\begin{matrix}C(OH):CH\\CH\quad:C(OH)\end{matrix}\right>\!N.C_6H_3Pr.CO_2H$ [3:4:1].

Formed by boiling $CH_2Cl.CO.NH.C_6H_3Pr.CO_2Me$ with alcoholic potash (Abenius, *J. pr.* [2] 40, 440). Insoluble powder.—Et_2A''. [193°].

OXYCYANCONIINE *v.* CYANCONIINE.

OXYCYANETHINE *v.* CYANETHINE.

OXY-CYCLOPIN $C_{15}H_{30}O_{16}$. A glucoside in Cape Tea split up by dilute acids into oxy-cyclopic acid $C_{19}H_{22}O_{12}$ and glucose (Greenish, *Ph.* [3] 11, 569).

DI-OXY-DICYMYL $C_{20}H_{26}O_2$ *i.e.* $C_6H_2Me(C_3H_7)(OH).C_6H_2Me(C_3H_7)(OH)$. [165·5°]. Formed by oxidising thymol with iron-alum (Dianin, *J. R.* 14, 135). Prisms or tables (containing aq), v. sol. alcohol.

OXY-CYMYL-ACRYLIC ACID $C_{13}H_{16}O_3$ *i.e.* [2:5:6:1] $C_6H_2Me(C_3H_7)(OH).CH:CH.CO_2H$. The anhydride [53°] (220°–230°) is formed by heating thymol with malic acid and H_2SO_4 (Pechmann a. Welsh, *B.* 17, 1647).

The isomeric (2, 5, 4, 1)- acid 280°] is formed from thymotic aldehyde, NaOAc, and Ac_2O

(Kotek, *B.* 16, 2104). It yields a crystalline methyl derivative [141°].

DI-OXY-DI-CYMYL-ETHANE $C_{22}H_{30}O_2$ *i.e.* $CH_3.CH(C_{10}H_{12}.OH)_2$. [185°]. Formed from thymol, paraldehyde, chloroform, and $SnCl_4$ (Steiner, *B.* 11, 287). Needles (from benzene). Yields $C_{22}H_{28}(OEt)_2$ and $C_{22}H_{28}(OAc)_2$ [100°].

DI-OXY-DI-CYMYL-ETHYLENE $CH_2:C(C_{10}H_{12}OH)_2$. [171°]. Formed, together with the preceding body, from $CCl_3.CH(C_{10}H_{12}OH)_2$ by boiling with alcohol and zinc-dust (Jaeger, *B.* 7, 1198; *C. J.* 31, 263). Oxidised by alkaline K_3FeCy_6 to $C_{44}H_{54}O_4$ [215°] and $C_{22}H_{26}O_2$ [215°].

DI-OXY-DI-CYMYL SULPHIDE $(C_6H_2MePr(OH))_2S$. [153°] (Tassinari, *G.* 17, 83).

DI-OXY-DECANE $C_{10}H_{22}O_2$. *Decylene glycol. Diamylene glycol.* The diacetyl derivative, formed from di-bromo-decane and AgOAc, yields on saponification with KOH the anhydride $C_{10}H_{20}O$ (diamylene oxide) (Bauer, *J.* 1862, 450).

Di-oxy-decane CMePr(OH).CMePr(OH). *Methyl propyl pinacone.* (c. 223°). Formed from methyl *n*-propyl ketone, water, and Na (Friedel, *J.* 1869, 513). Dilute H_2SO_4 converts it into the pinacolin $C_{10}H_{20}O$ (185° uncor.) (Szymanski, *B.* 19, 1532). The isomeric $CEt_2(OH).CEt_2(OH)$ [28°] is formed in like manner from di-ethyl-ketone (Schramm, *B.* 16, 1584).

Tetra-oxy-decane. *Anhydride* $<\begin{matrix}CMe(OH).CH_2.CMe\\CMe(OH).CH_2.CMe\end{matrix}>O$. (270°). Formed from $(CH_3.CO)_2CH_2$ and sodium-amalgam in presence of a dilute acid (Combes, *A. Ch.* [6] 12, 230). Liquid, v. sl. sol. water.

γ-OXY-DECOIC ACID. *Lactone* $C_{10}H_{18}O_2$ *i.e.* $C_6H_{13}.CH<\begin{matrix}CH_2.CH_2\\O\text{—}CO\end{matrix}$. (281° uncor.). Formed from bromo-decoic acid and Na_2CO_3 (Schneegans, *A.* 227, 92). Yields $Ba(C_{10}H_{19}O_3)_2aq$ and $AgC_{10}H_{19}O_3$.

Oxy-decoic acid $CH_2Pr.CH(OH).CHPr.CO_2H$. [120°]. Formed from isovaleric ether and Na (Wohlbrück, *B.* 20, 2332). Needles, v. sol. hot water.—BaA'_2.—$AgA'\frac{1}{3}AgOH$: amorphous.

Oxy-decoic acid $C_{10}H_{20}O_3$ *i.e.* $C_4H_9.CH(OH).CH(C_3H_7).CO_2H$. [120°]. Formed by the action of alcoholic potash at 110° on $C_4H_9.CH(OEt).CH(C_3H_7).CO_2Et$, which constitutes half the product of the action of sodium on isovaleric ether (Hantzsch, *A.* 249, 64).

DI-OXY-DECYLENE. *Di-valeryl-derivative* $C_4H_9C(O.COC_4H_9):C(O.COC_4H_9)C_4H_9$. (155°–165° at 12 mm.) (Klinger a. Schmitz, *B.* 24, 1275).

DI-OXY-DODECANE CEtPr(OH).CEtPr(OH). (255°). Formed from ethyl propyl ketone, water, and Na (Oechsner de Coninck, *Bl.* [2] 25, 10). Liquid. The isomeric 'methyl butyl pinacones' CHMeEt.CMe(OH).CMe(OH).CHMeEt (249°) and $CMe_3.CMe(OH).CMe(OH).CMe_3$ [69°] are prepared in like manner (Wislicenus, *A.* 219, 310; Friedel a. Silva, *J.* 1873, 340).

TRI-OXY-DODECINOIC ANHYDRIDE $C_{12}H_{18}O_3$ *i.e.* $\begin{matrix}CH_2.CH_2\\CHEt.O\end{matrix}>C:C<\begin{matrix}CH_2.CHEt\\CO\ .O\end{matrix}$. *Di-hexolactone.* (above 300°). Formed from oxy-hexoic lactone and NaOEt (Fittig, *A.* 256, 135). Liquid, sl. sol. water.

DI-OXY-DODECINENE $C_{12}H_{22}O_2$ *i.e.* $C_3H_5CH_2.CMe(OH).CMe(OH).CH_2C_3H_5$. (266°). S.G. $\frac{0}{0}$ ·963. C.E. (0°–24°) ·00082. Formed from allyl-acetone (Kablukoff, *J. R.* 1887, 513).

OXY-DODECOIC ACID $(C_5H_{11})_2C(OH).CO_2H$. *Diamoxalic acid.* [122°]. Formed from oxalic ether, isoamyl iodide, and zinc (Frankland a. Duppa, *A.* 142, 8). Yields EtA′ (262°) and $C_5H_{11}A'$ (280°–290°).

OXY-DURYL-ACETIC ACID [6:4:3:2:1] $C_6HMe_4.CH(OH).CO_2H$. [156°]. Formed from tetra-methyl-phenyl-glyoxylic acid, alcohol, and sodium-amalgam (Claus a. Foecking, *B.* 20, 3100; *J. pr.* [2] 38, 232). Prisms.—$NaA'1\frac{1}{2}aq$.—$CaA'_2 8aq$.—$BaA'_2 3aq$: v. sol. water. The isomeric (5, 4, 3, 2, 1)-acid [160° uncor.] yields $KA'4aq$, $BaA'_2 3aq$, and $CaA'_2 2\frac{1}{2}aq$.

DI-OXY-ENNANE $C_9H_{20}O_2$ *i.e.* $Pr.CH(OH).CH(OH).CH_2Pr$. [80°]. (232°). Formed by the action of alcoholic potash on a mixture of isobutyric aldehyde and valeric aldehyde (Fossek, *M.* 5, 120; Swoboda, *M.* 11, 384). Prisms (from water). On boiling with dilute H_2SO_4 it yields a pinacolin $C_{18}H_{36}O_2$ (274°). Cold conc. H_2SO_4 forms $C_9H_{18}O$ (150°).

Di-acetyl derivative $C_{13}H_{22}O_4$. (242°).

OXY-ENNENOIC ACID $C_9H_{16}O_3$. *Oxy-vinyl-iso-heptoic acid.* Found among the products got by passing CO over NaOAc mixed with sodic iso-amylate at 180° (Poetsch, *A.* 218, 78). Thick honey-yellow oil, not volatile with steam.—$C_9H_{14}Na_2O_3 8aq$.

Methyl ether $C_9H_{15}MeO_3$. (c. 250°).

OXY-ENNOIC ACID $CPr_2(OH).CH_2.CO_2H$. Formed by oxidising $CPr_2(OH).C_3H_5$ with $KMnO_4$ (Schirokoff, *J. pr.* [2] 23, 197). Syrup, sl. sol. hot water.—CaA'_2aq.—BaA'_2aq. S. (of BaA'_2) 9·3 at 20°.—PbA'_2. S. 1·6 at 19·5°.—AgA′: prisms.

Oxy-ennoic acid $Pr.CH_2.CH_2.CEt(OH).CO_2H$. Crystalline.—$BaA'_2$.—AgA′.

Ethyl ether EtA′. (225°). S.G. $\frac{13}{}$ ·940. A product of the action of isoamyl iodide and zinc on oxalic ether (Frankland a. Duppa, *A.* 142, 6; Beilstein, *Bn.* 1, 529).

OXY-ERUCIC ACID $C_{22}H_{42}O_3$. Formed from di-bromo-behenic acid $C_{22}H_{42}Br_2O_2$ and moist Ag_2O (Haussknecht, *A.* 143, 51). Oil, forming amorphous salts.

OXY-ETHANE PHOSPHONIC ACID $C_2H_7PO_4$ *i.e.* $CH_3.CH(OH).PO(OH)_2$. [76°]. Formed from aldehyde (4 mols.) and PCl_3 (1 mol.), followed by cold water (Fossek, *M.* 7, 32). Crystals decomposing at 120°.—CaA″.

OXY-ETHANE SULPHONIC ACID *v.* ISETHIONIC ACID.

Oxy-ethane disulphonic acid $C_2H_3(OH)(SO_3H)_2$. Formed, together with ethane tri-sulphonic acid, by boiling tri-bromo-ethane with a saturated solution of ammonium sulphite (Monari, *B.* 18, 1347).—$Na_2A''3\frac{1}{2}aq$.—$(NH_4)_2A''\frac{1}{2}aq$.—$BaA''2aq$: very soluble powder.

Oxy-ethane disulphonic acid $SO_3H.CH_2.CH(OH).SO_3H$. Formed from isethionic acid and H_2SO_4 at 100° (Meves, *A.* 143, 196; Engelhardt a. Latschinoff, *Z.* 1868, 271).—$K_2A''\frac{1}{2}aq$: needles, v. e. sol. water.

OXY-ETHENYL-AMIDO-PHENYL-MERCAPTAN C_8H_7NSO *i.e.* $C_6H_4<\begin{matrix}N\\S\end{matrix}>C.CH_2OH$ [175°]. Prepared by heating chloro-acetic acid with amido-phenyl-mercaptan (Hofmann, *B.* 13,

1234). Long fine needles. Insol. water, sol. alcohol and caustic alkalis.

DI-OXY-ETHENYL-o-PHENYLENE DI-AMINE $C_8H_6N_2O_2$. [above 280°]. Obtained by reduction of o-nitro-oxanilic acid with $SnCl_2$ (Aschan, *B.* 18, 2939). Sublimes in plates. Sol. acetic acid, sl. sol. water, alcohol, and ether, insol. benzene, ligroïn, and chloroform. It has weak acid properties, forming unstable salts.—$BaA'_2$2aq: white crystalline pp.

OXY-ETHYL-ACETOACETIC ETHER $CH_3CO.CH(CO_2H).CH_2.CH_2OEt$. Formed from acetoacetic ether, NaOEt, and glycol chlorhydrin (Chanlaroff, *A.* 226, 326). Liquid, yielding γ-oxy-butyric acid on boiling with baryta and alcohol.

Oxy-di-ethyl-acetoacetic ether. *Methyl derivative* $CH_2(OMe).CO.CEt_2.CO_2Et$. (c. 188°). Formed, together with an oil $C_7H_{14}O_2$ (c. 131°) by the action of NaOMe on chloro-di-ethyl-acetoacetic ether (James, *A.* 231, 240).

Di-oxy-di-ethyl-acetoacetic ether. *Dimethyl derivative* $CH(OMe)_2.CO.CEt_2.CO_2Et$. (c. 195°). Formed together with the compound $CH(OMe)_2.CO.CHEt_2$ (134°), by the action of NaOMe on $CHCl_2.CO.CEt_2.CO_2Et$.

OXY-ETHYL-DI-ALLYL-AMINE $(C_3H_5)_2NCH_2.CH_2OH$. (197°). Formed from di-allyl-amine and $CH_2Cl.CH_2OH$ (Ladenburg, *B.* 14, 1879). Liquid base.

OXY-ETHYL-*p*-AMIDO-BENZOIC ACID $CH_2OH.CH_2.NH.C_6H_4.CO_2H$. [187°]. Formed from *p*-amido-benzoic acid and ethylene oxide (Ladenburg, *B.* 6, 129). Prisms, sl. sol. cold water.—$HA'HNO_3$: crystals.

OXY-ETHYL-o-AMIDO-PHENOL $CH_2(OH).CH_2.NH.C_6H_4OH$. (290°–310°). Formed from o-amido-phenol and glycol chlorhydrin (Knorr, *B.* 22, 2095). Liquid, sol. water. Successive treatment with fuming HCl and NaOHAq forms the anhydride $C_6H_4{<}{\begin{smallmatrix}O\ .CH_2\\ NH.CH_2\end{smallmatrix}}$ (268°).

Methyl derivative $CH_2(OH).CH_2.NH.C_6H_4OMe$. (305° i. V.). Formed from o-anisidine.

OXY-ETHYL-AMIDO-QUINOLINE DI-HYDRIDE *v.* HYDRAZIDO-PHENYL-PROPIONIC ACID.

OXY-ETHYL-AMINE $CH_2(OH).CH_2NH_2$. *Amido-ethyl alcohol.* Formed by the action of ammonia on ethylene oxide or on glycol chlorhydrin (Wurtz, *C. R.* 49, 898; 53, 338). Formed also by the action of conc. H_2SO_4 on bromo-ethyl-phthalimide, by the action of HNO_3 on vinylamine, and by the action of $AgNO_3$ (2 mols.) on bromo-ethylamine hydrobromide (1 mol.) (Gabriel, *B.* 21, 569, 2666).

Salts.—B'HCl [below 100°].—$B'_2H_2PtCl_6$.—B'HBr: hygroscopic crystals.—$B'HNO_3$. [55°].—$B'C_6H_2(NO_2)_3OH$. [159°]. Yellow needles (from alcohol).

Picrate of the acetyl derivative $CH_2(OH).CH_2.NHAcC_6H_2(NO_2)_3OH$. [169°]. (Gabriel, *B.* 22, 2222).

Benzoyl derivative $CH_2(OH).CH_2NHBz$.—B'HBr. [143°].—$B'_2H_2PtCl_6$.—Picrate. [195°]. Crystalline pp.

Phenyl derivative $CH_2(OPh).CH_2.NH_2$ (229°). Formed from phenyl-oxyethyl-phthalamic acid and conc. HClAq (Schmidt, *B.* 22, 3256). Yields an acetyl derivative [78°] and a benzoyl derivative [93°] (Schreiber, *B.* 24, 189).—B'HCl. [215°].—$B'C_6H_2(NO_2)_3OH$.—Platinochloride $B'_2H_2PtCl_6$: golden needles.

p-Tolyl derivative (243°). Yields a benzoyl derivative [134°] and B'HCl [240°], $B'_2H_2PtCl_6$, and $B'C_6H_3N_3O_7$.

Oxy-tri-ethyl-amine $C_6H_{15}NO$ *i.e.* $NEt_2.CH_2.CH_2OH$. (161°). Formed from NEt_2H and glycol chlorhydrin (Ladenburg, *B.* 14, 1878; 15, 1144). Liquid, miscible with water.

Cinnamoyl derivative $NEt_2.CH_2.CH_2OCOC_8H_7$. Formed from the cinnamate of the base and dilute HCl. Yields $B'HAuCl_4$ and $B'C_6H_2(NO_2)_3OH$.

Ethylo-chloride $NEt_3Cl.CH_2.CH_2OH$. Prisms (Wurtz, *A. Suppl.* 7, 88).—*Gold salt* $C_8H_{20}NOAuCl_4$: golden plates.

Di-oxy-ethyl-amine. *Di-ethyl derivative* $CH_2(NH_2).CH(OEt)_2$. *Amido-acetal.* (162°). Formed from chloro-acetal and alcoholic NH_3 (Wohl, *B.* 21, 616; Wolff, *B.* 21, 1482). Colourless liquid, v. e. sol. water.—$B'_2H_2PtCl_6$: hexagonal plates, sl. sol. cold alcohol.

Di-oxy-di-ethyl-amine $NH(CH_2.CH_2OH)_2$. Formed from ethylene oxide or $ClCH_2.CH_2OH$ and ammonia (Wurtz).—$B'_2H_2PtCl_6$: tables.

Tri-oxy-tri-ethyl-amine $N(CH_2.CH_2OH)_3$. A product of the action of ethylene oxide on ammonia (Wurtz). With glycol chlorhydrin it yields $N(OH)(CH_2.CH_2OH)_4$. Both are syrupy.

Tetra-oxy-di-ethyl-amine. *Tetra-ethyl derivative* $NH(CH_2.CH(OEt)_2)_2$. (260°). S.14. Formed from chloro-acetal and NH_3Aq at 130° (Wolff, *B.* 21, 1484).—$B'_2H_2PtCl_6$. [121°].

α-OXY-ETHYL-AMINE-αων-TRI-SULPHONIC ACID $C_2H_9NS_3O_{10}$ *i.e.* $CH_3.C(HO)(SO_3H).CH(SO_3H).NH(SO_3H)$. The sodium salt Na_3A'''3aq is formed by shaking nitroso-acetone $CH_3.CO.CH(NOH)$ with a 30 p.c. solution of sodium bisulphite, and crystallises out on standing as a crystalline powder consisting of white needles. It is v. sol. water, insol. alcohol. By warming with dilute acids it is split up into methyl-glyoxal (pyruvic aldehyde) $CH_3.CO.CHO$, sodium sulphate, NH_3 and SO_2 (Pechmann, *B.* 20, 2543).

OXY-ETHYL-ANILINE $NHPh.CH_2.CH_2OH$. (286°). S.G. $\frac{0}{}$ 1·110. Formed from aniline and ethylene oxide (Demole, *B.* 6, 1024; Ladenburg, *B.* 6, 131; Knorr, *B.* 22, 2092). Liquid, with strong reducing properties.—$B'_2H_2PtCl_6$: reddish-brown crystals.

ω-Oxy-di-ethyl-aniline $C_6H_5NEtC_2H_4OH$. (268°). Formed from ethyl-aniline and ethylene chlorhydrin at 100° (Laun, *B.* 17, 677). Heavy oil.

Di-oxy-di-ethyl-aniline $NPh(CH_2.CH_2OH)_2$. (above 350°). Formed from the preceding and glycol chlorhydrin. Treatment with HClAq at 170°, followed by cold caustic soda solution, yields $NPh{<}{\begin{smallmatrix}C_2H_4\\ C_2H_4\end{smallmatrix}}{>}O$ [53°] (270°). The compound $NPh{<}{\begin{smallmatrix}C_2H_4\\ C_2H_4\end{smallmatrix}}{>}O_2$ [67°] is formed by the action of alcoholic $AgNO_3$ on the corresponding sulphur compound (Holzmann, *B.* 20, 1640).

OXY-ETHYL-BENZENE *v.* ETHYL-PHENOL.

Di-oxy-ethyl-benzene $C_6H_5.CH(OH).CH_2OH$. *Styrolene alcohol.* [68°]. (273° i.V.). Formed from styrene dibromide and boiling aqueous K_2CO_3 (Zincke, *A.* 216, 293). Needles (from

benzene-ligroïn). Converted by boiling dilute H_2SO_4 into oily C_8H_8O (260° at 50 mm.).

Di-acetyl derivative $C_8H_8Ac_2O_2$. (274° i.V.).

Di-benzoyl derivative. [97°]. Needles.

Di-oxy-ethyl-benzene $C_6H_3Et(OH)_2$ [1:3:4]. (295°). Formed from *p*-ethyl phenol sulphonic acid by potash-fusion (Sempotowski, *B.* 22, 2667). Coloured green by $FeCl_3$.

Di-oxy-tri-ethyl-benzene $C_6HEt_3(OH)_2$. [185°]. Formed by the action of HCl on $C_6HEt_3(OEt)(OH)$ (165° uncor. at 20 mm.) which is a product of the action of alcoholic potash and EtI on resorcin (Herzig a. Zeisel, *M.* 11, 306). White needles (from dilute alcohol). Yields $C_6HEt_3(OEt)(OAc)$ [65°] crystallising in monoclinic prisms.

OXY-ETHYL-BENZOIC ACID $C_9H_{10}O_3$ *i.e.* $C_6H_3Et(OH).CO_2H$. [120°]. Formed from sodium *o*-ethyl-phenol and CO_2 (Beilstein a. Kuhlberg, *A.* 156, 213). Coloured violet by $FeCl_3$.

Oxy-ethyl-benzoic acid. [112°]. Formed in like manner from sodium-phlorol (Oliveri, *G.* 13, 267). Needles (from water).—BaA'_2aq: scales.

β-Oxy-ethyl-benzoic acid $CH_3.CH(OH).C_6H_4CO_2H$.—AgA': needles.

Anhydride $C_9H_8O_2$. (276°). V.D. 74 (obs.). Formed by reducing acetophenone carboxylic acid with sodium-amalgam and acidifying (Gabriel a. Michael, *B.* 10, 2205). Crystalline at 0°.

Tri-oxy-ethyl-benzoic acid. *Methylene derivative* $CH_2{<}^{O}_{O}{>}C_6H_2(CH_2.CH_2OH).CO_2H$. '*ω-Oxyethylpiperonylcarboxylic acid.*' [146°]. Formed from the corresponding amido- acid $CH_2O_2.C_6H_2(C_2H_4NH_2)CO_2H$ (Perkin, jun., *C. J.* 57, 1021). Crystals. Converted at 120°–130° into the anhydride $C_{10}H_8O_4$ [127°].—$AgC_{10}H_9O_5$.—KA'.—NH_3MeA': crystals.

TRI-OXY-TRI-ETHYL BORATE $B(OC_2H_4OH)_3$. [162°]. Formed from BCl_3 and glycol (Councler, *J. pr.* [2] 18, 392). Deliquescent crystals.

DI-OXY-ETHYL-BUTYL GLYOXALINE $C_4H_9CH{<}^{CO.NEt}_{NH.CO}$. [135°]. (295°). Formed from isobutyl-hydantoïn, KOH, and EtBr (Pinner, *B.* 22, 685). Silky needles.

OXY-ETHYL-CARBAMIC ACID. *Anhydride* ${}^{CH_2.O}_{CH_2.NH}{>}CO$. [91°]. Formed from β-bromo-ethyl-amine and Ag_2CO_3 (Gabriel, *B.* 21, 568). Flat crystals (from alcohol), v. sol. water.

OXY-ETHYL-CONIINE *v.* CONIINE.

DI-OXY-ETHYLENE DIQUINOLINE OCTO-HYDRIDE $C_{20}H_{21}N_2O_2$ *i.e.*

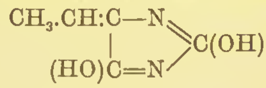
CH:CH — C.CH₂.CH₂.CH₂   CH₂.CH₂.CH₂.C — CH:CH
CH:C(OH).C ——— N.CH₂.CH₂.N ——— C.C(OH):CH

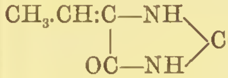
[233°]. Formed by heating oxy-quinoline tetra-hydride with ethylene bromide (Kohn, *C. J.* 49, 509). Small silky prisms.

DI-OXY-ETHYLIDENE-DI-NAPHTHOQUIN-ONE $C_6H_4{<}^{CO.C(OH)}_{CO.C.CHMe.C} \quad {}^{C(OH).CO}_{——CO}{>}C_6H_4$.

Phenyl hydrazide $\{C_{10}H_4(OH)O(N_2HPh)\}_2CHMe$. [258°]. Got by heating the phenyl-hydrazide of oxy-(α)-naphthoquinone with alcohol and aldehyde at 100° (Zincke a. Thielen, *B.* 21, 2205). Small red needles, v. sl. sol. alcohol.

TETRA-OXY-TETRA-ETHYLIDENE-PHOSPHONIUM CHLORIDE $(CH_3.C(OH))_4PCl$ [112°]. Formed from aldehyde, PH_3, and HCl (Messenger a. Engels, *B.* 21, 328). Dimetric crystals, with unpleasant smell, v. sol. alcohol, insol. ether. Decomposed by water. The corresponding $(CH_3.C(OH))_4PBr$ [88°] is also crystalline. The iodide $(CH_3.C(OH))_4PI$ [65°] is formed from aldehyde and phosphonium iodide (Girard, *A. Ch.* [6] 2, 11).

DI-OXY-ETHYLIDENE-METAPYRAZOLE $C_5H_6N_2O_2$ *i.e.*  or

 *Ethylidene-metapyrazolone.* Formed by heating chloro-crotonyl-urea, $CH_3.CH:CCl.CO.NH.CO.NH_2$, to its melting-point, HCl being evolved. Needles. M. sol. hot water (Pinner a. Lifschütz, *B.* 20, 2350).

α-OXY-ETHYL-MALONIC ACID $CEt(OH)(CO_2H)_2$. *Ethyltartronic acid* [98°]. Prepared by saponification of chloro-ethyl-malonic ether with baryta-water (Conrad, *B.* 14, 618). Decomposes at 180° into α-oxy-butyric acid and CO_2.

β-Oxy-ethyl-malonic acid $CH_3.CH(OH).CH(CO_2H)_2$. Formed from ethylidene-malonic acid and baryta-water (Komnenos, *A.* 218, 163). Syrup.—Ag_2A'': amorphous.

γ-Oxy-ethyl-malonic acid $CH_2(OH).CH_2.CH(CO_2H)_2$. — BaA'' $1\frac{1}{2}$aq. Got by boiling the lactonic acid with baryta.—Ag_2A''.

Lactonic acid $CH_2{<}^{CH_2.CH(CO_2H)}_{O—CO}$. Formed by boiling bromo-ethyl-malonic acid with water (Röder, *A.* 227, 19). Obtained also by boiling vinaconic acid with diluted H_2SO_4.—BaA'_2.

DI-OXY-DI-ETHYL OXIDE ×$O(CH(OH).CH_3)_2$. Alkoyl derivatives of this body are formed by the action of sodium salts on di-chloro-di-ethyl ether (Geuther, *A.* 226, 223; 245, 101).

Formyl derivative (c. 180°). S.G. $\frac{21}{}$ 1·134.

Acetyl derivative $O(CH(OAc).CH_3)_2$. (192°). S.G. $\frac{16}{}$ 1·071; $\frac{20}{}$ 1·067. Colourless liquid, slowly decomposed by water into aldehyde and acetic acid.

Propionyl derivative (c. 213°). S.G. $\frac{20}{}$ 1·027.

Butyryl derivative (c. 238°). S.G. $\frac{20}{}$ ·994.

Benzoyl derivative $C_{18}H_{18}O_5$. Needles.

Succinyl derivative $O(CMeH)_2C_4H_4O_4$.

Di-methyl ether $O(CH(OMe).CH_3)_2$. (127°). S.G. $\frac{12.5}{}$ ·953. Formed from αα-di-chloro-di-ethyl oxide, MeOH, and NaOMe. Oil, decomposing on standing into di-methyl-acetal and aldehyde.

Di-ethyl ether. (153° cor.). S.G. $\frac{14}{}$ ·891.

Di-propyl ether. (184° cor.). S.G. $\frac{14}{}$ ·895.

Di-isobutyl ether. (175° cor.). S.G. $\frac{11}{}$ ·879.

Di-isoamyl ether. (227°). S.G. $\frac{11}{}$ ·874.

DI-OXY-DI-ETHYL-DIPHENYL. *Di-ethyl ether.* [3:4:1]$C_6H_3Et(OEt).C_6H_3Et(OEt)$[1:3:4].

[120° cor.]. Formed from di-amido-di-ethyl-diphenyl, alcohol, and nitrous acid (Schultz, *B.* 17, 475). White plates, sl. sol. cold alcohol.

Tetra-oxy-ethyl-diphenyl. *Tetra-acetyl derivative.* $C_{12}H_5Et(OAc)_4$. [138°]. Formed from the tetra-ethyl derivative by successive treatment with HIAq and Ac_2O (Herzig, *M.* 11, 418). Needles (from alcohol).

Tetra-ethyl derivative $C_{12}H_5Et(OEt)_4$. [92°]. A product of the action of EtI and alcoholic potash on tetra-oxy-diphenyl (Herzig, *M.* 11, 417). Plates, v. sol. alcohol.

OXY-ETHYL-PHTHALIMIDE $C_{10}H_9NO_3$ *i.e.* $C_6H_4(CO)_2N.CH_2.CH_2OH$. [127°]. Formed from bromo-ethyl-phthalimide and KOHAq (Gabriel, *B.* 21, 571). Needles or plates, sol. hot water.

Phenyl derivative $C_6H_4(CO)_2N.C_2H_4OPh$. [130°]. Formed from $PhOC_2H_4Br$ and potassium phthalimide (Schmidt, *B.* 22, 3255). On warming with potash it yields the acid $C_{16}H_{15}NO_4$ [125°].

p-Tolyl derivative [135°]. Crystals. Yields a di-nitro- derivative [88°] (Schreiber, *B.* 24, 190).

OXY-ETHYL-PIPERIDINE $C_7H_{15}NO$ *i.e.* $C_5H_{10}NC_2H_4OH$. (199°). Formed by heating piperidine with ethylene chlorhydrin (Ladenburg, *B.* 14, 1876). Liquid, sol. water.—$B'HAuCl_4$: plates.

Phenyl-acetyl derivative $C_{15}H_{21}NO_2$. Oil, formed by heating phenylacetic acid with oxyethyl-piperidine and HCl.—$B'HAuCl_4$ [c. 100°].—B'HI.—$B'HI_3$. Brown needles.

Benzoyl derivative $C_{14}H_{19}NO_2$.—B'HI.—$B'_2H_2PtCl_6$: silky needles.

Oxy-ethyl-piperidine $C_5H_{10}(C_2H_4OH)N$. [32°]. (227°). Formed by reducing oxy-α-ethyl-pyridine with sodium-amalgam (Ladenburg, *B.* 22, 2586). Hygroscopic mass. Yields an oily nitrosamine.—$B'_2H_2PtCl_6$. [158°]. Large crystals.

OXY-ETHYL-PYRIDINE $C_5H_4N.C_2H_4OH$. (179° at 25 mm.). S.G. $\frac{0}{}$ 1·1111. Formed from (α)-methyl-pyridine and formic aldehyde (Ladenburg, *B.* 22, 2584). Syrup, v. sol. water, not volatile with steam. Yields vinyl-pyridine on distillation.—$B'_2H_2PtCl_6$. [170°]: prisms, m. sol. cold water.

An isomeride $C_5H_4N.(CH(OH).CH_3$ is got by distilling barium α-oxy-pyridyl-propionate (Hardy a. Calmels, *Bl.* [2] 48, 230).

Oxy-di-ethyl-pyridine $NC_5H_3Et(C_2H_4OH)$. (148° at 18 mm.). Formed from methyl-ethyl-pyridine (aldehyde collidine) and formic aldehyde at 165° (Prausnitz, *B.* 23, 2725). Oil. —$B'_2H_2PtCl_6$. [159°]. Red cubes.

OXY-ETHYL-PYRIDINE TETRAHYDRIDE $CH_2{<}{CHEt.CO \atop CH_2\ \ .CH_2}{>}NH$. [68°]. Formed by heating δ-amido-heptoic acid at 220° (Aschan, *B.* 23, 3694). Plates, smelling like coniine.

OXY-ETHYL-PYRIDINE CARBOXYLIC ACID $NC_5H_2Et(OH).CO_2H$. Formed from comanic acid and ethylamine (Ost, *J. pr.* [2] 29, 380). Prisms (containing ½aq), v. sol. water.

Di-oxy-ethyl-pyridine carboxylic acid $NC_5HEt(OH)_2CO_2H$ [c. 210°]. Formed from ethylamine and comenamic acid (Meunel, *J. pr.* [2] 32, 178). Prisms (containing 2aq). Coloured violet by $FeCl_3$. Reduces ammoniacal $AgNO_3$. Ac_2O at 160° forms acetyl-ethyl-pyromeconamic acid $C_9H_{11}NO_3$ whence boiling water forms $C_7H_9NO_2$ [166°].

Ethyl ether EtA'. [115°]. Needles (from water).—EtA'½HCl.—$Ba(C_6H_2Et_2NO_4)_2$: needles.

OXY-ETHYL-QUINAZOLINE DIHYDRIDE $C_6H_4{<}{CH_2.NEt \atop NH.CO}$. *Benzylene-ethyl-urea.* [95°]. Formed from ω-oxy-tolyl-ethyl-thio-urea, alcohol, and HgO (Soderbaum a. Widman, *B.* 22, 2937). Needles (from alcohol).—$B'_2H_2PtCl_6$. [c. 205°].—$B'HAuCl_4$: golden scales.

(*Py.* 3:4)-**OXY-ETHYL-QUINOLINE** $C_6H_4{<}{CH:CH \atop NEt.CO}$, *Ethyl-pseudo-carbostyril.* [55°]. Formed together with (*Py.* 3)-ethoxy-quinoline by the ethylation of carbostyril (*Py.* 3-oxy-quinoline) (Friedländer a. Weinberg, *B.* 18, 1528). Glistening white needles. Sl. sol. water, v. sol. other solvents. Scarcely volatile with steam. Dissolves in strong HCl.

(*Py.* 1, 3)-**Di-oxy-**(*Py.* 2)-**ethyl-quinoline.** Formed from chloro-oxy-ethyl-quinoline and HCl (Rügheimer a. Schramm, *B.* 21, 301). Prisms, v. e. sol. alcohol.

DI-OXY-ETHYL-ISOQUINOLINE $C_6H_4{<}{CH_2.CO \atop CO\ .NEt}$. [105°]. Formed by distilling o-carboxy-phenyl-acetic acid with ethylamine (Pulvermacher, *B.* 20, 2493). Needles, v. sol. alcohol. With diazobenzene chloride it yields $C_9H_6ONEt:N_2HPh$ [139°].

Di-oxy-di-ethyl-isoquinoline $C_6H_4{<}{CEt_2.CO \atop CO\ .NH}$. [144°]. Formed from di-oxy-isoquinoline (vol. i. p. 706). NaOEt and EtI (P.). White plates. With alcoholic potash and EtI it produces di-oxy-tri-ethyl-isoquinoline $C_6H_4{<}{CEt_2.CO \atop CO\ .NEt}$ [50°] (309°).

(*Py.* 3, 2)-**OXY-ETHYL-QUINOLINE DIHYDRIDE** $C_6H_4{<}{CH_2.CHEt \atop NH.CO}$. *Ethylhydrocarbostyril.* [88°]. Formed from phenyl-valeric acid by nitration and reduction (Baeyer a. Jackson, *B.* 13, 119). Crystals. Occurs also in an unstable modification [76°]. PCl_5 gives chloro-ethyl-quinoline and $C_{11}H_{11}NO$ [168°].

(*B.* 2)-Oxy-(*Py.* 4)-ethyl-quinoline tetrahydride. *Methyl derivative* $C_{12}H_{17}NO$. *Ethyl-thalline.* (287°). Formed from thallin and EtI (Skraup, *M.* 6, 779). Thick liquid.—B'HCl.—B'EtI. [133°].—$(B'EtCl)_2PtCl_4$: orange needles.

(*B.* 4)-Oxy-(*Py.* 4)-ethyl-quinoline tetrahydride ${CH:CH—C.CH_2.CH_2 \atop CH:C(OH).C.NEt.CH_2}$. [76°]. Prepared by heating (*B.* 4)-oxy-quinoline tetrahydride with EtI or EtBr (O. Fischer, *B.* 16, 717; Fischer a. Renouf, *B.* 17, 756; Fischer a. Kohn, *B.* 19, 1044; *C. J.* 49, 508). Monoclinic prisms or tables, sol. alcohol and ether, sl. sol. water. $FeCl_3$ colours its alcoholic solution brown. —B'HCl. *Kairine A.* Trimetric prisms; $a:b:c$ = ·595:1:·957, v. sol. water. Febrifuge.—B'EtI. [160°]. Prisms (from alcohol).

Ethyl ether $C_{13}H_{19}NO$. [33°]. (270°). Formed from the ethyl ether of (*B.* 4)-oxy-quinoline tetrahydride and EtBr at 130°. Silky plates, insol. water.—B'EtI. [137°]. Prisms.—$B'_2Et_2PtCl_6$ [183°].

Acetyl derivative $C_{11}H_{14}AcNO$. [64°].

(*B.* 1)-Oxy-(*Py.* 4)-ethyl-quinoline tetrahydride $\begin{matrix}CH.C(OH).C.CH_2.CH_2\\CH.CH—C.NEt.CH_2\end{matrix}$. [73°]. Formed by ethylating the corresponding oxy-quinoline tetrahydride (Riemerschmied, *B.* 16, 724). Crystals, sol. alcohol.—B'HCl aq.

(*Py.* 3)-**OXY-**(*Py.* 2)-**ETHYL-QUINOLINE-DIHYDRIDE** (*Py.* 2)-**CARBOXYLIC ETHER** (?)$C_6H_4<\begin{matrix}CH_2.CEt.CO_2Et\\ |\\ N{=}C(OH)\end{matrix}$. [114°]. Obtained by reduction of o-nitro-benzyl-ethyl-malonic ether with zinc and acetic acid (Lellmann a. Schleich, *B.* 20, 440). Colourless silky needles.

OXY-ETHYL-SUCCINIC ACID $C_6H_{10}O_5$. —BaA''3aq.—CaA'' 3aq.—Ag_2A''. *Anhydride* $C_6H_8O_4$ *i.e.* $CHMe<\begin{matrix}O.CO.CH_2\\CH(CO_2H)\end{matrix}>$. *Methyl-paraconic acid.* [84°]. Formed from aldehyde, succinic acid, and Ac_2O (Fittig a. Fränkel, *A.* 255, 17). Small plates.—BaA'_2 3½aq. —CaA'_2 2½aq.—AgA'.

Reference. — Tri-chloro-oxy-ethyl-succinic acid.

DI-OXY-DI-ETHYL SULPHIDE $S(CH_2.CH_2OH)_2$. Formed from ethylene chlorhydrin and aqueous K_2S (V. Meyer, *B.* 19, 3259). Syrup. With PCl_3 it yields $S(C_2H_4Cl)_2$ whence K_2S yields insoluble $C_4H_8S_2$. A soluble $C_4H_8S_2$ is formed from $C_2H_4(SNa)_2$ and ethylene bromide.

OXY-ETHYL-*p*-TOLUIDINE $C_9H_{13}NO$ *i.e.* $C_7H_7NH.CH_2.CH_2OH$. [37°]. (287°). Formed from *p*-toluidine and ethylene oxide (Demole, *B.* 7, 635; *A.* 173, 123). Crystals, sol. water.—$B'_2H_2PtCl_6$. [148°].—$B'H_2SO_4$. [111°].—$B'_2H_2C_2O_4$. [122°].

Di-oxy-di-ethyl-*p*-toluidine $C_7H_7N(C_2H_4OH)_2$. (339°).—$B'_2H_2PtCl_6$.

OXY-ETHYL-UREA. *p-Tolyl-derivative* $NH_2.CO.NH.C_2H_4OC_7H_7$. [158°]. Formed from tolyloxyethylamine hydrochloride and potassium cyanate solution at 100° (Schreiber, *B.* 24, 193).

OXY-FLAVOLINE *v.* Flavenol.

OXY-FLUORENE CARBOXYLIC ACID $\begin{matrix}C_6H_4\\C_6H_3(CO_2H)\end{matrix}>CH(OH)$. [203°]. Formed by reducing diphenylene ketone carboxylic acid with zinc-dust and ammonia (Graebe, *A.* 247, 283). Crystals (from hot water or benzene).

OXYGEN. O. (Older names were *vital air*, *pure air*, *dephlogisticated air.*) At. w. 15·96 (*v. infra*). Mol. w. 31·92. Boils −181·4° at 740 mm. (Olszewski, *W.* 31, 58). Has not been solidified (*v. infra*). S.G. (liquid; compared with water at 4°) ·899 at −130° (Wroblewski, *W.* 20, 860), ·7555 at −129·6°, ·8788 at −139·3°, ·8544 at −137·5°, ·8772 at −139·4°, 1·124° at −181·4° [= b. p.] (Olszewski, *M.* 5, 124; *W.* 31, 58); Wroblewski (*l.c.*) gives S.G. for temperature from −118° to −200° as $= 1·212 + ·00428T - ·0000529T^2$, where T = absolute temperature. S.G. (gaseous, at 3000 atmos. referred to water = 1) 1·1054 (Amagat, *C. R.* 107, 522). Critical temp. c. −118°; critical pressure c. 50 atmos. V.D. 15·96 (*v. infra*) S.H.p. (equal weight of water = 1) ·21751 from 13° to 207° (Regnault, *Acad.* 26, 1); S.H.v. (equal wt. of water = 1) ·1551 (Clausius, *Mechan. Wärmetheorie*, 1, 62). C.E. (21° to 98° at 760 mm.) ·0036743 (Jolly, *P. Jubelbd.* 82). S. ·0489 at 0°, ·04286 at 5°, ·03802 at 10°, ·03415 at 15°, ·03103 at 20°, ·02616 at 30° (Winkler, *B.* 22, 1764; S. is given for each degree from 0° to 30°, and the results are compared with those of Bunsen). S. (alcohol, 0° to 24°) ·28397 (Carius, *A.* 94, 134; *cf.* Timofejeff, *Z. P. C.* 6, 141). Compressibility-coefficient = ·00025 at 1000–1500 atmos., ·00016 at 1500–2000 atmos., ·000115 at 2000–2500 atmos., ·000091 at 2500–3000 atmos. (Amagat, *C. R.* 107, 522). O exhibits several very different emission-spectra under different conditions; for measurements of lines *v. B. A.* 1884. 432. The absorption-spectrum of O at pressures up to 90 atmos. has been examined by Liveing a. Dewar (*P. M.* [5] 26, 286; *Pr.* 46, 222); for the absorption-spectrum of liquid O *v.* Olszewski, W. A. B. 95 [2nd part], 257 (*cf.* L. a. D. *Pr.* 46, 422; Janssen, *C. R.* 101, 649; 102, 1332; Egoroff, *C. R.* 101, 1143).

Occurrence.—Uncombined in the atmosphere, of which it forms one-fifth by volume. Compounds of O are very numerous, and occur in enormous quantities. O forms eight-ninths of water by weight, and about one-half of silica, alumina, and chalk, which are the three most plentiful constituents of the solid earth; almost every widely distributed rock or mineral contains O, the principal exceptions being rock-salt, fluorspar, blende, galena, and pyrites. As O is slightly sol. in water, this gas is found uncombined in all natural waters. O is a constituent of all living tissues; according to Wurster (*B.* 21, 1525), O_2H_2 occurs in the juices of plants. According to H. Draper, O occurs in the sun (*Am. S.* [3] 14, 89; *cf.* J. C. Draper, *ibid.* 16, 256).

O was prepared for the first time by Priestley, in 1774, by heating HgO; a year later the gas was discovered by Scheele. Lavoisier was the first to recognise the importance of the discovery of O, and to study its chemical properties.

References to older memoirs on Oxygen.—Priestley, 'Experiments and Observations on different kinds of Airs' [London, 1775–1777], 2, 29; 3, 1; Priestley, 'Experiments and Observations relating to various branches of Natural Philosophy' [London, 1779], 1, 192; Scheele, 'Abhandlungen von der Luft und dem Feuer' [Upsala a. Leipzig, 1777]; also *Crell. Annal.* 1785, 2, 229, 291; Lavoisier's memoirs appeared in *Acad.* from 1774 to 1788; Berzelius, *Lehrbuch der Chemie* [3rd ed.], 5, 46.

Formation.—The processes wherein O is formed may be divided into groups: I. *From air.*—1. BaO is heated in air to dull redness, when BaO_2 is formed; the pressure is decreased, and the BaO_2 is heated, when O is evolved, and BaO remains.—2. Hg is heated in air at c. 300° when HgO is slowly formed; on strongly heating HgO, O and Hg are produced.—3. MnO_2 is heated with NaOH in air; Na_2MnO_4 and H_2O are produced ($4NaOH + 2MnO_2 + O_2 = 2Na_2MnO_4 + 2H_2O$); the product is heated to dull redness in steam, when NaOH, Mn_2O_3, and O are formed ($2Na_2MnO_4 + 2H_2O = 4NaOH + Mn_2O_3 + 3O$); by again passing air over the residue, Na_2MnO_4 is reformed (Tessié du Motay, *D. P. J.* 186, 230).—4. When air is pressed into water, more O than N is dissolved; by reducing pressure on the water O and N are evolved; by pressing the evolved gases again

into water, again reducing pressure, and pressing the gases into a fresh quantity of water, and repeating these processes eight times, nearly pure O (about 2–3 p.c. N) is obtained (Mallet, *D. P. J.* 199, 112). For details of the methods for obtaining O from air *v.* DICTIONARY OF APPLIED CHEMISTRY. II. *From Oxides.*—5. Several metallic oxides give off O when heated; *e.g.* HgO, MnO_2, PbO_2, Au_2O_3, Bi_2O_5.—6. When water is electrolysed, O separates at the positive electrode.—7. O is obtained by passing a mixture of H_2O and Cl through a red-hot tube; the issuing gas is passed through NaOHAq to absorb HCl and excess of Cl.—8. When steam is passed over $CuCl_2$ at 100°–200° an oxychloride of Cu is formed which is reduced to $CuCl_2$ at c. 400°, with evolution of O (Vogel, *W. J.* 1861. 177; Mallet, *C. R.* 64, 226; 66, 349).—9. O is obtained by the reaction of H_2O_2Aq with Ag_2O ($Ag_2O + H_2O_2 = H_2O + 2Ag + O_2$).—10. MnO_2, PbO_2, CrO_3, BaO_2, Bi_2O_5, and other metallic peroxides yield sulphates, H_2O, and O when heated with conc. H_2SO_4.—11. CO_2 is decomposed by fresh parsley, mint, and other green plants, when the plant is placed in water charged with CO_2 and exposed to direct sunlight. III. *From compounds other than oxides.*—12. $KClO_3$ is heated, either alone or mixed with MnO_2 or Fe_2O_3.—13. $CaCl_2O_2$ is heated, when $CaCl_2$ and O are formed; or dry Cl is passed over CaO heated to redness.—14. Conc. HNO_3 is dropped into a red-hot Pt flask; $2HNO_3 = H_2O + O + 2NO_2$. — 15. Conc. H_2SO_4 is dropped on to red-hot Pt, or on to red-hot bricks; the gases produced are passed through milk of lime; $H_2SO_4 = H_2O + SO_2 + O$ (Deville a. Debray, *C. R.* 51, 822).—16. By strongly heating dry $ZnSO_4$, O and SO_2 are evolved and ZnO remains (D. a. D., *l.c.*).—17. $Ba(NO_3)_2$ yields O, mixed with N, when strongly heated.—18. A mixture of O and N, containing about 60 p.c. O is obtained by heating $NaNO_3$ with two parts dry ZnO (*v.* Pepper, *C. N.* 6, 218).—19. Conc. H_2SO_4 is heated with $K_2Cr_2O_7$ or $KMnO_4$; sulphates of K and Cr (or Mn) and H_2O are formed and O is evolved.—20. A fairly conc. solution of bleaching powder is heated with addition of a small quantity of a salt of Co; Co_2O_3 is formed (by the action of the CaO on the Co salt), and this is probably oxidised to CoO_3, which is again reduced to Co_2O_3 with evolution of O (Winkler, *J. pr.* 98, 340; Fleitmann, *A.* 134, 64; Reinsch, *Z.* [2] 2, 31; Böttger, *J. pr.* 95, 309, 375; Stolba, *J. pr.* 97, 309). A modification of this process consists in passing Cl into warm thick milk of lime containing a little $Co2NO_3$ (W., *l.c.*).

Preparation.—1. Pure $KClO_3$, which has been fused, is well mixed with c. half its weight of pure dry MnO_2, and the mixture is heated in a flask of hard glass to c. 210°–220°. As the O thus obtained contains a little Cl, the gas is passed through NaOHAq or milk of lime. It is then dried by H_2SO_4, and passed in a rapid stream through a glass tube heated to redness. After a time the stream of O may be allowed to slacken, and the glass tube need not be kept hot. The rapid stream of O, passing through the hot tube, washes out the last trace of air, which very obstinately adheres to glass at ordinary temperatures (Houzeau, *C. R.* 70, 39). Any ozone present is also decomposed. The small quantity of air which adheres to the glass may also be removed, according to Ilosva (*Bl.* [3] 2, 734), by passing the O over Pt foil at 280°–250°, or Pt black at c. 250°, whereby combination of O with the N present occurs, with formation of nitrites and nitrates, which may be absorbed in NaOHAq. The Pt loses the power of inducing the combination of N and O after a time, but regains this power when heated in a stream of H at c. 250° (I., *l.c.*). If the O is required quite dry, it is passed through conc. boiled H_2SO_4, and then over a long layer of P_2O_5. Regarding the part played by MnO_2 and other substances in causing O to be evolved from $KClO_3$ at temperatures lower than that at which this salt gives off O when heated alone, *v.* Hornsby, *Ph.* 15, 352; Witt, *ibid.* 411, 503; Brown, *ibid.* 469; Wiederhold, *P.* 116, 171; 118, 186; Baudrimont, *J. Ph.* [4] 14, 81, 161; Krebs, *Z.* 6, 243; Mills a. Donald, *C. J.* 41, 18; Mills a. Stevenson, *C. J.* 41, 23.—2. Pure MnO_2 is heated to full redness in a hard glass tube; the gas is passed through milk of lime to absorb CO_2, then over Pt black at c. 250° to cause combination of N (which is generally present) with O, then through NaOHAq to absorb nitrites and nitrates produced, and the O is then dried by conc. H_2SO_4, $CaCl_2$, and P_2O_5. It is difficult to obtain O by this method quite free from every impurity.—3. Böttger (*J. pr.* 103, 316; 107, 48) says that pure O is obtained by gently heating $KMnO_4$, or by the reaction of dilute HNO_3Aq, S.G. c. 1·064, with a mixture of PbO_2 and BaO_2.—4. Fairly pure O may be obtained in a regular stream, at the ordinary temperature, by compressing into small cylinders a mixture of two parts BaO_2, one part MnO_2, and one part $CaSO_4$, and acting on these, in a Kipp's apparatus, with HClAq, S.G. 1·2, diluted with an equal volume of water (Neumann, *B.* 20, 3058).

Properties.—A colourless, odourless, tasteless gas. Condensed to a liquid at very low temperatures and great pressures. Liquid O is bright blue when viewed in layers 30–40 mm. thick (Olszewski, *W.* 42, 663). Pictet supposed that O was solidified when pressure was suddenly reduced, and the liquid was allowed to issue into the air (*C. R.* 86, 37); but, according to more recent experiments by Wroblewski a. Olszewski (*C. R.* 100, 350, 979), solid O has not been obtained. Light appears bluish when observed through liquid O, or through a column of the gas very strongly compressed (Liveing a. Dewar, *P. M.* [5] 26, 286). One litre O at 0° and 760 mm. weighs 1·424488 grms. at the latitude of 45°, multiplying mean result of Regnault (*Acad.* 21, 158) and Jolly (*W.* 6, 520) for weight of one litre H by mean S.G. of O, referred to H, obtained by Scott and Rayleigh (*v. N.* 37, 418). The atomic volume of O $\left(\frac{\text{At. weight}}{\text{S.G. of liquid}}\right)$ is c. 14 (*v.* Wroblewski, *C. R.* 102, 1010). The atomic volume of O in compounds varies according to the number of atoms with which the O is directly united, and perhaps to a small extent according to the nature of these atoms. Kopp gives 12·2 for O^{I} and 7·8 for O^{II} (*v.* PHYSICAL METHODS, section *Volumetrical*). The effect of the atom of O on the magnetic rotatory

power of O compounds is not yet determined with certainty (Perkin, *C. J.* 45, 558; *v.* PHYSICAL METHODS, section *Optical*). O is absorbed by molten Ag or Pt, and given off again as the metal solidifies. O is also absorbed by charcoal. One vol. cocoa-nut charcoal absorbs c. 18 vols. O at 0° and 760 mm. (Hunter, *P. M.* [4] 29, 116; *v.* also Saussure, *G. A.* 47, 113). According to Angus Smith (*Pr.* 28, 322), the vol. of O absorbed by C is eight times that of H under the same conditions. O absorbed by charcoal brings about oxidation of H_2S, PH_3, C_2H_6O, &c., fairly rapidly (Calvert, *C. J.* [2] 5, 293; *cf.* CARBON, vol. i. p. 686).

O is the most negative of the elements except F. It combines directly with all elements except F, Cl, Br, I, Au, and Pt. At least one binary compound of O with each element, except F and Br, is known. Compounds containing O exhibit the same diverse properties. The oxides of the positive elements, as a class, are basic, and those of the negative elements are acidic (*v.* OXIDES, p. 658; ANHYDRIDES, vol. i. p. 267; BASE, vol. i. p. 445). O is a constituent of the greater number of acids; the compounds of O with H and non-metallic elements are acids. When H is combined with one of the less positive metals and a relatively large quantity of O, the compound so produced is generally an acid (*v.* ACIDS, vol. i. p. 47). The process of combining O with another element or with a compound is called oxidation (*v.* OXIDATION, p. 657; *cf.* DEOXIDATION, vol. ii. p. 377). When the process is attended with the production of so much heat that the products become self-luminous, it is called combustion (*v.* COMBUSTION, vol. ii. p. 241; *cf.* FLAME, vol. ii. p. 549). O is more closely related chemically to S, Se, and Te than to the other elements. It belongs to Group VI., which contains the even-series elements O, Cr, Mo, W, and U, and the odd-series elements S, Se, and Te (*v.* CHROMIUM GROUP OF ELEMENTS, vol. ii. p. 168, and OXYGEN GROUP OF ELEMENTS, this vol. *infra*). O exhibits allotropy; the allotropic modification is called *Ozone* (*v.* art. OZONE).

Atomic weight of oxygen.—The value 16·01 was obtained by Berzelius and Dulong in 1819, by burning H by CuO and weighing the water formed (*A. Ch.* 15, 386). In 1842 Dumas, by the same method, arrived at the number 15·98 (*A. Ch.* [3] 8, 189). In the same year, Erdmann a. Marchand conducted very carefully a series of five experiments by the same method; their mean result was 16·005. Ostwald (*Lehrbuch der Allgemeinen Chemie*, 1, 43) shows that the value 15·84 is obtained from Stas's experiments on the ppn. of NH_4ClAq by Ag. In 1805 Gay-Lussac a. Humboldt (*G. A.* 20, 38) determined the ratio in which H and O combine, by volume, to be 2:1. Using the values for S.G. of these gases obtained by Biot a. Arago, the atomic weight of O became 15·1. If Regnault's more accurate determinations of S.G. of H and O are made use of, and it is assumed that H and O combine in the ratio 2:1 by volume, then the atomic weight of O becomes 15·964. In recent years Scott has made a series of direct determinations of the relative densities of H and O (*Pr.* 1887. 398; *B. A.* 1887. 668; *Pr.* 42, 396; *N.* 37, 439). Keiser (*B.* 20, 2323; *Am.* 10, 249) caused Pd to occlude H, and then drove out the H over hot CuO, and weighed the water produced. In this way a direct weighing of the H burnt was obtained. Keiser's final value for O was 15·9492. Cooke a. Richards (*Am.* 10, 81) weighed H in a large balloon, and then burnt it to H_2O; they obtained $O = 15·953$. Lord Rayleigh, in 1888, pointed out a source of error in all experiments wherein a gas is weighed by pumping the air out of a glass globe, and thus allowing the gas to enter (the error is due to the shrinkage of the globe when evacuated). From his own experiments, Rayleigh gave $O = 15·884$ (*Pr.* 43, 356); and applying his correction to Scott's most carefully determined values (*Pr.* 42, 396), he obtained the value $O = 15·912$. Cooke a. Richards applied Rayleigh's correction to their experimental data, and arrived at the conclusion that $O = 15·869$ (*Am.* 10, 191). The mean of the results obtained by directly weighing H and then burning it to H_2O is 15·888. The most probable value obtained by weighing H by occluding it in Pd, driving out by heat, and weighing Pd before and after, is 15·9492. The mean of the values obtained by burning H to H_2O, weighing O by loss of weight of CuO, and determining H by difference between weights of H_2O and O, is 15·992. For a criticism of the methods and results up to 1885, *v.* Ostwald's *Lehrbuch der Allgemeinen Chemie*, 1, 41. As the atomic weights of many elements are determined by directly referring them to O, some chemists take the atomic weight of O as 16 (H thus becomes a little more than 1). Most chemists at present take $O = 15·96$, which is the value used in this Dictionary.

Reactions and Combinations.—The reactions and combinations of O are too many to be described here; it must suffice to indicate them in a general way. Reference should be made to the various elements and compounds for details. 1. All *non-metals*, except F, Br, Cl, and I, combine directly with O; compounds of all, except F and Br, with O are known.—2. All *metals*, except Au and Pt, combine directly with O; compounds of all with O are known.—3. Many *lower oxides* are changed to higher oxides by heating in O, *e.g.* BaO, Bi_2O_2, NO, P_2O_3, PbO, FeO; many other lower oxides form higher oxides when O is produced in contact with the lower oxides (*cf.* OXIDATION, p. 657, and OXIDES, p. 658).—4. Innumerable *compounds* are decomposed by O, with formation of more oxidised compounds, *e.g.* NH_3Aq, H_2S, PbS, and $Na_2S_2O_3Aq$; with many compounds O combines directly, *e.g.* P_2O_3, HNO_2Aq, SO_2Aq, NO.

Certain oxidations do not occur when very dry O is heated with the substance to be oxidised after it has been thoroughly dried (*v.* CARBON, vol. i. p. 687; *Carbon monoxide*, vol. i. p. 690; *v.* also PHOSPHORUS; SULPHUR).

Detection of free oxygen.— Uncombined O changes an alkaline pyrogallol solution to dark-brown; white indigo becomes blue; NO combines with O to form red-brown NO_2, easily soluble in water; $CrCl_2Aq$ rapidly absorbs O, changing from blue to green (for preparation of $CrCl_2Aq$, *v.* NITROGEN, *Preparation* No. 1, p. 557).

OXYGENATED WATER. An older name for HYDROGEN DIOXIDE (*q. v.*, vol. ii. p. 722).

OXYGEN GROUP OF ELEMENTS. *Oxygen, sulphur, selenion, and tellurium.* Oxygen was

prepared by Priestley in 1774; sulphur has been known from early times; selenion was discovered by Berzelius in 1817; tellurium was found by Klaproth, in 1798, in gold-ore from the *Siebengebirge*. The name oxygen was given by Lavoisier to express the fact that many compounds of this element are acidic; the word sulphur is supposed to be derived from *sal* = salt and πῦρ = fire (burning salt or stone); the name tellurium is derived from *tellus* = the earth; selenion received its name from σελήνη = the moon, because of its association with and likeness to tellurium. The following table presents some of the chief properties of the four elements:—

The elements S, Se, and Te show very distinct resemblances in their chemical properties. All form hydrides MH_2, which are gases at ordinary temperatures; SH_2 and SeH_2 in water redden litmus, and react as very weak acids. TeH_2 is not acidic; these hydrides are decomposed by heat, stability in this respect decreasing as at. w. of M increases. These hydrides are produced by passing H over molten S, Se, or Te; also by reacting on various sulphides, selenides, and tellurides, with dilute acids. The hydride of O, viz. OH_2, is analogous in composition, and is formed similarly to those of S, Se, and Te; OH_2 is neutral. H_2O_2 and H_2S_2 are also similar in composition and many pro-

	Oxygen	Sulphur	Selenion	Tellurium
Atomic weights	15·96	31·98	78·8	125
Molecular weights	31·92 (47·88 as ozone)	63·96 (? 191·88 at lower temps.)	157·6 (? 236·4 at c. 800°)	250
	One or more compounds of each element have been gasified; specific heats of solid S, Se, and Te have been determined directly.			
Melting points (approx.)	(not solidified)	112°–117°	c. 200°	455°
Boiling points (approx.)	– 181·4° at 760 mm.	449°	680°	below 1400°
Spec. grav. (approx.)	1·12 (liquid at B.P.)	1·96–2·05	4·3–4·8	6·2
Atom. weight / *Spec. grav.* (approx.)	13·3	16	17·5	20
Occurrence and preparation	Very large quantities of O occur uncombined in air; O is a constituent of almost all rocks and minerals, and also of all living organisms; it forms $\frac{8}{9}$ths of water.	In large quantities in Sicily, Spain, &c.; sulphides and other S compounds are common minerals; S compounds are found in many living organisms.	Uncombined in very small quantities; compounds of Se with S, Fe, Cd, Hg, Pb, &c., occur very sparingly.	Uncombined, also in combination with Au, Pb, S, Sb, Bi, &c., but in very small quantities.
	By heating various compounds, chiefly oxides of metals, and in many other ways.	Prepared by refining crude sulphur, also by roasting various sulphides in absence of air.	By passing SO_2 into H_2SeO_3Aq; also by adding HClAq to KSeCNAq.	From solution of a salt of H_2TeO_3, by passing in SO_2, or by Zn.
Physical properties	A colourless, odourless gas, bluish when much compressed; condensed to a colourless liquid, appearing blue in thick layers, at great pressures and low temperatures; has not been solidified.	A yellow, brittle crystalline, solid; also a plastic semi-fluid, amorphous mass. Very bad conductor of electricity.	A red-grey, lustrous crystalline, solid; also an amorphous, vitreous, grey-black solid. The amorphous form is a very bad conductor of electricity; the crystalline form conducts fairly, and conductivity increases when exposed to sunlight.	A lustrous, white, metal-like, crystalline, brittle, solid; also as an amorphous powder. Bad conductor of electricity.

	Oxygen	Sulphur	Selenion	Tellurium
Chemical properties	Combines directly with all elements except F, Cl, Br, I, Au, and Pt; oxides are known of all elements except F and Br. Compounds exhibit very different properties. O is a constituent of most acids, and of all alkalis. Compound with H, OH_2, is a neutral oxide; H_2O_2 is a peroxide.	Combines directly with most elements. Sulphides are basic, or acidic, or neutral, according to nature and relative quantity of element combined with S. S is a constituent of several acids. H_2S is feebly acidic.	Compounds with several elements are known; they resemble sulphides. H_2Se is very feebly acidic. H_2SeO_3 and H_2SeO_4 are much weaker acids than H_2SO_3 and H_2SO_4.	Combines with several elements (compounds not studied very fully). Binary compounds resemble those of Se. H_2Te is not acidic. TeO_2 and TeO_3 do not form acids by acting with water; but these oxides are obtained by heating the acids H_2TeO_3 and H_2TeO_4.

perties. Se_2H_2 and Te_2H_2 have not been prepared. Binary compounds of S, Se, and Te with metals are analogous in composition to the metallic oxides. Chlorides of the form MCl_2 are known, M = O, S, Se, Te; no compound of S, Se, or Te analogous to O_2Cl is known, nor has a compound of O and Cl analogous to SCl_4, $SeCl_4$, and $TeCl_4$ been obtained. The stability of the chlorides towards heat increases in passing from O to Te. The oxides of S, Se, and Te—MO_2 and MO_3—are acidic (SeO_3 is not known), acidity decreasing rapidly as at. w. of M increases; TeO_3 is scarcely acidic, but a corresponding acid H_2TeO_4 exists; TeO_3 combines with some strong anhydrides to form compounds of the type of salts. The oxyacids H_2MO_3 and H_2MO_4 are analogous in composition, but the acids of S are very much stronger than those of Se or Te; those acids yield oxychlorides, $MOCl_2$ and MO_2Cl_2, by reacting with PCl_5. Many other oxyacids of S are known.

The elements of the O family exhibit allotropy; O and S in a very marked way, Se less markedly, and Te only slightly. The allotropic forms of O exist as gases; their molecular formulæ are O_2 and O_3; the allotropic forms of S, Se, and Te are known with certainty only as solids. It is doubtful whether molecules of S or Se, other than S_2 and Se_2, exist as gases through any considerable range of temperature; the only molecule of Te existing as a gas is Te_2. The mol. w. of S in solution is certainly greater than S_2, and probably varies according to the solvent.

The elements S, Se, and Te form the odd-series members of Group VI., of which group O forms the first even-series member; the other even-series members are Cr, Mo, W, and U. All the members of Group VI. are characterised by forming acidic oxides MO_3; as the at. w. increases these oxides become less acidic. Only the odd-series members, and O, form hydrides. All form chlorides MCl_2, the stability of which towards heat increases from O to U; the higher members also form several other stable chlorides. Group VI. falls into two families, (i.) S, Se, Te; (ii.) Cr, Mo, W, U; O is the typical element of the group (*cf.* Chromium group of elements, vol. ii. p. 168; *v.* also Oxygen, Sulphur, Selenion, Tellurium). M. M. P. M.

α-OXY-GLUTARIC ACID $CO_2H.CH(OH).CH_2.CH_2.CO_2H$. *Glutanic acid.* [73°] ? (M.). Formed from amido-glutaric acid and HNO_2 (Ritthausen, *J. pr.* 103, 239; Markownikoff, *A.* 182, 348). Occurs in beetroot molasses (Lippmann, *B.* 15, 1156). Readily yields the lactonic acid.—$CaA''\frac{1}{2}aq$.—$MgA''4aq$.—$PbA''\frac{1}{2}aq$.—$ZnA''3aq$.—$Ag_2A''\frac{1}{2}aq$.

Lactonic acid $C_5H_6O_4$ *i.e.* $CH_2\left<\begin{matrix}CO\ .O\\ CH_2.CH.CO_2H\end{matrix}\right.$. [50°]. Very hygroscopic needles (Wolff, *A.* 260, 126).—$CaA'_2 2aq$.—BaA'_2.—$ZnA'_2 2aq$. Yields glutaric acid [98°] on reduction by HI.

β-oxy-glutaric acid. *Methyl derivative* $CO_2H.CH_2.CH(OMe).CH_2.CO_2H$. Formed by oxidising di-allyl-carbinol with 5 p.c. solution of $KMnO_4$ (Rjabinin, *J. pr.* [2] 23, 274). Extracted with ether (*v.* Oxypyrotartaric acid).

Salts.—CaA'' (at 100°). Syrup, covered by crystalline crusts.—BaA''.—Ag_2A''. Prisms.

αβ-Di-oxy-glutaric acid $CO_2H.CH_2.CH(OH).CH(OH).CO_2H$ [156°]. Formed by boiling glutaconic-acid-di-bromide with water and $CaCO_3$. Needles (from water), or six-sided tables (from alcohol). V. e. sol. water, v. sol. alcohol. Its Ca salt is easily soluble (Kiliani, *B.* 18, 2517).

αγ-Di-oxy-glutaric acid $CO_2H.CH(OH).CH_2.CH(OH).CO_2H$. Formed by heating the di-oxy-propane-tri-carboxylic acid, which is obtained by oxidising isosaccharic acid with HNO_3. Colourless prisms. V. e. sol. water, v. sol. alcohol, sl. sol. ether. Its Ca salt is sparingly soluble (Kiliani, *B.* 18, 2516).

Tri-oxy-glutaric acid $C_5H_8O_7$. [127°]. Formed from arabinose or sorbin by oxidation with HNO_3 (S.G. 1·2) (Kiliani, *B.* 21, 3006, 3276).—K_2A'': monoclinic plates.

OXYGUANIDINE. Obtained by boiling cyanamide with alcoholic hydroxylamine hydrochloride (Prætorius a. Seidler, *J. pr.* [2] 19, 399).—$(CN_3H_5O)_2H_2PtCl_6$: ruby-red prisms.

OXY-HÆMOGLOBIN *v.* Hæmoglobin.

OXYHALOID COMPOUNDS. Compounds of F, Cl, Br, or I, with O and another element. Oxyhaloid compounds of non-metals are often formed by reacting with PCl_5, PBr_5, or PI_5 on oxyacids, *e.g.* SO_2Cl_2 from $SO_2(OH)_2$; they are also produced sometimes by heating together an

oxide and chloride, *e.g.* BOCl by heating B_2O_3 with BCl_3; sometimes the halogen is directly combined with an oxide, *e.g.* $COCl_2$ and NOCl by combining CO and NO with Cl, and $BOCl_3$ by heating Cl with B_2O_3 mixed with C. Metallic oxyhaloid compounds are formed by decomposing the haloid compounds of the metals by water or steam; by heating together oxides and haloid compounds; and in some cases by the incomplete ppn. of haloid compounds in solution by alkali. Non-metallic oxyhaloid compounds are decomposed by water to haloid acids and other oxides or oxyacids of the non-metal present. Some metallic oxyhaloid compounds are also decomposed by hot water to haloid acids and metallic oxides; in this respect the oxyfluorides are the most stable, and the oxyiodides, as a class, are more stable than the oxybromides and oxychlorides. The oxyhaloid compounds of H are acids. All elements form one or more oxyhaloid compounds. A metal which readily forms many oxyhaloid compounds generally forms one or more oxides with acidic reactions, and is otherwise more or less non-metallic in its chemical properties. M. M. P. M.

DI-OXY-HENDECOIC ACID $C_{11}H_{20}(OH)_2O_2$. [85°]. Formed by the oxidation, in alkaline solution, of hendecenoic acid derived from castor oil (Hazura a. Grüssner, *M.* 9, 952). Needles, sol. hot water.

OXY-HENICOSOIC ACID $C_{19}H_{38}(CH_2OH)(CO_2H)$. [103·5°]. Occurs in the soda soap from carnaüba wax (*q. v.*). Crystalline powder (from petroleum), sl. sol. alcohol, m. sol. isobutyl alcohol (whence it separates as a jelly) (Stärcke, *A.* 223, 310). As its alcoholic solution is not ppd. by acetate of Mg, Cu, or Pb, it is possibly a lactone $C_{19}H_{38}{<}{\genfrac{}{}{0pt}{}{CH_2}{CO}}{>}O$. Heated with soda lime it splits off H_2, forming a dibasic acid $C_{19}H_{38}(CO_2H)_2$ [90°].

PENTA-OXY-HEPTANE. The oily anhydride $C_7H_{11}(OH)_3O$ is formed by the action of HOCl followed by KOH on di-allyl-carbinol (Reformatsky, *J. R.* 21, 295). The acetyl derivative $C_7H_{11}(OAc)_5$ (169·5°) S.G. $\frac{0}{}$ ·919 is described by Saytzeff (*A.* 185, 129).

OXY-HEPTANE PHOSPHONIC ACID $C_7H_{17}PO_4$ *i.e.* $C_6H_{13}.CH(OH).PO(OH)_2$. [185°]. Formed from œnanthol and PCl_3 followed by water (Fossek, *M.* 7, 27). Monoclinic tables: $a{:}b{:}c = 1·844{:}1{:}1·957$; $\beta = 74°$.—CaA″.

The compound $(C_6H_{13}.CH(OH))_2PO.OH$ [160°] is formed by heating œnanthol with hypophosphorous acid (Ville, *C. R.* 109, 72). It yields the salts $BaA'_2$3aq, $PbA'_2$3aq, KA′4aq, and $(C_6H_{13}CH(OAc))_2PO_2H$ [94°].

OXY-HEPTENOIC ACID $CHMe(OH).CH(C_3H_5).CO_2H$. Formed from allyl-acetoacetic ether and sodium-amalgam (Zeidler, *A.* 187, 45). Syrup, miscible with water.—BaA'_2.—Zn(OH)A′.

Oxy-heptenoic acid. *Nitrile* CHEt:CMe.CH(OH).CN. Formed from methyl-ethyl-acroleïn and HCy (Johanny, *M.* 11, 401). Converted by hydrochloric acid into the amide $CHEt{:}CMe.CH(OH).CONH_2$ [101°]. The nitrile yields an oily acetyl derivative (114° at 22 mm.), v. sol. ether.

Oxy-heptenoic lactone *v.* MESITONIC ACID.

OXYHEPTIC ACID $C_7H_{10}O_3\frac{1}{3}$aq? [185°]. A product of the action of bromine, followed by alcoholic potash on isobutyl-acetoacetic ether (Demarçay, *C. R.* 86, 1135). Pearly scales (from water). Yields $C_7H_9O(OEt)_2NH_2$? [87°].

α-OXY-HEPTOIC ACID $C_7H_{14}O_3$ *i.e.* $Pr.CH_2.CH_2.CH(OH).CO_2H$. [60°] (Helms, *B.* 8, 1167); [65°] (Ley, *J. R.* 9, 141). Formed by heating aqueous potassium bromo-heptoate at 140°. Prisms.—MeA′. [160°-165°].

Amide [147°]. Hexagonal tables.

α-Oxy-heptoic acid $C_5H_{11}.CH(OH).CO_2H$. [60·5°]. Formed from its ether, EtA′ (203°), which is produced, as well as the ethyl derivative thereof $C_5H_{11}CH(OEt).CO_2Et$ (c. 224°) by the action on oxalic ether of zinc and isoamyl iodide at 100°, followed by water (Frankland a. Duppa, *Pr.* 14, 191). Scales.—BaA'_2.—CuA'_2.

β-Oxy-heptoic acid $CHMe_2.CH(OH).CMe_2.CO_2H$. [112°]. The chief product of the action of sodium on isobutyric ether (Hantzsch, *A.* 249, 60). Silky needles, m. sol. water, volatile with steam.—$BaA'_2 4\frac{1}{2}$aq.

Ethyl derivative of the ethyl ether $Pr.CH(OEt).CMe_2.CO_2Et$. (181° cor.). Oil.

β-Oxy-heptoic acid $CHMe(OH).CMe.EtCO_2H$. Formed by reducing $CH_3.CO.CMeEt.CO_2Et$ with sodium-amalgam (Saur, *A.* 188, 266). Syrup, v. e. sol. water.—$CuC_7H_{12}O_3$.—$AgC_7H_{13}O_3$: plates, m. sol. hot water.

β-Oxy-heptoic acid $CMePr(OH).CH_2.CO_2H$. Formed by oxidising $CMePr(OH).C_3H_5$ with $KMnO_4$ (Semljanitzin, *J. pr.* [2] 23, 267). Syrup. —CaA'_2 (at 100°).—BaA'_2.—AgA′: prisms.

β-Oxy-heptoic acid $CEt_2(OH).CH_2.CO_2H$. [39°]. Formed by oxidising $CEt_2(OH).C_3H_5$ with $KMnO_4$ (Schirokoff, *J. pr.* [2] 23, 201). Thin needles. — LiA′aq. — CaA'_2aq. — $BaA'_2$2aq. — $PbA'_2$2aq. S. 6 at 19°.—$CuA'_2$5aq.—AgA′.

γ-Oxy-heptoic acid $CHPr(OH).CH_2.CH_2.CO_2H$. Syrup.—BaA'_2.—AgA′: curdy pp.

Lactone $Pr.CH{<}{\genfrac{}{}{0pt}{}{CH_2.CH_2}{O\quad .CO}}{>}$. (235° i.V.). Formed by the action of HI and P on the hexa-oxy-heptoic acid obtained from dextrose (Kiliani, *B.* 18, 3066; 19, 1128). Obtained also from propyl-paraconic acid $Pr.CH{<}{\genfrac{}{}{0pt}{}{CH(CO_2H)}{O-CO}}{>}CH_2$ by distilling, converting the resulting $CHPr{:}CH.CH_2.CO_2H$ into γ-bromo-heptoic acid, and boiling this with water (Fittig, *B.* 20, 3180; *A.* 255, 76).

An isomeric lactone (220° cor.) is obtained in like manner from levulose.

γ-Oxy-isoheptoic acid $CHPr(OH).CH_2.CH_2.CO_2H$. Very unstable.—BaA'_2.—AgA′.

Lactone $C_7H_{12}O_2$. (225° uncor.). S. 3 in the cold. Formed from γ-bromo-isoheptoic acid and also by distilling isopropyl-paraconic acid (Fittig a. Zanner, *A.* 255, 94). Liquid, volatile with steam.

γ-Oxy-heptoic acid.—BaA'_2.—AgA′.

Lactone $C_7H_{12}O_2$. [11°]. (220° i.V.). S. 8·3 at 0°. Formed from tetracrylic acid and cold HBrAq (Fittig a. Krafft, *A.* 208, 86). Liquid.

γ-Oxy-heptoic acid. *Lactone* $CHMe{<}{\genfrac{}{}{0pt}{}{CH_2.CMe_2}{O-CO}}$ [52°]. (86° at 15 mm.). Formed by reducing β-acetyl-valeric acid with

sodium-amalgam (Anschütz, *A.* 247, 107). Large crystals.

γ-Oxy-heptoic acid $CH_3.CH(OH).CH_2.CHEt.CO_2H$. Formed by reducing β-acetyl-valeric acid with sodium-amalgam (Young, *C. J.* 43, 173; *A.* 216, 38). The free acid changes quickly, especially on boiling, to the lactone.—BaA'_2.—AgA': curdy pp.

Lactone $CH_3.CH<\begin{smallmatrix}CH_2.CHEt\\O\quad .CO\end{smallmatrix}$. (219·5° i.V.). S.G. $\frac{16}{}$ ·992. Liquid, m. sol. water. A solution saturated at 0° becomes turbid at 17° and clear again at 95°.

Hexa-oxy-heptoic acids are formed from levulose, dextrose, and galactose by successive treatment with HCy and alkalis (Kiliani, *B.* 18, 3066; 19, 767; 22, 521). The free acids change to lactones $C_7H_{12}O_7$. The hexa-oxy-heptoic acid from galactose crystallises in needles [145°] and forms the salt KA' ½aq.

DI-OXY-HEPTYLENE $C_7H_{12}(OH)_2$. [89·5°]. (195·6° cor.). V.D. 63·6. A product of the distillation of resin (Morris, *C. J.* 41, 169). White mass. Forms a hydrate $C_7H_{14}O_2$ aq [c. 106°].

Acetyl derivative $C_7H_{12}(OAc)_2$. [69°].

TETRA-OXY-TETRA-HEPTYL-PHOSPHONIUM IODIDE $(C_6H_{13}.CH(OH))_4PI$. [122°]. Formed from PH_4I and heptoic aldehyde (De Girard, *A. Ch.* [6] 2, 40). Laminæ.

OXY-HEPTYL-PYROTARTARIC ACID *Lactonic acid* $C_{12}H_{20}O_4$. *Methylhexylparaconic acid.* [107°]. Formed from œnanthol, pyrotartaric acid, and Ac_2O (Riechelmann, *A.* 255, 132). Plates, v. sol. ether.—BaA'_2 3aq.—CaA'_2 aq.—AgA': needles (from water).

β-OXY-HEPTYL-SUCCINIC ACID $C_{11}H_{20}O_5$ *i.e.* $C_6H_{13}.CH(OH).CH(CO_2H).CH_2CO_2H$. *Hexitamalic acid.* The salts are got by boiling the lactonic acid with bases.—CaA'' (at 100°).—BaA'' (at 130°).—Ag_2A''.

Lactonic acid

$C_6H_{13}.CH<\begin{smallmatrix}CH(CO_2H)\\O.CO\end{smallmatrix}>CH_2$. *Hexyl paraconic acid.* [89°]. Formed from œnanthol, Ac_2O, and barium succinate at 120° (Schneegans, *A.* 227, 85). Needles, sl. sol. water.—CaA'_2 2aq.—AgA'; flocculent pp.

DI-OXY-HEXADECANE $C_{16}H_{32}(OH)_2$. Formed from $C_{16}H_{32}Br_2$ and AgOAc followed by KOH (Krafft a. Grosjean, *B.* 23, 2352).

Di-acetyl derivative $C_{16}H_{32}(OAc)_2$. [56°].

DI-OXY-HEXANE $C_6H_{14}O_2$ *i.e.* $CHMe(OH).CH_2.CH_2.CHMe(OH)$. (220° i.V.). S.G. $\frac{0}{0}$ ·976; $\frac{24}{0}$ ·961. C.E. (0°–24°) ·00064 (Sorokin, *J. pr.* [2] 23, 18). Formed from diallyl by successive treatment with HI, AgOAc, and KOH (Wurtz, *A. Ch.* [4] 3, 162). Liquid, sol. water.

Mono-acetyl derivative (210°).

Di-acetyl derivative $C_6H_{12}(OAc)_2$. (225°).

Di-oxy-hexane (207°). S.G. $\frac{0}{}$ ·9669. Obtained from hexylene derived from mannite (Wurtz; Hecht, *B.* 11, 1154). The corresponding oxide, $C_6H_{12}O$ (110°), is formed from $C_6H_{13}OCl$ and KOH (Eltekoff, *J. R.* 1882, 355).

Di-acetyl derivative (215°–220°). S.G. $\frac{0}{}$ 1·014.

Di-oxy-hexane $CH_3.CH(OH).CH_2.CH_2.CH_2.CH_2(OH)$. *Hexylene δ-glycol.* (235° at 710 mm.). S.G. at 0° = ·9809. Prepared by reduction of aceto-butyl alcohol $CH_3.CO.CH_2.CH_2.CH_2.CH_2.OH$ with sodium-amalgam (Lipp, *B.* 18, 3282). Thick colourless fluid of slight smell and bitter taste. V. sol. water and alcohol, more sparingly in anhydrous ether. By heating with HCl it is converted into hexylene-δ-chlorhydrin, and by prolonged action into hexylene-di-chloride. By heating with H_2SO_4 (65 p.c.) it splits off H_2O, forming hexylene-δ-oxide.

Di-oxy-hexane CHMe(OH).CHPr(OH). [c. 0°]. (207°). Formed from aldehyde, isobutyric aldehyde, and alcoholic potash (Fossek, *M.* 5, 119; Swoboda, *M.* 11, 389). Thick liquid, sol. water. Dilute H_2SO_4 forms, on heating, (β)-pinacolin $C_{12}H_{24}O_2$ (210°).

Isomeride *v.* PINACONE.

Tri-oxy-hexane $C_6H_{14}O_3$ *i.e.* $CH_2(OH).CH(OH).CH_2.CMe_2(OH)$. *Hexyl-glycerin.* (190° at 50 mm.). S.G. $\frac{0}{}$ 1·0936.

Formation.—1. By addition of bromine to $CMe_2(OH).CH_2.CH:CH_2$ and decomposition of the product with baryta (Orloff, *Bl.* [2] 47, 167). 2. From di-methyl-allyl-carbinol by successive treatment with HOCl and aqueous KOH, or with Br and baryta (Orloff, *Bl.* [2] 45, 253; *A.* 233, 351; Reformatsky, *J. pr.* [2] 31, 318; 40, 398).

Properties.—Syrup, sol. water and alcohol, insol. ether.

Tri-acetyl derivative. Oil.

Tri-oxy-hexane $CH_2(OH).CH(OH).CH_2.CH_2.CHMe(OH)$. (181° at 10 mm.). S.G. $\frac{0}{4}$ 1·1012. Formed by heating its tri-acetyl derivative with PbO. Liquid, sol. water.

Tri-acetyl derivative $C_6H_{11}(OAc)_3$. (c. 283°). S.G. $\frac{0}{4}$ 1·109. C.E. ·000873. Formed by heating methyl-butenyl-carbinol (from allyl-acetone) with Ac_2O (Markownikoff a. Kabloukoff, *Bl.* [2] 34, 347; 37, 346; 43, 111). Heavy oil. Yields an oxide $C_6H_{12}O_2$ (178°).

Tri-oxy-hexane $CHEt(OH).CMe(OH).CH_2OH$. (170°–176° at 53 mm.). Formed by boiling the dibromide of methyl-ethyl-allyl-carbinol with water (Lieben a. Zeisel, *M.* 4, 41). Liquid.

Tri-acetyl derivative (c. 270°). Oil.

Tetra-oxy-hexane $C_6H_{14}O_4$. [95°]. Formed by oxidising diallyl with $KMnO_4$ (Wagner, *B.* 21, 3343). Plates, v. sol. water, m. sol. cold alcohol, insol. ether.

OXY-HEXANE DISULPHONIC ACID $C_6H_{12}O(SO_3H)_2$. Formed from methyl-ethyl-acroleïn and SO_2 at 80° (Ludwig, *M.* 9, 667).—BaA'' 2aq converted by sodium-amalgam in presence of acids to hygroscopic sodium oxy-hexane sulphonate $C_6H_{13}O(SO_3Na)$.

OXY-HEXENOIC ACID $C_6H_{10}O_3$. A product of the action of boiling water on the dibromide of hydrosorbic acid (Fittig, *A.* 200, 57). Liquid. —CaA'_2 1½aq: plates.

OXY-HEXIC ACID $C_6H_8O_3\frac{1}{3}$aq or $C_7H_{10}O_4$. [174°]. Formed from propyl-acetoacetic ether by successive treatment with Br and alcoholic potash (Demarçay, *C. R.* 88, 289). Small pearly plates, v. e. sol. hot water. Is perhaps identical with terebic acid (Gorboff, *J. R.* 1887, 605). Reduced by Zn and H_2SO_4 to $C_7H_{12}O_4$ (?) [93°]. Yields an amide $C_{14}H_{21}O_5(NH_2)_3$ (?) [215°] and an amic ether $C_{10}H_{10}NO_3$ (?) [79°].

Iso-oxy-hexic acid. [187°]. Formed in like manner from isopropyl-acetoacetic ether (D.). Reduced by Zn and H_2SO_4 to $C_7H_{12}O_4$ (?) [113°].

Yields $C_{18}H_{21}O_5(NH_2)_5$ (?) [240°] and another amide $C_6H_7O(NH_2)(OEt)_2$ (?) [95°].

DI-OXY-HEXINENE *v.* Di-oxy-hexylene.

α-OXY-HEXOIC ACID $C_6H_{12}O_3$ *i.e.* $CH_2Pr.CH(OH).CO_2H$. *Leucic acid.* Mol. w. 132. [73°]. Formed by the action of nitrous acid on leucine (Strecker, *A.* 68, 55; Thudichum, *C. J.* 14, 307; Waage, *A.* 118, 297). Needles, v. sol. water, alcohol, and ether.—BaA'_2: silky laminæ (from hot alcohol).—CaA'_2.—CoA'_2.—CuA'_2.—ZnA'_2aq. S. ·33 at 16°; ·5 at 100°.—$ZnA'_2$2aq (Körner, *G.* 13, 356).—AgA′: crystalline pp.

An isomeric or identical oxy-hexoic acid [62°] is formed by the action of Na_2CO_3 on bromo-hexoic acid got from fermentation hexoic acid (Jelisafoff, *J. R.* 12, 367; *Bn.* 1, 523). It yields the salts CaA'_2, BaA'_2, MgA'_2 2aq, ZnA'_2 2aq (S. ·14 at 16°; ·21 at 100°), CuA'_2, and AgA′. It forms a crystalline amide [142°].

α-Oxy-hexoic acid $CEt_2(OH).CO_2H$. [80°]. S. 35 at 17·5°. Formed from its ether which is got from oxalic ether by the action of $ZnEt_2$ followed by water (Frankland, *Pr.* 12, 396; Frankland a. Duppa, *Pr.* 13, 140; *A.* 135, 26; Geuther, *Z.* 1867, 705; Fittig, *A.* 200, 21). Triclinic crystals, v. sol. water, alcohol, and ether. Yields di-ethyl ketone on oxidation.—NH_4A'. -BaA'_2.—BaA'_2 5aq.—ZnA'_2. S. ·33 at 16°. – CuA_2.—AgA′aq: needles.

Methyl ether MeA′. (165°). S.G. $\frac{16·5}{}$ ·987.

Ethyl ether EtA′. (175°). V.D. 5·24 (calc. 5·53). S.G. $\frac{18·7}{}$ ·961. Oil. Formed from $COCl.CO_2Et$ and $ZnEt_2$ (Henry, *B.* 5, 949).

Isoamyl ether (225°). S.G. $\frac{13}{}$ ·933.

Nitrile $CEt_2(OH).CN$. Formed from $COEt_2$ and HCy (Tiemann a. Friedländer, *B.* 14, 1974). Oil.

α-Oxy-hexoic acid $CH_2Pr.CH(OH).CO_2H$. [56°]. Got by saponification of its nitrile, which is formed from isovaleric aldehyde and HCy (Erlenmeyer a. Sigel, *B.* 7, 1109; Ley, *B.* 10, 231). Formed also by heating isobutyl-tartronic acid at 180° (Guthzeit, *A.* 209, 239). Plates. —ZnA'_2 2aq. S. ·12 at 16°.

Nitrile. Oil, lighter than water.

β-Oxy-hexoic acid $CHMe(OH).CHEt.CO_2H$. Formed from ethyl-acetoacetic ether and sodium-amalgam (Waldschmidt, *A.* 188, 240). Syrup.—NaA′.—CuA'_2.—AgA′: plates.

α-Oxy-hexoic acid $CMe_3.CH(OH).CO_2H$. [88°]. Formed by reducing tri-methyl-pyruvic acid with sodium-amalgam (Glücksmann, *M.* 10, 780). Monoclinic crystals.—AgA′.

β-Oxy-hexoic acid $CHEt(OH).CHMe.CO_2H$. Formed by reducing propionyl-propionic acid (Hantzsch a. Wohlbrück, *B.* 20, 1320).—NaA′.

γ-Oxy-*n*-hexoic acid $CHEt(OH).CH_2.CH_2.CO_2H$. The salts are formed by the action of bases on the lactone. The free acid quickly changes to lactone.—CaA'_2.—BaA_2.—AgA′.

Lactone $C_6H_{10}O_2$ *i.e.* $CHEt\!<\!\begin{array}{l}CH_2.CH_2\\O\text{—}CO\end{array}$. (220°). *Formation.*—1. By boiling with water the bromo-hexoic acid formed by the union of hydrosorbic acid with HBr (Fittig, *B.* 13, 955; *A.* 208, 67).—2. By heating glutaconic acid with HI and P (Kiliani a. Kleeman, *B.* 17, 1300).—3. By reduction of metasaccharin with HI (Kiliani, *B.* 18, 642).—4. By warming hydrosorbic acid with dilute (1:1)H_2SO_4 (Fittig, *A.* 256, 134).

Properties.—Liquid, m. sol. water. Volatile with steam. Its aqueous solution becomes turbid when heated to 40°, but clear again at 80°. K_2CO_3 separates it from the solution. HI and P reduce it to *n*-hexoic acid.

Amide $CHEt(OH).CH_2.CH_2.CONH_2$. [74°]. Formed by heating the lactone with alcoholic NH_3 at 100°. Prisms, v.e. sol. water and alcohol, sl. sol. ether.

γ-Oxy-isohexoic acid $CMe_2(OH).CH_2.CH_2.CO_2H$. Crystalline, but very unstable.—BaA'_2 (at 100°).—AgA′.

Lactone $C_6H_{10}O_2$. (207° i. V.). Formed from terebic acid by distillation, by successive treatment with HBr and water, or by boiling with dilute H_2SO_4 (Fittig a. Bredt, *A.* 200, 58, 259; Geisler, *A.* 208, 43; Erdmann, *A.* 228, 181). Formed also by oxidising isohexoic acid with $KMnO_4$ (Bredt, *A.* 208, 59). Liquid, v. sol. water. Neutral in reaction. Its aqueous solution becomes turbid at 35°, clear again at 80°. Yields on oxidation with HNO_3 the acid $C_6H_8O_4$ [68°], whence $CaC_6H_8O_8$ 7aq and $AgC_6H_7O_4$. Boiling NaOEt forms an anhydride $C_{12}H_{18}O_3$ [106°], whence HClAq forms $C_{11}H_{20}O_2$ (209°).

γ-Oxy-hexoic acid $CH_2(OH).CH_2.CHEt.CO_2H$. Formed from $CH_3.CO.CEt(CH_2.CH_2OH).CO_2Et$ by boiling with baryta-water (Chanlaroff, *A.* 226, 335). Thick liquid, changing to the lactone on boiling its solution. $Ba(C_6H_{11}O_3)_2$: crystals (from alcohol).—CaA'_2.—AgA′; needles (from water).

Lactone $CH_2\!<\!\begin{array}{l}CH_2.CHEt\\O\text{—}CO\end{array}$. (215°). S.G. $\frac{16}{}$ 1·035. Liquid, m. sol. cold water.

γ-Oxy-hexoic acid $CHMe(OH).CH_2.CHMe.CO_2H$. Formed by reduction with sodium-amalgam from β-acetyl-isobutyric acid derived from α-bromo-propionic ether and sodium acetoacetic ether (Fittig a. Gottstein, *A.* 216, 30). Formed also by reducing saccharin or isosaccharin with HI and P (Liebermann a. Scheibler, *B.* 16, 1821; Kiliani, *B.* 18, 635).—BaA'_2.

Lactone. (206°). Liquid, sol. 20–25 volumes of water. An isomeric anhydride [137°] is also formed by reducing isosaccharin.

γ-Oxy-hexoic acid $CHMe(OH).CHMe.CH_2.CO_2H$. Formed by reducing β-acetyl-*n*-butyric acid (Gottstein, *A.* 216, 36). Yields a lactone (210°).

δ-Oxy-hexoic acid $CHMe(OH).CH_2.CH_2.CH_2.CO_2H$. Obtained by reducing γ-acetyl-*n*-butyric acid with sodium-amalgam at 30° (Fittig a. Wolff, *A.* 216, 133). When boiled with water it is partly converted into the lactone. When the lactone is boiled with water it is partly converted into the acid. Equilibrium occurs with 65 p.c. lactone and 35 p.c. acid.—AgA′.

Lactone. [19°]. (c. 231° i. V.). Colourless liquid, solidifying below 0°. Miscible with water but separated by K_2CO_3.

Oxy-hexoic acid $C_6H_{12}O_3$. [108°]. Formed by oxidising oil of millet with $KMnO_4$ (Kassner, *Ar. Ph.* [3] 25, 1081). Plates, v. sol. water. Yields an acetyl derivative [71°].

Di-oxy-hexoic acid. [141°]. Formed from ethyl-crotonic acid by successive treatment with

bromine and with water at 100° (Fittig a. Howe, *A.* 200, 39). Trimetric prisms, $a:b:c = \cdot 96:1:\cdot 33$. V. sol. water and alcohol.—$CuA'_2\ 3\frac{1}{2}aq$: bright-blue needles.

Di-oxy-hexoic acid $CHMe(OH).CEt(OH).CO_2H$. [96°]. Formed by oxidising ethyl-crotonic acid with $KMnO_4$ (Fittig, *B.* 21, 920).

Di-oxy-hexoic acid $CHEt(OH).CMe(OH).CO_2H$. [152° cor.]. Formed by oxidation of methyl-ethyl-acroleïn (Lieben a. Zeisel, *M.* 4, 65). Needles or prisms.—$CaA'_2\ 3aq$: crystalline mass.

Hexa-oxy-hexoic acid $C_6H_{12}O_7$. *Arabinose-carboxylic acid.* Formed from arabinose by the action of aqueous HCy, followed by saponification (Kiliani, *B.* 29, 3033; 20, 339). When liberated from its salts it immediately forms the lactone.—CaA'_2: amorphous.

Amide. Minute needles.

Lactone $C_6H_{10}O_6$. [145°–150°]. $[\alpha]_D = -54\cdot 8$. Needles or prisms. Yields metasaccharic acid dilactone $C_6H_6O_6$ on oxidation by HNO_3 and *n*-hexoic acid on reduction by HI and P.

DI-OXY-HEXYLENE $C_6H_{12}O_2$. *Hexinene glycol.* (218°–225°). Formed from epichlorhydrin and Na (Hübner a. Miller, *A.* 159, 186). Is perhaps di-oxy-hexinene (Claus, *B.* 10, 556).

OXY-HIPPURIC ACID $C_9H_9NO_4$ *i.e.* $C_6H_4(OH).CO.NH.CH_2.CO_2H$. Formed from *m*-amido-hippuric acid by the diazo-reaction (Griess, *B.* 1, 190; Conrad, *J. pr.* [2] 15, 259). Needles, v. sol. hot water.

OXY-HYDRASTININE *v.* HYDRASTINE.

OXYHYDROANTHRANOL *v.* OXYANTHRANOL HYDRIDE.

TRI-OXY-HYDROBENZAMIDE *v.* OXY-BENZOIC ALDEHYDE.

OXYHYDROBENZOIC ACID $C_7H_8O_3$. [275° cor.]. Formed from oxy-uvitic acid and aqueous $KMnO_4$ (Oppenheim a. Emmerling, *B.* 9, 327). Needles. Yields benzoic acid by potash-fusion. —$CaA'_2\ 3aq$.—AgA': v. sl. sol. water.

OXY-HYDRO-COUMARILIC ACID *v.* COUMARILIC ACID.

OXY-HYDRONAPHTHOQUINONE *v.* HYDROJUGLONE.

OXY-HYDROQUINOLINE *v.* OXY-QUINOLINE HYDRIDE.

OXY-HYDROQUINONE *v.* TRI-OXY-BENZENE.

OXY-DIHYDROQUINOXALINES *v.* OXY-QUINOXALINE DIHYDRIDE.

OXYHYPOGÆIC ACID $C_{16}H_{30}O_3$. [34°]. Formed from di-bromo-palmitic acid and Ag_2O (Schröder, *A.* 143, 36). White mass.

OXY-DIIMIDODIAMIDOIASTIN *v.* ISATIN.

OXY-IMIDO-METHYL-PYRIMIDINE DIHYDRIDE $C(NH){<}\begin{smallmatrix}NH.CMe\\NH.CO\end{smallmatrix}{>}CH$. *Imido-methyl-uracil.* [270°]. Formed from guanidine, alcohol, and acetoacetic ether (Jaeger, *A.* 262, 365). Prisms, v. sol. hot water. Yields a dibromido [160°]. MeI forms $C_5H_6MeN_3O$ [312°], whence B'_2HI [212°], B'HClaq, and $B'_2H_2SO_4$ [270°].

Salts.—B'HCl. [295°].—$B'H_2SO_4$. [180°]. —$B'HNO_3$: needles.

Oxy-imido-di-methyl-pyrimidine dihydride $C(NH){<}\begin{smallmatrix}NH.CMe\\NH.CO\end{smallmatrix}{>}CMe$. [320°]. Formed from guanidine and methyl-acetoacetic ether. —$B'H_2SO_4$. [265°].—$B'HNO_3$. [200°]. Plates.

OXY-IMIDO-PHENYL-PYRIMIDINE DIHYDRIDE $C(NH){<}\begin{smallmatrix}NH.CPh\\NH.CO\end{smallmatrix}{>}CH$. *Imido-phenyl-uracil.* [294°]. Formed from guanidine and benzoyl-acetic ether (Jaeger, *A.* 262, 372). Amorphous powder, insol. water and alcohol.

OXY-IMIDO-DIPHENYL SULPHIDE $NH{<}\begin{smallmatrix}C_6H_4\text{———}\\C_6H_3(OH)\end{smallmatrix}{>}S$. Formed from oxydiphenylamine by heating with S (Bernthsen, *A.* 230, 182). Colourless mass, v. sol. alcohol and ether. $FeCl_3$ forms a chocolate pp. of $N{<}\begin{smallmatrix}C_6H_4\\C_6H_3\end{smallmatrix}{>}S$, insol. water.
$|$
O ⁄

DI-OXY-IMIDO-DIPHENYL SULPHIDE $NH{<}\begin{smallmatrix}C_6H_3(OH)\\C_6H_3(OH)\end{smallmatrix}{>}S$. Formed by reducing thionol $N{<}\begin{smallmatrix}C_6H_3(OH)\\C_6H_3\text{———}\end{smallmatrix}{>}S$ which is itself got
$|$
O ⁄

by the action of conc. H_2SO_4 on imido-diphenyl sulphide (Bernthsen, *A.* 230, 188). Colourless needles, v. sl. sol. water. Yields a tri-acetyl derivative [156°].

DI-OXY-IMIDO-PYRIDINE DIHYDRIDE *v.* DI-OXY-AMIDO-PYRIDINE.

DI-OXY-DI-IMIDO-QUINONE $C_6(NH)_2(OH)_2O_2$. Formed by oxidising tetra-oxy-di-amido-benzene by $FeCl_3$ (Nietzki, *B.* 16, 2094; 18, 503). Plates, v. sl. sol. alcohol.

OXY-INDAZOLE $C_7H_5(OH)N_2$. [215°–266°](?). Formed by boiling diazo-indazole with water (Witt, Noelting, a. Grandmougin, *B.* 23, 3642). Needles, sl. sol. cold water.

OXY-INDOLE *v.* OXINDOLE.

(α)-OXY-INDONAPHTHENE C_9H_8O *i.e.* $C_6H_4{<}\begin{smallmatrix}CO\\CH_2\end{smallmatrix}{>}CH_2$. *(α)-Hydrindone.* [40°]. (244°). Formed by heating *o*-cyano-benzyl-acetic ether with conc. HClAq (Gabriel a. Hausmann, *B.* 22, 2018). Colourless tables. Conc. HClAq at 100° forms $(C_9H_6)_n$, not melted at 280°.

Oxim $C_9H_8(NOH)$. [146°]. White needles (from alcohol), sol. alkalis.

Phenyl-hydrazide $C_9H_8(N_2HPh)$. [c. 120°]. White prisms, converted by conc. HClAq into $C_{15}H_{11}N$ [235°].

References.—DI-BROMO- and CHLORO-DI-OXY-INDONAPHTHENE.

OXY-ITACONIC ACID $C_5H_6O_5$. Formed by boiling aconic acid with baryta-water (Meilly, *A.* 171, 153). Oil.—BaA'' (at 160°).—Ag_2A'': flocculent pp.

OXY-JUGLONE *v.* JUGLONE.

OXY-LEPIDINE *v.* OXY-METHYL-QUINOLINE.

OXY-LEUCOTIN *v.* COTOÏN.

OXY-LUTIDINE *v.* OXY-DI-METHYL-PYRIDINE.

OXY-MALONIC ACID *v.* TARTRONIC ACID.

OXY-MARGARIC ACID $C_{17}H_{34}O_3$. [80°]. Occurs in adipocere (Ebert, *B.* 8, 775).—AgA': amorphous.

OXY-TRIMELLITIC ACID $C_9H_6O_7$ *i.e.* $C_6H_2(OH)(CO_2H)_3$ [5:4:2:1]. [c. 245°]. Formed by fusing sulpho-trimellitic acid with potash (Jacobsen a. Meyer, *B.* 16, 192). Prisms (containing 2aq). With HClAq at 240° it yields *m*-oxy-benzoic acid.—$Ba_3A'''_2\ 5aq$: small prisms.

OXY-TRIMESIC ACID $C_9H_6O_7$ *i.e.* $C_6H_2(OH)(CO_2H)_3$ [2:5:3:1]. S. ·5 at 10°. Formed by heating [2:1]$C_6H_4(ONa)CO_2Na$ in a current of CO_2 (Ost, *J. pr.* [2] 14, 95; 15, 302; 17, 284), and by fusing $C_6H_2(SO_2NH_2)(CO_2H)_3$ with potash (Jacobsen, *A.* 206, 204). Nodules (containing aq) or needles (containing 2aq). Decomposes at 180°.—$Ca_3A'''_2$ 8aq.—$Ca(H_2A''')_2$.—$Ba_3A'''_2$ 8aq.—Ag_3A''' 3aq.

Ethers Et_2HA'''aq. [148°].—Et_2NaA'''aq.—Et_3A'''. [84°].—$Et_3NaC_9H_2O_7$: prisms, insol. water.

OXY-MESITENE CARBOXYLIC ACID *v.* Aceto-acetic acid.

ω-OXY-MESITYLENE $C_6H_3Me_2.CH_2OH$. (220°). Heavy oil (Wispek, *B.* 16, 1577).

Acetyl derivative (230°). S.G. $\frac{16}{}$ 1·09. Formed from ω-bromo-mesitylene and KOAc.

Isomeride *v.* Mesitol.

Di-ω-oxy-mesitylene $C_6H_3Me(CH_2OH)_2$. *Mesitylenic glycol.* (280°). S.G. $\frac{25}{}$ 1·23. S. 5. S. (ether) 50. Obtained by prolonged boiling of ω-di-chloro-mesitylene [41·5°] with water and lead carbonate (Robinet a. Colson, *C. R.* 96, 1863). Liquid, with bitter taste, v. sol. alcohol.

Di-acetyl derivative $C_6H_3Me(CH_2OAc)_2$. (244° at 120 mm.). S.G. $\frac{20}{}$ 1·12. Oil.

Isomeride *v.* Tri-methyl-resorcin.

Tri-ω-oxy-mesitylene $C_9H_9O_3$ *i.e.* $C_6H_3(CH_2OH)_3$. *Mesicerin.* Obtained by boiling tri-ω-bromo-mesitylene with water (40 pts.) and lead carbonate (Colson, *A. Ch.* [6] 6, 95). Syrup, gradually crystallising in a desiccator. Sol. alcohol, insol. chloroform and ether.

o-OXY-MESITYLENIC ACID $C_9H_{10}O_3$ *i.e.* $C_6H_2Me_2(OH)CO_2H$ [5:3:2:1]. [179°]. Formed by potash-fusion from mesitylene sulphonic acid (Fittig a. Hoogewerff, *A.* 150, 333), from mesitol (Jacobsen, *A.* 195, 274), (a)-sulpho-mesitylenic acid (Remsen, *Am.* 3, 220), and mesitylene disulphonic acid (Barth a. Herzig, *M.* 1, 812). Formed also from *o*-amido-mesitylenic acid (Jacobsen, *B.* 11, 2055). Prepared from *m*-xylenol, Na, and Co_2 (Jacobsen, *B.* 14, 44). Needles (from dilute alcohol). $FeCl_3$ colours its solution blue. — NH_4A'.—KA'. — CaA'_2 5aq.—BaA'_2 5aq. — ZnA'_2 2aq: four-sided prisms.—MeA'. Oil.

***p*-Oxy-mesitylenic acid** $C_6H_2Me_2(OH)CO_2H$ [5:3:4:1]. [223°]. Formed from *p*-sulphamido-mesitylenic acid by potash-fusion (Jacobsen, *B.* 12, 606; *A.* 206, 197). Formed also from *p*-amido-mesitylenic acid (Emerson, *Am.* 8, 268). Needles, insol. cold water. Yields *c*-xylenol on heating with HClAq at 200°.—BaA'_2.—AgA'.—MeA'. [130°].—EtA'. [113°]. Needles or prisms, volatile with steam.

OXY-METHACRYLIC ACID. Appears to be a product of the action of KCy followed by potash on CH_2:CCl.CH_2Cl (Claus, *A.* 170, 126).

Methyl derivative CH_2:C(CH_2OMe).CO_2H. (c. 238°). Formed by heating $C(OMe)_2(CO_2H)_2$ at 140° (Kleber, *A.* 246, 103). Liquid, miscible with water. With HI and P it yields MeI and isobutyric acid.

OXY-METHANE *v.* Methyl alcohol.

Di-oxy-methane *v.* Formic aldehyde.

Tri-oxy-methane *v.* Formic acid.

OXY-METHANE SULPHONIC ACID $CH_2(OH)SO_3H$. Formed from methyl alcohol, H_2SO_4, and SO_3 (Max Müller, *B.* 6, 1031). Crystalline, not decomposed by boiling water or acids. Yields sodium sulphide on warming with soda and spongy platinum (Loew, *B.* 23, 3125).

Oxy-methane disulphonic acid CH_4SO_7 *i.e.* $CH(OH)(SO_3H)_2$. Formed from methyl alcohol and SO_3.—K_2A'': needles.

Oxy-methane tri-sulphonic acid $C(OH)(SO_3H)_3$. Formed from $C(SH)(SO_3K)_3$ and bromine-water (Albrecht, *A.* 161, 129). Deliquescent mass.—K_3A''' aq: needles. S. 1·2 at 21°.—$(NH_4)_3A'''$.—$Ba_3A'''_2$ 8aq.—$Hg_6O_3A'''_2$ 15aq. — $PbK_{18}A'''_6(OH)$ 5aq. — $Pb_4A'''_2Ac_2$ 8aq. — Ag_3A''' aq: needles, v. sol. warm water.

OXY-METHENYL-DI-AMIDO-DIBENZOIC ACID. *Ethyl derivative* $C(OEt)\begin{matrix}\nearrow N\ .C_6H_4.CO_2H \\ \searrow NH.C_6H_4.CO_2H\end{matrix}$. [223°]. Formed from o-amido-benzoic acid hydrochloride and NH:$C(OEt)_2$ (Sandmeyer, *B.* 19, 2656). Needles, v. sl. sol. hot water.—AgHA'': white pp.

OXY-METHENYL-AMIDO-PHENOL $C_6H_4{<}{}^{N}_{O}{>}COH$ or $C_6H_4{<}{}^{NH}_{O}{>}CO$. [137°]. Formed by heating oxy-phenyl-urea made by the action of $ClCO_2Et$ on o-amido-phenol (Grönvick, *Bl.* [2] 25, 177; Kalckhoff, *B.* 16, 1828), and by heating o-amido-phenyl ethyl carbonate (Bender, *B.* 19, 2265, 2950). Plates. EtI and KOEt form $C_6H_4{<}{}^{NEt}_{O}{>}CO$. [29°].

Ethyl derivative $C_6H_4{<}{}^{N}_{O}{>}COEt$. (225°–230°). Formed from $C_6H_4(OH).NH_3Cl$ and NH:$C(OEt)_2$ (Sandmeyer, *B.* 19, 2655). Oil, insol. alkalis.

OXYMETHENYL-AMIDO-PHENYL-MERCAPTAN C_7H_5NOS *i.e.* $C_6H_4{<}{}^{N}_{S}{>}C(OH)$. [136°]. Formed by the action of hot water or alcohol on C_7H_4ClSN which is got by heating phenyl thiocarbimide with PCl_5 (Hofmann, *B.* 12, 1128; 13, 10). Crystals (from alcohol), sl. sol. water.

Ethyl derivative $C_6H_4NS(COEt)$. [25°]. From C_7H_4ClSN and NaOEt.—$B'_2H_2PtCl_6$.

Acetyl derivative $C_6H_4NS(COAc)$. [60°].

OXY-TETRAMETHENYL DIHYDRIDE CARBOXYLIC ACID $\begin{matrix}CH_2.CH.CO_2H \\ CH_2.CO\end{matrix}$. [183°]. Formed by heating inactive amido-glutaric acid (Wolff, *A.* 260, 125). Prisms, v. sol. hot water.

OXY-METHENYL-PHENYLENE-DIAMINE *v.* Phenylene-urea.

OXY-METHYL-ACETOACETIC ETHER. *Ethyl derivative* $CH_2(OEt)$.CO.CHMe.CO_2Et. (190°–195°). S.G. $\frac{22}{}$ ·976. Formed from chloro-methyl-acetoacetic ether and NaOEt (Isbert, *A.* 234, 194). Liquid.

ω-OXY-METHYL-AMIDO-BENZOIC ACID $C_6H_3(CH_2OH)(NH_2).CO_2H$ [2:4:1]. Formed by dissolving amido-phthalide [178°] in hot aqueous potash (Hoenig, *B.* 18, 3452).—CuA'_2: dark-grey pp.

Oxy-dimethylamide-benzoic acid. *Anhydride of the methylo-hydroxide* $C_{10}H_{13}NO_3$ *i.e.* $C_6H_3(OH){<}{}^{NMe_3}_{CO}{>}O$. Formed by the action of MeI and KOH on amido-salicylic acid (Griess, *B.* 12, 2307). White needles (containing 4aq), v. sol. water. Tastes bitter. Gives a violet colour with $FeCl_3$. Converted on heating into

crystalline $C_6H_3(OH)(NMe_2)CO_2Me$.—B'HCl.—B'HI.—$B'_2H_2PtCl_6$ 4aq: small yellow prisms.

Oxy-methylamido-benzoic acid. *Methyl derivative* $C_6H_3(OMe)(NHMe)CO_2H$. [above 200°]. Formed from potassium amido-anisate and MeI (Griess, *B.* 5, 1042; 6, 588). Slender needles, v. sl. sol. hot water. Yields B'HClAq. Further treatment with MeI and KOH forms $C_6H_3{<}\begin{smallmatrix}NMe_3\\CO\end{smallmatrix}{>}O$ 5aq which gives the salts $B'_2H_2PtCl_6$ and B'HI aq, and on distillation yields $C_6H_3(NMe_2)(OMe)CO_2H$ (288°).

β-OXY-METHYL-α-AMIDO-BUTYRIC ACID CHMe(OH).CH(NHMe).CO_2H. S. 56 at 12°. Formed from β-methyl-glycidic acid and methylamine at 100° (Selinsky, *Bl.* [2] 43, 247). Crystals.

o-OXY-TETRA-METHYL-DI-p-AMIDO-TRI-PHENYL CARBINOL $C_{23}H_{26}N_2O_2$ *i.e.* $C_6H_4(OH).C(OH)(C_6H_4NMe_2)_2$. Formed by oxidising the leuco- base obtained by condensation of salicylic aldehyde with dimethylaniline (O. Fischer, *B.* 14, 2522). Dyes yellowish-green.

o-OXY-TETRA-METHYL-DI-p-AMIDO-TRI-PHENYL-METHANE $C_{23}H_{26}N_2O$ *i.e.* $C_6H_4(OH).CH(C_6H_4NMe_2)_2$. *Leuco-base of salicyl-aldehyde-green.* [128°]. Prepared by heating a mixture of dimethylaniline (24 pts.), salicylic aldehyde (10 pts.), and $ZnCl_2$ (20 pts.) to 100° for 7 or 8 hours; the yield being nearly theoretical (Fischer, *B.* 14, 2522). Colourless rosettes. Sol. hot alcohol and benzene, nearly insol. water. Combines with both acids and bases. On gentle oxidation it gives a green of yellow shade.

Acetyl derivative $C_{23}H_{25}N_2(OAc)$. Iridescent plates. [144°].

The isomeride [163°] from p-oxybenzoic aldehyde yields a green dye and forms an acetyl derivative [146°] crystallising in prisms.

Di-oxy-tetra-methyl-di-amido-tri-phenyl-methane. *Methyl derivative* $C_6H_3(OH)(OMe).CH(C_6H_4NMe_2)_2$. [136°]. Formed from vanillin, $PhNMe_2$, and $ZnCl_2$ (O. Fischer a. Schmidt, *B.* 17, 1895). Crystals, v. sol. alcohol.

OXY-TETRA-METHYL-AMMONIUM HYDROXIDE $CH_2(OH).NMe_3OH$. Formed from $CH_2I.NMe_3I$ and moist Ag_2O (Hofmann, *J.* 1859, 377). Yields $(CH_2OH.NMe_3Cl)_2PtCl_4$ crystallising in octahedra.

DI-OXY-METHYL-AMYL-KETONE. *Dimethyl derivative.* $CH(OMe)_2.CO.CHEt_2$. (134°). S.G. $\frac{15}{}$ ·886. Formed as one of the products of the action of NaOMe upon $CHCl_2.CO.CEt_2.CO_2Et$ (James, *A.* 231, 243; *C. J.* 49, 57). Oil. Miscible with alcohol and with ether, burns with pale flame. Does not combine with $NaHSO_3$ or react with Ac_2O.

OXY-METHYL-AMYL-PYRROLE CARBOXYLIC ETHER $C_5H_{11}N{<}\begin{smallmatrix}.CMe\\CO.CH_2\end{smallmatrix}{>}C.CO_2Et$. [52°]. (188° at 16 mm.). Formed from acetosuccinic ether, amylamine, and alcohol in the cold (Emery, *A.* 260, 150). White plates (from CS_2).

DI-OXY-DI-METHYL-ANILINE *v.* TETRA-METHYL-DI-AMIDO-DI-PHENYL-DI-OXIDE.

OXY-METHYL-ANTHRANOL. *Acetyl derivative.* $C_6H_4{<}\begin{smallmatrix}C(OAc)\\C(OAc)\end{smallmatrix}{>}C_6H_3Me$. [217°]. Formed from methyl-anthraquinone [177°], Ac_2O, NaOAc, and zinc-dust (Liebermann, *B.* 21, 1172). Plates.

OXY-METHYL-ANTHRAQUINONE $C_{15}H_{10}O_3$ *i.e.* $C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_2Me(OH)$ $\left[\begin{smallmatrix}1\\6\end{smallmatrix}\ 4\ 3\right]$. [262°]. Formed by heating o-cresol-phthaleïn or a mixture of phthalic anhydride, o-cresol, and H_2SO_4 at 160° (Baeyer a. Fraude, *B.* 12, 241; *A.* 202, 163). Yellow leaflets.

Bromo- derivative [205°].

Oxy-methyl-anthraquinone $C_6H_4{:}C_2O_2{:}C_6H_2Me(OH)$ [1:6:2:5]. [170°]. Formed in like manner from p-cresol (Drewson, *A.* 212, 346; Birukoff, *B.* 20, 2069). Orange needles (by sublimation).

Acetyl derivative [180°]. Needles.

Oxy-methyl-anthraquinone $C_{14}H_6MeO_2(OH)$. [178°]. Formed from amido-methyl-anthraquinone [202°] by the diazo- reaction (Römer a. Link, *B.* 16, 699). Yellow needles (by sublimation).

Acetyl derivative [177°]. Plates.

Di-oxy-methyl-anthraquinone $C_6H_3(OH){:}C_2O_2{:}C_6H_2Me(OH)$. [162°]. Mol. w. 254. S. (boiling 86 p.c. alcohol) ·45. The yellow colouring matter of rhubarb, the wall lichen (*Parmelia parietina*), and of the root of *Rumex obtusifolius* (Rochleder a. Heldt, *A.* 48, 12; Döpping a. Schlossberger, *A.* 50, 215; De la Rue a. Müller, *C. J.* 10, 298; Thann, *A.* 107, 324). It occurs also in the root of *Rheum pyramidale*, *Rumex palustris*, and of other varieties of *Rumex* (Grothe, *P.* 113, 190) and in senna leaves (Batka, *C. C.* 1864, 622). Formed by passing air through an alkaline solution of chrysarobin (Liebermann a. Seidler, *A.* 212, 36). Golden plates (from alcohol), forming a cherry-red solution in NaOHAq. Insol. Na_2CO_3Aq. Conc. H_2SO_4 forms a red solution. Conc. HNO_3 forms a tetra-nitro- derivative. Yields methyl-anthracene on distilling with zinc-dust. Does not dye mordants. Zinc, HOAc, and HClAq form $C_{15}H_{12}O_3$ [200°-206°] whence $C_{30}H_{20}Ac_6O_7$ [231°] (Liebermann, *B.* 21, 437).

Di-acetyl derivative [200°]. Plates.

Di-benzoyl derivative [c. 201°].

Di-oxy-methyl-anthraquinone $C_6H_4{:}C_2O_2{:}C_6HMe(OH)_2$ [1:6:3:2:5]. *Methyl-quinizarin.* [160°]. Formed from hydrotoluquinone, phthalic anhydride, and H_2SO_4 at 140° (Nietzki, *B.* 10, 2011). Red needles (from alcohol). Yields methyl-anthracene when distilled with zinc-dust.

Acetyl derivative [185°]. Needles.

Di-oxy-methyl-anthraquinone $C_6H_4{:}C_2O_2{:}C_6HMe(OH)_2$ [1:6:4:3:2]. *Methyl-alizarin.* [252°]. Formed by potash-fusion from bromo- or oxy-methyl-anthraquinone (O. Fischer, *B.* 8, 675; Fraude, *B.* 12, 241). Orange needles, which may be sublimed. Dyes mordants like alizarin.

Alkannin (vol. i. p. 125) is probably a di-oxy-methyl-anthraquinone as it yields methyl-anthracene on distillation with zinc-dust (Liebermann a. Römer, *B.* 20, 2428).

Di-oxy-di-methyl-anthraquinone $C_6H_2Me(OH){:}C_2O_2{:}C_6H_2Me(OH)$. *Di-methyl-anthrarufin.* [300°]. Got, together with the two following isomerides, by the action of H_2SO_4 on s-oxy-toluic acid (Kostanecki a. Niementowski, *B.* 18, 255, 2140; *A.* 240, 276). Yellow needles

(from benzene). Its alkaline solutions are yellow. Does not dye mordants.

Di-acetyl derivative [237°]. Tables.

Di-oxy-di-methyl-anthraquinone $C_{14}H_4Me_2(OH)_2O_2$. *Di-methyl-anthraflavic acid.* Needles or small yellow plates (by sublimation); not solid at 360°. Does not dye mordants.

Di-acetyl derivative [223°]. Needles.

Di-oxy-di-methyl-anthraquinone (benz-). [213°]. Yellow needles, yielding $C_{16}H_{10}Ac_2O_4$ [188°].

Tri-oxy-methyl-anthraquinone $C_{15}H_{10}O_5$. *Emodin.* [254°]. Occurs in rhubarb root (Warren de la Rue a. Hugo Müller, *C. J.* 10, 304), in the bark and berries of *Rhamnus frangula* (Liebermann a. Waldstein, *B.* 8, 970; 9, 1775; Schwabe, *Ar. Ph.* [3] 26, 569), and in the lichen *Nephroma Lusitanica* (Bachmann, *C. C.* 1888, 47). Orange-red monoclinic prisms (containing aq). Yields methyl-anthracene on distilling with zinc-dust. Its alkaline solution is dark cherry-red.

Mono-acetyl derivative [180°].

Tri-acetyl derivative [190°].

Tri-oxy-methyl-anthraquinone $C_6H_3Me:C_2O_2:C_6H(OH)_3$ [1:6:2:3:4]. *Methyl-anthragallol.* [c. 375°]. Made by heating gallic acid with *p*-toluic acid at 130° for 15 hours (Cahn, *B.* 19, 2335; *A.* 240, 284). Orange-red needles (by sublimation). Its solution in conc. KOHAq is green, becoming violet on dilution. Hot NH_3Aq forms a blue solution. Conc. H_2SO_4 forms a red liquid turned green by a trace of HNO_3, decolourised by more HNO_3.

Tri-acetyl derivative [204°].

Tri-oxy-methyl-anthraquinone [2':1':6'] $C_6H_3Me:C_2O_2:C_6H(OH)_3$ [1:6:2:3:4]. *Methyl-anthragallol.* [298°]. Formed by heating gallic acid with o-toluic acid (C.). Minute yellow needles. Forms a green solution in conc. KOHAq turned violet on dilution. Dyes like anthragallol. Conc. H_2SO_4 gives a red solution turned green by HNO_3.

Tri-acetyl derivative [210°]. Tables.

(2, 3, 4)-**Tri-oxy-3' and 5'-methyl-anthraquinones** (*methyl-anthragallols*). These two isomerides are formed simultaneously by heating gallic acid with *m*-toluic acid at 130°-135°. The one melts at [312°] and gives an acetyl derivative which forms needles melting at [190°]. The other isomeride melts at [235°-240°], and its acetyl derivative, which crystallises in small prisms, melts at 218°. Their other properties are almost the same as those of the other methyl-anthragallols (Cahn, *B.* 19, 2336).

Tri-oxy-methyl-anthraquinone [3:2:1:6] $C_6H_2(OH)_2:C_2O_2:C_6H_2Me(OH)$ [1':6':2':5']. *Methyl-oxy-alizarin.* Formed by saponifying its di-methyl ether which is produced by heating hemipic acid with *p*-cresol and H_2SO_4 (Liebermann a. Kostanecki, *A.* 240, 303). Brownish-yellow flakes, v. sol. alcohol. Dyes like alizarin.

Di-methyl ether $C_{17}H_{14}O_5$. Flakes.

Tri-oxy-di-methyl-anthraquinone [4':2':1':6'] $C_6H_2Me_2:C_2O_2:CH(OH)_3$ [1:6:2:3:4]. Formed by heating (4,2,1)-di-methyl-benzoic acid with gallic acid and H_2SO_4 (Birukoff, *B.* 20, 871; *A.* 240, 287). Yellowish-red needles. Forms a red solution in conc. H_2SO_4. Yields di-methyl-anthracene [224°], when distilled with zinc-dust.

Tri-oxy-tri-methyl-anthraquinone [4':3':2':1':6'] $C_6HMe_3:C_2O_2:C_6H(OH)_3$ [1:6:2:3:4]. *Tri-methyl-anthragallol.* [244°]. Formed from tri-methyl-benzoic (durylic) acid, gallic acid, and H_2SO_4 (Wende, *B.* 20, 867). Brown needles. Yields tri-methyl-anthracene [236°].

Acetyl derivative [174°]. Plates.

Tetra-oxy-di-methyl-anthraquinone [2':4':5':1':6'] $C_6HMe(OH)_2:C_2O_2:C_6HMe(OH)_2$ [1:6:2:3:4]. *Di-methyl-anthrachrysone.* [above 360°]. Formed by heating di-oxy-*o*-toluic acid with H_2SO_4 (10 pts.) at 100° (Cahn, *B.* 19, 755). Reddish-yellow plates (by sublimation). Does not dye mordants.

Tetra-acetyl derivative [234°].

OXY-METHYL-BENZOIC ACID *v.* Oxy-toluic acid.

Oxy-di-methyl-benzoic acid $C_6H_2Me_2(OH).CO_2H$ [6:3:2:1]. *Oxy-isoxylylic acid.* [142°]. Formed by fusing ethyl-*p*-xylene sulphonic acid with potash (Stahl, *B.* 23, 991). Needles. Gives a bluish-violet colour with $FeCl_3$.

Oxy-di-methyl-benzoic acid. $C_6H_2Me_2(OH).CO_2H$ [5:4:2:1]. *Oxy-p-xylylic acid.* [199°]. Formed from ψ-cumenol by potash-fusion (Reuter, *B.* 11, 30; Jacobsen, *B.* 12, 436). Needles, volatile with steam. Gives a bluish-violet colour with $FeCl_3$. HClAq at 220° gives xylenol [61°].—BaA'_2. S. 1·1 at 0°.

Oxy-di-methyl-benzoic acid $C_6H_2Me_2(OH)CO_2H$. [4:2:5:1]? [170·5°]. Formed by fusing $C_6H_2Me_2BrCO_2H$ (Gunter, *B.* 17, 1608). Scarcely volatile with steam. Gives no colour with $FeCl_3$.

Oxy-di-methyl-benzoic acid [137°]. Formed from *p*-xylenol, Na, and CO_2 at 180° (Oliveri, *G.* 12, 166). Needles, coloured violet by $FeCl_3$.—BaA'_2 4aq.

Oxy-di-methyl-benzoic acid $C_6H_2Me_2(OH)CO_2H$ [6:3:4:1]. [153°]. Got from $C_6H_2Me_2Br.CO_2H$ and KOH. Not coloured blue by $FeCl_3$.

Oxy-di-methyl-benzoic acid. *Xyletic acid.* [155°]. Formed from crude xylenol, Na, and CO_2 (Wroblewsky, *Z.* 1868, 233).—CaA'_2 2aq.—BaA'_2aq: needles.

Di-oxy-di-methyl-benzoic acid $C_6HMe_2(OH)_2CO_2H$ [5:3:6:2:1]. [196°]. Formed from betorcin, $NaHCO_3$, and water at 130° (Kostanecki, *B.* 19, 2323). Prisms. Coloured blue by $FeCl_3$.

Oxy-tri-methyl-benzoic acid $C_6HMe_3(OH)CO_2H$ [6:4:3:2:1]. *Oxydurylic acid.* [148°]. Formed by fusing durenol with potash (Jacobsen a. Schnapauff, *B.* 18, 2844). Needles. —CaA'_2 aq: prisms, m. sol. water.

Di-oxy-tetra-methyl-benzoic acid. *Tetra-hydride of the methylene derivative* $CH_2O_2C_6H_3Me_4CO_2H$. *Piperhydronic acid.* [96°]. Formed from (β)-hydropiperic acid and sodium-amalgam (Buri, *A.* 216, 178).—CaA'_2 aq: crystals (from water).

OXY-TRI-METHYL-BENZOIC ALDEHYDE $C_6HMe_3(OH)CHO$ [1:3:4:6:5]. [106°]. Formed by the action of chloroform on an alkaline solution of ψ-cumenol (Auwers, *B.* 17, 2976). Needles. $FeCl_3$ gives a blue colour.

OXY-METHYL-BUTYL-PYRROLE CARBOXYLIC ETHER $C_4H_9.N\left\langle\begin{matrix}CMe:C(CO_2Et)\\CO\ .CH_2\end{matrix}\right.$ [68°].

(175° at 15 mm.). Formed from aceto-succinic ether (10 g.) and isobutylamine (3·4 g.) in the cold (Emery, *A.* 260, 149). Needles (from CS_2).

OXY-METHYL-CINNAMIC ACID. *Anhydride* $\left[6:4:\frac{1}{2}\right]C_6H_2Me(OH)<\begin{smallmatrix}CH:CH\\O-CO\end{smallmatrix}$. [248°]. *Homoumbelliferon.* Formed by heating orcin with malic acid and H_2SO_4 (Pechmann a. Welsh, *B.* 17, 1649). Tables, sol. alcohol and aqueous alkalis. Conc. H_2SO_4 forms a solution with blue fluorescence. Potash-fusion gives orcyl aldehyde and KOAc.

Acetyl derivative [127°]. Formed by heating orcyl aldehyde with Ac_2O and NaOAc (Tiemann a. Helkenberg, *B.* 12, 1002). Needles.

OXY-METHYL-COUMARILIC ACID $C_{10}H_8O_4$ *i.e.* $\left[4\frac{1}{2}\right]C_6H_3(OH)<\begin{smallmatrix}CMe\\O\end{smallmatrix}>C.CO_2H$. [226°]. Formed by saponification of its ethyl-ether, which is obtained by boiling chloro-acetacetic ether (1 mol.) with a conc. alcoholic solution of mono-sodium resorcin $C_6H_4(OH)(ONa)$. Needles (containing $\frac{1}{2}$aq). V. sol. hot water. On distillation it loses carbonic acid, giving oxy-methyl-coumarone $C_6H_3(OH)<\begin{smallmatrix}CMe\\O\end{smallmatrix}>CH$ [97°].

Ethyl ether A'Et. [178°]; white needles; v. sol. ether; its dilute solutions have a blue fluorescence (Hantzsch, *B.* 19, 2928).

Di-oxy-methyl-coumarilic acid $C_{10}H_8O_5$ *i.e.* $\left[6:4:\frac{1}{2}\right]C_6H_2(OH)_2<\begin{smallmatrix}CMe\\O\end{smallmatrix}>C.CO_2H$. [281°]. Formed by saponification of its ethyl ether, which is obtained by boiling chloro-acetacetic ether (1 mol.) with a conc. alcoholic solution of mono-sodium-phloroglucin $C_6H_3(OH)_2(ONa)$ (1 mol.). Crystals (containing $\frac{1}{2}$aq). The acid and its ether give an indigo-blue colour with warm conc. H_2SO_4.

Ethyl ether A'Et: [242°]; small white needles; the alkaline solution is fluorescent (Lang, *B.* 19, 2934).

OXY-METHYL-COUMARONE *v.* COUMARONE.

OXYMETHYLENE *v.* FORMIC ALDEHYDE.

OXY-TRIMETHYLENE-DIAMINE $CH(OH)(CH_2NH_2)_2$. Formed by heating with HClAq the compound got by the action of epichlorhydrin or (α)-dichlorhydrin on potassium phthalimide (Goedeckemeyer, *B.* 21, 2689; Gabriel, *B.* 22, 225).—$B''H_2Cl_2$. [184°]. Hygroscopic mass.—$B''H_2PtCl_6$. [240°].—$B''H_2Br_2$. [200°]. Needles.—$B''2C_6H_2(NO_2)_3OH$: yellow needles. [230°].

OXY-TRIMETHYLENE-DIPHTHALAMIC ACID $CH(OH)(CH_2NH.COC_6H_4CO_2H)_2$. [c. 120°]. Formed by boiling oxytrimethylene-diphthalimide with potash (Goedeckemeyer, *B.* 21, 2690). Hygroscopic needles. Yields oxy-trimethylene-diamine on evaporating with HClAq.

OXYMETHYLENE-PHTHALIDE? $C_9H_6O_3$. [146°]. A crystalline body formed in the action of Br and HOAc on acetophenone carboxylic acid (Gabriel a. Michael, *B.* 11, 1010).

Phenyl derivative $C_6H_4<\begin{smallmatrix}C:CH.OPh\\CO.O\end{smallmatrix}$. [144°]. Made by heating phthalic anhydride with phenoxy-acetic acid and NaOAc (Gabriel, *B.* 14, 922). Needles. The homologous *p-tolyl derivative* [174°] is also crystalline.

OXYTRIMETHYLENE - DIPHTHALIMIDE $CH(OH)(CH_2NC_8H_4O_2)_2$. [205°]. Formed from potassium phthalimide and (α)-dichlorhydrin at 150° (Goedeckemeyer, *B.* 21, 2689; Gabriel, *B.* 22, 224). Needles (from HOAc). Fuming HBr at 200° converts it into $CHBr(CH_2NH_2)_2$.

OXY-METHYL-ETHYL-BENZOIC ACID $C_6H_2MeEt(OH).CO_2H$. [149°]. Made by fusing *s*-di-methyl-ethyl-benzene sulphonic acid with potash (Jacobsen, *A.* 195, 284). Long needles from dilute alcohol). Turned blue by $FeCl_3$.

OXY-METHYL-ETHYL KETONE. *Ethyl derivative* $CH_2(OEt).CO.Et$. (100°–105°). (Formed from $CH_2(OEt).CO.CHMe.CO_2Et$ and alcoholic KOH at 120° (Isbert, *A.* 234, 196).

OXY - METHYL - ETHYL - PYRIMIDINE $C_7H_{10}N_2O$ *i.e.* $CEt<\begin{smallmatrix}N.CMe\\N:C(OH)\end{smallmatrix}>CH$. [160°]. Formed by the action of a 10 p.c. solution of NaOH (1 mol.) upon a mixture of propionamidine hydrochloride (1 mol.) and acetacetic ether (1 mol.) (Pinner, *B.* 18, 2847; *B.* 22, 1619). Fine white needles. V. sol. water and alcohol. Reduced by zinc-dust to methyl-ethyl-pyrimidine.

Salts.—B'HCl: [240°–246°]; very soluble thick prisms.—$B'_2H_2Cl_2PtCl_4$: [236°]; thick yellow prisms.

Oxy-methyl-di-ethyl-pyrimidine $CEt<\begin{smallmatrix}N.CMe\\N:C(OH)\end{smallmatrix}>CEt$. [135°]. Formed from propionamidine hydrochloride, ethyl-acetoacetic ether, and dilute (10 p.c.) NaOHAq (Pinner, *B.* 22, 1621). Needles, v. sol. water.

Oxy-methyl-di-ethyl-pyrimidine $C_9H_{14}N_2O$ *i.e.* $CEt<\begin{smallmatrix}N.CEt\\N:C(OH)\end{smallmatrix}>CMe$. [155°]. Formed from propionamidine hydrochloride, propionyl-propionic ether, and KOH (Meyer, *J. pr.* [2] 39, 264). When warmed with a solution of nitrous acid in HOAc it yields $C_9H_{12}N_4O_5$ and a little $C_9H_{13}N_3O_2$ [205°].

Oxy-di-methyl-ethyl-pyrimidine $CMe<\begin{smallmatrix}N.CMe\\N:C(OH)\end{smallmatrix}>CEt$. [146°]. Formed from acetamidine and ethyl-acetoacetic ether (Pinner, *B.* 22, 1618). Needles, v. sol. water.

Oxy-di-methyl-ethyl-pyrimidine $CEt<\begin{smallmatrix}N.CMe\\N:C(OH)\end{smallmatrix}>CMe$. [165°]. Formed from propionamidine and methyl-acetoacetic ether (P.). Needles, v. e. sol. water and alcohol.

Oxy-di-methyl-ethyl-pyrimidine $CMe<\begin{smallmatrix}N.CEt\\N:C(OH)\end{smallmatrix}>CMe$. [168°]. Formed from acetamidine and propionyl-propionic ether (E. von Meyer, *J. pr.* [2] 40, 304).

Di-oxy-methyl-ethyl-pyrimidine $C_4H_2MeEt(OH)_2N_2$ *i.e.* $CO<\begin{smallmatrix}NH.CMe\\NEt.CO\end{smallmatrix}>CH$. *Methyl-ethyl-uracil.* [195°]. Formed, together with di-oxy-methyl-di-ethyl-pyrimidine [53°], by heating potassium methyl-uracil with EtBr at 155° (Hoffmann, *A.* 253, 68). Prisms (from EtBr) or needles (from alcohol).

OXY-METHYL-ETHYL-PYRROLE CARBOXYLIC ETHER $\begin{smallmatrix}NEt.CMe\\CO\ .CH_2\end{smallmatrix}>C.CO_2Et$. [76°]. (165° at 14 mm.). Formed from acetyl-succinic ether and cold aqueous ethylamine (Emery, *A.* 260, 148). Needles.

Oxy-methyl-ethyl-pyrrole dihydride carboxylic acid $\begin{matrix}CO\ .NEt\\ CH_2.CH_2\end{matrix}\!\!>CMe.CO_2H$. [123°]. Obtained, as nitrile, by heating acetyl-propionic (levulic) ether with HCy and alcoholic ethylamine (Kühling, *B.* 23, 709). Needles, v. sol. water and alcohol.

Nitrile $C_8H_{12}N_2O$. Syrup.

Amide $C_8H_{14}N_2O_2$. [183°]. Needles.

Thioamide [176°]. Formed from the nitrile and alcoholic H_2S.

Amidoxim [c. 160°]. Formed from the thioamide by boiling with hydroxylamine hydrochloride.

OXY-(*B.* 2-*Py.* 2)-DI-METHYL-(*Py.* 3)-ETHYL-QUINOLINE $C_{13}H_{14}(OH)N$. [45°]. (312°–316° at 720 mm.). Colourless crystals. Formed by fusing di-methyl-ethyl-quinoline sulphonic acid with KOH.—A'K^x: easily soluble colourless plates (Harz, *B.* 18, 3390).

Di-oxy-methyl-ethyl-quinoline
$C_6H_3Me\!<\!\begin{matrix}C(OH):CEt\\ N{=\!=}C.OH\end{matrix}$. [c. 220°]. Formed from chloro-ethyl-oxy-*o*-toluquinoline and dilute HCl at 165° (Rügheimer a. Schramm, *B.* 20, 1235; 21, 302). Needles (from HOAc); insol. water.

Reference. — CHLORO-OXY-METHYL-ETHYL-QUINOLINE.

α-OXY-α-METHYL-GLUTARIC ACID
$C_6H_{10}O_5$ *i.e.* $CO_2H.CMe(OH).CH_2.CH_2.CO_2H$. Formed from the lactone of oxy-isohexoic acid by oxidation with dilute nitric acid (Fittig a. Bredt, *A.* 208, 63; 236, 225). Made also by saponification of the nitrile formed by combination of β-acetyl-propionic (levulic) acid with HCy (Kreckeler a. Tollens, *B.* 18, 2018; *A.* 238, 287). The free acid at once changes to the lactonic acid. BaA″ 4aq. — SrA″ 4aq. — CaA″ 7aq. — ZnA″.— Ag_2A'': white flocculent pp.

Lactonic acid $CMe(CO_2H)\!<\!\begin{matrix}CH_2.CH_2\\ O\ —\ CO\end{matrix}$.
[70°]. Deliquescent prisms, v. sol. ether. Converted by hot H_2SO_4 into CO_2 and levulic acid. $CaA'_2\,4\frac{1}{2}aq$.—MeA'. (252°).—EtA'. (262°).

Amide of the lactonic acid. [c. 124°].

Nitrile of the lactonic acid. [c. 33°].

β-Oxy-β-methyl-glutaric acid
$CMe(OH)(CH_2.CO_2H)_2$. Formed by oxidising methyl-di-ethyl-carbinol with $KMnO_4$ (Sorokin, *J. pr.* [2] 23, 278).—CaA″: amorphous.—ZnA″ (dried at 110°).—$Cu_2A''(OH)_2$ 5aq: small tablets. Ag_2A''.

Oxy-tri-methyl-glutaric acid. *Lactonic acid* $CMe_2\!<\!\begin{matrix}CH_2.CMe.CO_2H\\ CO\ .O\end{matrix}$? [104°]. Formed from α-bromo-tri-methyl-glutaric anhydride and KOHAq at 0° (Auwers a. V. Meyer, *B.* 23, 307). Crystals, v. sol. water.—AgA': crystalline powder.

Di-oxy-di-methyl-glutaric acid?
$CH_2(CMe(OH).CO_2H)_2$? [96°]. Formed by dissolving di-α-bromo-di-α-methyl-glutaric anhydride in cold 10 p.c. caustic soda solution (Auwers a. Jackson, *B.* 23, 1614). Six-sided plates, v. sol. cold water.

OXY-METHYL-INDONAPHTHENE
$C_6H_3Me\!<\!\begin{matrix}CH_2\\ C(OH)\end{matrix}\!\!>CH$. [59°]. Formed by condensing *m*-tolyl-propionic acid by means of hot H_2SO_4 (Von Miller, *B.* 23, 1899). White needles with characteristic odour. Volatile with steam. The isomeride from *p*-tolyl-propionic acid melts at 63°.

Oxy-methyl-indonaphthene
$C_6H_4\!<\!\begin{matrix}CH_2\\ C(OH)\end{matrix}\!\!>CMe$. (246° at 719 mm.). Formed from β-phenyl-isobutyric acid and H_2SO_4 at 150° (Von Miller, *B.* 23, 1888). Heavy oil smelling of peppermint, volatile with steam. Yields phthalic acid on oxidation. Gives a phenyl-hydrazide [116°].

OXY-METHYL-INDOLE. *Ethyl-derivative*
$C_6H_4\!<\!\begin{matrix}NH—\\ C(OEt)\end{matrix}\!\!>CMe$ or $C_6H_4\!<\!\begin{matrix}NH\\ CH\end{matrix}\!\!>C.CH_2OEt$
[142°]. Formed by heating at 90° the phenyl-hydrazide of $CH_3.CO.CH_2OEt$ (Fittig, *B.* 21, 2649). Crystals (from alcohol).

OXY-METHYL-JULOLE DIHYDRIDE
$\begin{matrix}CH_2\!<\!\begin{matrix}CH_2.CH_2\\ C{=\!=}C\end{matrix}\!\!>N.CO\\ CH\!<\!\begin{matrix}\\ CH\ .CH\end{matrix}\!\!>C.CMe\end{matrix}\!\!>CH$. [130° cor.]. Formed by boiling quinoline tetrahydride with acetoacetic ether (Reissert, *B.* 24, 845). White needles, v. sol. alcohol, insol. alkalis, sol. conc. HClAq. — B'HCl $1\frac{1}{2}$aq. — $B'_2H_2PtCl_6$: orange needles.

OXY-METHYL-MALONAMIC ACID
$C_4H_7NO_4$ *i.e.* $CMe(OH)(CONH_2)(CO_2H)$. Formed from pyruvic acid and KCy followed by conc. HClAq (Böttinger, *B.* 14, 88). Syrup.— $ZnA'_2\,x$aq: crystalline, v. e. sol. water.

DI-OXY-DI-METHYL-MALONIC ACID. *Di-methyl derivative* $(CH_3O.CH_2)_2C(CO_2H)_2$. [138°]. Formed from sodium-malonic ether, chloro-di-methyl oxide and NaOEt (Kleber, *A.* 246, 111). Prisms, v. sol. water. Its salts are very hygroscopic.

Di-ethyl ether $C_5H_{10}O_2(CO_2Et)_2$. (c. 240°).

OXY-DI-METHYL-PENTAMETHENYL HYDRIDE $CO\!<\!\begin{matrix}CH\ :CMe\\ CH_2:CHMe\end{matrix}$ or
$CO\!<\!\begin{matrix}CH{=\!=}CMe\\ CHMe.CH_2\end{matrix}$. '*Di-methyl-ketopentene.*' (119°). Made from methyluvic acid by prolonged boiling (Dietzel, *A.* 250, 195). Oil, lighter than water.

Oxy-methyl-heptamethenyl trihydride?
$C_8H_{12}O$ *i.e.* $CH\!\!<\!\begin{matrix}CMe.CH_2.CH_2\\ CO\ \ .CH_2.CH_2\end{matrix}$? (189°). An oil, smelling like camphor, formed by heating its dicarboxylic ether which is formed by distilling $CO_2Et.CHAc.CH_2.CH_2.CHAc.CO_2Et$ (Perkin a. Obrembsky, *B.* 19, 2051). Reacts with phenyl-hydrazine.

DI-OXY-DI-METHYL-HEPTAMETHYLENE
$C_9H_{18}O_2$ *i.e.* $CH_2\!<\!\begin{matrix}CH_2.CH_2.CMe(OH)\\ CH_2.CH_2.CMe(OH)\end{matrix}$? (201° at 180 mm.). Formed by reducing $CH_2(CH_2.CH_2Ac)_2$ with sodium (Kipping a. W. H. Perkin, jun., *C. J.* 59, 220). Thick oil with burning taste, smelling of thyme. Does not form an oxim or a phenyl-hydrazide. Yields deliquescent $C_9H_{17}NaO_2$ aq. Forms an oily product of condensation $C_{18}H_{34}O_3$ (305°–310° at 200 mm.).

Di-acetyl derivative $C_9H_{16}Ac_2O_2$. (201° at 65 mm.). Liquid, insol. cold water.

OXY-METHYL-(α)-NAPHTHOQUINOLINE
$C_{14}H_{11}NO$ *i.e.* $C_{10}H_6\!<\!\begin{matrix}C(OH):CH\\ N{=\!=}CMe\end{matrix}$. [292°]. (K.); [over 300°] (C. a. L.). Formed by boiling with

HCl α-naphthyl-β-imido-butyric ether, which is formed by condensation of acetoacetic ether with (α)-naphthylamine (Knorr, *B.* 17, 543; Conrad a. Limpach, *B.* 21, 531). Needles (from alcohol).—$B'_2H_2PtCl_6$: v. sl. sol. hot water.

The isomeride derived from (β)-naphthylamine crystallises in flat needles [286°] (K.) or [above 300°] (C. a. L.) decomposed by distillation.

OXY-DI-METHYL-(β)-NAPHTHOQUINOLINE DISULPHONIC ACID $C_{15}H_{11}(OH)(SO_3H)N\,1\frac{1}{2}aq$. Formed by potash-fusion from the disulphonic acid of di-methyl-(β)-naphthoquinoline (Reed, *J. pr.* [2] 35, 309): small needles, insol. water and alcohol.

DI-OXY-METHYL-NAPHTHOQUINONE (?) $C_{11}H_8O_4$. [170°]. Extracted from tubers of *Drosera Whittakeri* (Rennie, *C. J.* 51, 376). Forms a deep-red solution in KOHAq.

Tri-oxy-methyl-naphthoquinone (?) $C_{11}H_8O_5$. [c. 193°]. A substance of this empirical composition may be extracted from tubers of *Drosera Whittakeri* (Rennie, *C. J.* 51, 371). Red plates (from alcohol or glacial HOAc). V. sl. sol. water. Gives a violet solution in KOHAq or NH_3Aq. Reduced by $SnCl_2$ to $C_{11}H_{10}O_5$. [217°].

OXY-METHYL-ISO-OXAZOLE $CMe{<}{\begin{smallmatrix}CH_2.CO\\N-O\end{smallmatrix}}$. [170°]. Formed from acetoacetic ether, hydroxylamine hydrochloride, and NaOH at 50° (Hantzsch, *B.* 24, 497). Satiny needles, sl. sol. cold water, sol. HClAq.—Ac_2O forms on heating a compound [136°] possibly $\begin{smallmatrix}N-O\\CMe.CH\end{smallmatrix}{>}C.C{<}\begin{smallmatrix}-CMe:N\\C(OAc).O\end{smallmatrix}$.—$NH_4A'$. [207°].—$BaA'_2\,2aq$.—$CuA'_2$.—AgA: gelatinous.

Di-oxy-di-methyl-di-iso-oxazyl $\begin{smallmatrix}O.CO\\N:CMe\end{smallmatrix}{>}CH.CH{<}\begin{smallmatrix}CO.O\\CMe:N\end{smallmatrix}$. Formed by warming isocarbopyrotritaric ether with hydroxylamine and HOAc on the water-bath (Knorr, *B.* 22, 161). Hair-like needles which explode at 190°.

OXY-TETRA-METHYL-PHENYL-ACETIC ACID [6:5:3:2:1] $C_6HMe_4.CH(OH).CO_2H$. [146°]. Formed from tetra-methyl-phenyl-glyoxylic acid by reduction with sodium-amalgam (Claus a. Foecking, *B.* 20, 3102). Nodules.—$BaA'_2\,2aq$.—$CaA'_2\,8aq$: needles.

Oxy-tetra-methyl-phenyl-acetic acid [6:5:4:3:1] $C_6HMe_4.CH(OH).CO_2H$. [160°]. Formed in like manner (Claus, *J. pr.* [2] 38, 233). Hexahedra, m. sol. hot water.

Oxy-tetra-methyl-phenyl-acetic acid [6:4:3:2:1] $C_6HMe_4.CH(OH).CO_2H$. [156°]. Prisms, v. sol. alcohol and ether.—$NaA'\,1\frac{1}{2}aq$.—$CaA'_2\,8aq$.—$BaA'_2\,3aq$: small crystals.

OXY-TRI-METHYL-PHENYL-METHYL-PYRAZOLE $C_{13}H_{16}N_2O$ *i.e.* $C_6H_2Me_3.N{<}\begin{smallmatrix}CO.CH_2\\N{=}CMe\end{smallmatrix}$. [155°]. Formed by heating the ψ-cumyl-hydrazide of acetoacetic ether at 140° for two hours (Haller, *B.* 18, 706). Glistening crystals, v. sol. alcohol. Yields a nitrosamine $C_{12}H_{15}N_3O_2$ [156°] and a methyl derivative $C_{14}H_{18}N_2O$ [106°].

OXY-TETRA-METHYL-PHENYL-DI-METHYL-PYRIDINE CARBOXYLIC ACID $C_6HMe_4N{<}\begin{smallmatrix}CMe:C(CO_2H)\\CMe:CH.CO\end{smallmatrix}{>}$. [145°]. Made by heating tetramethyl phenyl-amido-crotonic ether at 280° (Conrad a. Limpach, *B.* 21, 1655).

OXY-METHYL-ISOPHTHALIC ACID $C_6H_2Me(OH)(CO_2H)_2$ [4:5:3:1]. [c. 270°]. Formed by heating $C_6H_2Me(SO_3H)(CO_2H)_2$ with conc. HClAq at 220° (Jacobsen, *B.* 14, 2115). Needles (from hot water). Not coloured by $FeCl_3$.

OXY-DI-METHYL-PROPIONAMIDINE $CH_3.CH(OH).C(NHMe):NMe$. The crystalline hydrochloride B'HCl [215°], formed by the action of methylamine on the hydrochloride of $CH_3.CH(OH).C(OC_5H_{11}):NH$, is v. sol. water and m. sol. alcohol (Pinner, *B.* 23, 2948).

OXY-METHYL-PROPYL-BENZOIC ACID. *Methyl derivative* $C_6H_2MePr(OMe)CO_2H$ [3:6:1:4]. [139°]. Formed from its amide [149°], which is made by the action of $ClCONH_2$ on $C_6H_3MePr(OMe)$ in CS_2 in presence of $AlCl_3$ (Gattermann, *A.* 244, 68). The ethyl derivative [159°] and its amide $C_6H_2MePr(OEt).CONH_2$ [127°] are got in like manner.

Oxy-methyl-isopropyl-benzoic acid $C_6H_2MePr(OH)CO_2H$ [3:5:2:1]. *Cymenotic acid.* [147°]. Formed from (4,2,1)-cymenol, sodium, and CO_2 (Jesurun, *B.* 19, 1414). Slender needles (from water).—$BaA'_2\,4aq$.—AgA'.—MeA'. [148°].

Isomeric acids *v.* CARVACROTIC ACID and THYMOTIC ACID.

OXY-METHYL-PROPYL-CINNAMIC ACID [1:4:3:6] $C_6H_2(CH_3)(C_3H_7)(OH).C_2H_2.CO_2H$. *Thymo-acrylic acid.* [280°]. Prepared by heating *p*-thymotic aldehyde with acetic anhydride and sodium acetate (Kobek, *B.* 16, 2104). White microscopic crystals.

Methyl derivative $C_6H_2(CH_3)(C_3H_7)(OMe).C_2H_2.CO_2H$. [141°]. Needles, v. sol. alcohol, sl. sol. water.

OXY-METHYL-PROPYL-CINNAMIC ANHYDRIDE *v.* METHYL-PROPYL-COUMARIN.

OXY-METHYL-PROPYL KETONE. *Ethyl ether* $EtO.CH_2.CO.Pr$. (112°–115°). Formed from $EtO.CH_2.CO.CHEt.CO_2Et$ and alcoholic KOH at 120° (Isbert, *A.* 234, 195). Lighter than water; smells like a ketone.

DI-OXY-METHYL-ISOPROPYL-PYRIMIDINE $CMe_2(OH).C{<}\begin{smallmatrix}N:CMe\\N.C(OH)\end{smallmatrix}{>}CH$. [98°]. Formed from oxy-isobutyramidine hydrochloride, acetoacetic ether, and NaOH in equivalent proportions (Pinner, *B.* 22, 2625). Needles (from acetone), v. sol. most solvents.

OXY-METHYL-PROPYL-PYRROLE CARBOXYLIC ETHER $C_3H_7N{<}\begin{smallmatrix}CMe\\CO.CH_2\end{smallmatrix}{>}C.CO_2Et$. [50°]. (172° at 15 mm.). Formed from aceto-succinic ether and propylamine in the cold (Emery, *A.* 260, 148). Needles.

OXY-METHYL-PURIN $C_5H_2Me(OH)N_4$ *i.e.* $CO{<}\begin{smallmatrix}NH-C.CH:N\\NMe.C\text{——}N\end{smallmatrix}{>}CH$. [233°]. Made by heating di-chloro-oxy-methyl-purin with HI (Fischer, *B.* 17, 332). Prisms, v. sol. water. Alkaline in reaction.—B'HI.—$B'_2H_2PtCl_6$.

Oxy-di-methyl-purin $C_5H_2Me(OMe)N_4$? [112°]. Formed from di-chloro-oxy-di-methyl-purin and HIAq (Fischer, *B.* 17, 334). Slender needles, v. sol. water, insol. alkalis.

Di-oxy-di-methyl-purin $C_7H_8N_4O_2$. Formed by reducing the ethyl derivative of chloro-di-oxy-di-methyl-purin with HI. Sparingly soluble crystals.

Di-ethyl derivative $C_{11}H_{16}N_4O_3$ *i.e.* $C(OEt)<\begin{matrix}N:C(OEt).C.NMe\\ N\text{———}C.NMe\end{matrix}>CO$? [127°]. Formed from di-chloro-oxy-di-methyl-purin and alcoholic NaOH. Fine plates, sol. HClAq, insol. alkalis.

Tri-oxy-methyl-purin *v.* METHYL-URIC ACID.

OXY-METHYL-PYRAZOLE $C_4H_6N_2O$ *i.e.* $CMe<\begin{matrix}CH_2.CO\\ N—NH\end{matrix}$. [215°]. Formed by warming acetoacetic ether with hydrazine and water (Curtius a. Jay, *J. pr.* [2] 39, 52). Prisms (from water), sl. sol. hot alcohol. Has a sweet taste.

OXY-DI-METHYL-PYRIDINE. *Ethyl derivative* $C_9H_{13}NO$ *i.e.* $N<\begin{matrix}CMe\ \ \ \ .CH\\ C(OEt):CH\end{matrix}>CMe$. (246°). Formed from acetoacetic ether and ammonia-zinc chloride (Canzoneri a. Spica, *G.* 16, 449). Oil.

Oxy-di-methyl-pyridine. *Methyl derivative* $N<\begin{matrix}CMe:CH\\ CMe:CH\end{matrix}>C.OMe$. (203°). S.G. $\frac{24}{15}$ 1·011. Formed from chloro-di-methyl-pyridine, NaOMe, and MeOH at 160° (Conrad a. Eckhardt, *B.* 22, 81). Oil.—$B'_2H_2PtCl_6$.—B'MeI. [204°]. Prisms (from water).

Ethyl derivative C_7H_8EtNO. (215°).—B'MeI. [196°]. Crystals (from water).

Oxy-di-methyl-pyridine C_7H_9NO *i.e.* $NH<\begin{matrix}CMe.CH\\ CO—CH\end{matrix}>CMe$. *ψ-Lutidostyril.* [176°]. (304°). Formed by heating oxy-tri-methyl-pyridine (methyl-ψ-lutidostyril) in a current of HCl (Hantzsch, *B.* 17, 2904). Formed also by distilling its carboxylic acids (Collie, *B.* 20, 446; Nieme a. Pechmann, *A.* 261, 205), and by passing dry NH_3 over mesitene-lactone at 160° (Anschütz, *A.* 259, 169). Needles (from alcohol).—B'HCl 2aq: prisms. — $B'_2H_2PtCl_6$. — C_7H_8KNO: silvery spangles, sl. sol. KOHAq.

Oxy-di-methyl-pyridine C_7H_9NO *i.e.* $CO<\begin{matrix}CH:CMe\\ CH:CMe\end{matrix}>NH$. *Lutidone.* [231°] (Collie, *C. J.* 59, 177). (350°). Formed by heating its carboxylic or dicarboxylic acid at 280°; and also by heating dehydracetic acid with NH_3 at 100° (Haitinger, *B.* 18, 452; Conrad a. Guthzeit, *B.* 20, 156). Formed also from di-acetyl-acetone and NH_3Aq (Feist, *B.* 22, 1571). Monoclinic pyramids (containing 3aq). PCl_5 gives chloro-di-methyl-pyridine (178°). $FeCl_3$ gives a brownish-red colour.—$B'_2H_2PtCl_6$ (at 100°). [231° cor.].—$B'_2H_2Cr_2O_7$. [125°].—$B'C_6H_2(OH)(NO_2)_3$. [220°].

Oxy-tri-methyl-pyridine $C_8H_{11}NO$ *i.e.* $CO<\begin{matrix}CH:CMe\\ CH:CMe\end{matrix}>NMe$. *Methyl-lutidone.* [245°]. Formed by heating its dicarboxylic acid (Conrad a. Guthzeit, *B.* 20, 159). Needles (containing 3aq) [111°], v. sol. water.—B'HI. [242°]. Formed by heating lutidone with MeI and MeOH at 140° (Conrad a. Eckhardt, *B.* 22, 80). Crystals.

Oxy-tri-methyl-pyridine $C_8H_{11}NO$ *i.e.* $NMe<\begin{matrix}CMe:CH\\ CO—CH\end{matrix}>CMe$. *Methyl-ψ-lutidostyril.* [92°]. (292°). Formed by heating 'dicarbo-collidylium dehydride' with H_2SO_4 or HCl at 150°–180° (Hantzsch, *B.* 17, 1025, 2903). Formed also by methylation of ψ-lutidostyril. Very hygroscopic crystals, not volatile with steam. V. sol. water, v. sl. sol. ether.—B'HCl $\frac{1}{2}$aq.—B'_2HI.—$B'_2H_2PtCl_6$2aq.—$B'_2H_2PtCl_6$2EtOH.—$B'_2H_2PtCl_6$: long yellowish-red needles.

Di-oxy-tri-methyl-pyridine. *Di-ethyl-derivative* $N<\begin{matrix}CMe:C(OEt)\\ CMe.C(OEt)\end{matrix}>CMe$. (218°) at 726 mm. Formed from di-bromo-collidine and NaOEt (Pfeiffer, *B.* 20, 1350). Oil.—$B'_2H_2PtCl_6$.

OXY-DI-METHYL-PYRIDINE CARBOXYLIC ACID $\begin{matrix}CMe.NH.CMe\\ CH—CO.C.CO_2H\end{matrix}$. *Lutidone carboxylic acid.* [258° cor.]. Got by saponifying its ether. Crystals (containing aq).—BaA'_2.—CuA'_2.—AgA': amorphous. *Ethyl ether.* [164° cor.]. (240°–250°). Formed in small quantity in distilling β-amido-crotonic ether under reduced pressure (Collie, *A.* 226, 310; *C. J.* 59, 174). Needles, sol. water, sl. sol. alcohol. Does not react with Ac_2O or phenylhydrazine. Yields a bromo-derivative $C_{10}H_{12}BrNO_3$ [250°]. PCl_5 forms $C_{10}H_{12}ClNO_2$ (264° cor.) which yields a chloro-di-methyl-pyridine (177°–180°) on heating.

Oxy-di-methyl-pyridine carboxylic acid $CO<\begin{matrix}CH:CMe\\ NH.CMe\end{matrix}>C.CO_2H$. [258°]. Formed from isodehydracetic acid and ammonia (Nieme a. Pechmann, *A.* 261, 206).

Oxy-methyl-pyridine dicarboxylic acid *v.* METHYL-CHELIDAMIC ACID, vol. i. p. 729.

Oxy-di-methyl-pyridine dicarboxylic acid $CO<\begin{matrix}CH:C(CH_2.CO_2H)\\ NH.CMe:C(CO_2H)\end{matrix}>$. *ψ-Lutidostyril dicarboxylic acid.* [201°]. Formed from citracumalic acid and NH_3Aq (N. a. P.). Needles, v. sl. sol. cold water and alcohol.

Oxy-di-methyl-pyridine carboxylic acid $CO<\begin{matrix}CH:CMe\\ NH.CMe\end{matrix}>C.CO_2H$. *Ethyl ether* EtA'. *ψ-Lutidostyril-carboxylic ether.* [137°]. Formed by passing dry NH_3 through mesitene carboxylic acid lactone at 160° (Anschütz, *A.* 259, 173). It is also a product of the condensation of amido-acetoacetic ether and of β-amido-crotonic ether (Collie, *B.* 20, 445). Needles (from hot water). The corresponding acid is an insoluble crystalline powder [300°].

Oxy-di-methyl-pyridine dicarboxylic acid $CO<\begin{matrix}C(CO_2H):CMe\\ C(CO_2H):CMe\end{matrix}>NH$. [267°]. Made by saponifying its ether. Prisms (from water).—KA'.—CaA'' 2aq.—CuA'' $1\frac{1}{2}$aq (dried at 100°).

Ethyl ether Et_2A''. [221°]. S. (alcohol) 1 at 20°. Formed by adding NH_3Aq to an alcoholic solution of $CO<\begin{matrix}C(CO_2Et):CMe\\ C(CO_2Et):CMe\end{matrix}>O$ obtained from cupric acetoacetic ether and $COCl_2$ (Conrad a. Guthzeit, *B.* 19, 24; 20, 154). Forms an acetyl derivative $C_{15}H_{19}NO_6$ [65°].—$B'_2H_2PtCl_6$. [190°]. Orange pp.

Oxy-tri-methyl-pyridine dicarboxylic acid $CO<\begin{matrix}C(CO_2H):CMe\\ C(CO_2H):CMe\end{matrix}>NMe$. [245°]. Formed by saponifying its ether (C. a. G.).—Na_2A'': crystalline, v. sol. water.—Et_2A''. [193°]. Formed by the action of methylamine on dimethyl pyrone dicarboxylic ether, which is obtained from cupric acetoacetic ether and $COCl_2$. Needles (Gerichten, *B.* 19, 25; Conrad a. Eckhardt, *B.* 22, 80).

OXY-METHYL-PYRIDYL-PROPIONIC ACID *v.* ECGONINE.

OXY-DI-METHYL-PYRIMIDINE $CMe{<}\begin{smallmatrix}N.CMe\\N:C(OH)\end{smallmatrix}{>}CH$. [192°]. Formed from acetamidine hydrochloride, acetoacetic ether, and dilute (10 p.c.) NaOHAq (Pinner, *B.* 18, 2845; 22, 1616). Needles, v. e. sol. ordinary solvents.

Ethyl derivative. [55°]. (259°). Prisms.

Oxy-tri-methyl-pyrimidine $CMe{<}\begin{smallmatrix}N.CMe\\N:C(OH)\end{smallmatrix}{>}CMe$. Formed from acetamidine hydrochloride, methylacetoacetic ether, and dilute NaOHAq (Pinner, *B.* 22, 1617). Needles, v. sol. water.

Di-oxy-methyl-pyrimidine $CO{<}\begin{smallmatrix}NH.CMe\\NH.CO\end{smallmatrix}{>}CH$. *Methyl-uracil.* Formed by boiling β-uramido-crotonic acid with acids (Behrend, *A.* 229, 8; 231, 256). Needles (from alcohol). Decomposes at 270°–280°. By heating with potash it is converted into $C_{10}H_{12}I_2N_4O_5$. Potash and MeI at 140° forms a dihydride $C_5H_8N_2O_2$ [219°] and di-oxy-tri-methyl-pyrimidine. A mixture of PCl_5 and $POCl_3$ at 125° forms oily $C_5H_3Cl_3N_2$ (246°), S.G. $\frac{21\cdot8}{22\cdot6}$ 1·6273. Yields deep-violet coffin-like crystals of di-iodide $C_5H_6N_2O_2I_2$ (Hoffmann, *A.* 253, 74).

Di-oxy-tri-methyl-pyrimidine $CO{<}\begin{smallmatrix}NMe.CMe\\NMe.CO\end{smallmatrix}{>}CH$ [109°]. Formed by methylation of the preceding body (Behrend; Hagen, *A.* 244, 2). Plates, v. sol. water and alcohol, sl. sol. ether. Yields methylamine on heating with baryta-water at 200°. Dry Br forms $C_6H_9NO_4Br_2$, aqueous bromine yields $CO{<}\begin{smallmatrix}NMe.CMe(OH)\\NMe.CO\end{smallmatrix}{>}CBr_2$ [163°], whence boiling alcohol gives bromo-oxy-tri-methyl-pyrimidine [126°], converted by conc. aqueous ammonia into oxy-amido-tri-methyl-pyrimidine $CO{<}\begin{smallmatrix}NMe.CMe\\NMe.CO\end{smallmatrix}{>}C.NH_2$ [167°], a body that is changed by potassium cyanate and HCl into crystalline $CO{<}\begin{smallmatrix}NMe.CMe\\NMe.CO\end{smallmatrix}{>}C.NH.CO.NH_2$.

OXY-METHYL-PYRROLE. *Dihydride* $\begin{smallmatrix}CH_2.CO\\CH_2.CHMe\end{smallmatrix}{>}NH$. *γ-Amido-valeric lactam.* [37°]. Formed by heating γ-amido-valeric acid and by the action of sodium-amalgam and HOAc at 280° on the phenyl-hydrazide of levulic acid (Tafel, *B.* 20, 250; 22, 1862). Yields an oily nitrosamine, which produces valerolactone on distillation. –B′HCl. [110°]. Needles, v. sol. water.—$B'_4H_2PtCl_6$.

ν-**Oxy-di-methyl-pyrrole** C_6H_9NO *i.e.* $\begin{smallmatrix}CH:CMe\\CH:CMe\end{smallmatrix}{>}NOH$. Made by heating its carboxylic acid (Knorr, *A.* 236, 302). Reduces silver solution in the cold and Fehling's solution on boiling. Gives a red substance with acids, and exhibits the pine-wood reaction.

Oxy-tri-methyl-pyrrole ? $C_7H_{11}NO$. *Tri-methyl-pyrrolone.* (175°). S.G. $\frac{0}{}$ ·945. Formed from sodio-ethyl cyanide and MeI (Hanriot a. Bouveault, *Bl.* [3] 1, 175).

Di-oxy-tri-methyl-pyrrole *v.* ACETONAMINES, vol. i. p. 27.

OXY-METHYL-PYRROLE CARBOXYLIC ACID $CO{<}\begin{smallmatrix}NH.CMe\\CH_2:C.CO_2H\end{smallmatrix}$. *Ethyl ether* EtA′. [134°]. Formed by heating α-amido-ethylidene-succinic ether at 150° (Emery, *A.* 260, 144). Needles, v. sol. alcohol. Yields an acetyl derivative [142°].

Oxy-di-methyl-pyrrole carboxylic acid. *Ethyl ether* $CO{<}\begin{smallmatrix}NH.CMe\\CHMe.C.CO_2Et\end{smallmatrix}$ [127°]. Formed from methyl-acetosuccinic ether and alcoholic NH_3 at 0° (Emery, *A.* 260, 151). Small white prisms (from HOAc).

Oxy-di-methyl-pyrrole carboxylic acid. *Ethyl ether* $CO{<}\begin{smallmatrix}NMe.CMe\\CH_2.C.CO_2Et\end{smallmatrix}$ [42°]. (160° at 11 mm.). Formed from acetosuccinic ether and alcoholic methylamine (E.). Bunches of needles, v. sol. ether.

Oxy-di-methyl-pyrrole carboxylic acid $C_7H_9NO_3$ *i.e.* $\begin{smallmatrix}N(OH).CMe\\CMe\;:CH\end{smallmatrix}{>}C.CO_2H$. Formed by boiling oxy-di-methyl-pyrrole dicarboxylic ether with NaOHAq (Knorr, *A.* 236, 301). Slender needles, v. sol. alcohol. Gives off CO_2 at 138°.

Oxy-di-methyl-pyrrole dicarboxylic acid $N(OH){<}\begin{smallmatrix}CMe:C.CO_2H\\CMe:C.CO_2H\end{smallmatrix}$.

Mono-ethyl ether EtHA″. Formed by boiling the di-ethyl ether with alcoholic potash (Knorr, *A.* 236, 299). Crystals (from alcohol). Decomposes at 185° into CO_2 and oxy-dimethyl-pyrrole carboxylic ether.

Di-ethyl ether Et_2A''. [99°]. Formed by heating di-acetyl-succinic ether with hydroxylamine hydrochloride, NaOAc, and HOAc (Knorr). Yields the salt $C_{12}H_{16}KNO_5$.

OXY-METHYL-PYRROLE DIHYDRIDE CARBOXYLIC ACID. *Nitrile* $\begin{smallmatrix}CH_2.CH_2\\CO\;.NH\end{smallmatrix}{>}CMe.CN$. [141°]. Formed by heating $CH_3.CO.CH_2.CH_2.CO_2Et$ with HCy and ammonia in a closed tube (Kühling, *B.* 22, 2369; 23, 708). Octahedra (from hot alcohol). Successive treatment with cold H_2SO_4 and water converts it into the corresponding amide [161°]. Hydroxylamine yields the amidoxim [156°].

OXY-METHYL-PYRROLE DIHYDRIDE THIOCARBOXYLIC AMIDE $\begin{smallmatrix}CH_2.CH_2\\CO\;.NH\end{smallmatrix}{>}CMe.CS.NH_2$. [220°]. Formed by passing H_2S through an ammoniacal solution of the nitrile of oxy-methyl-pyrrole dihydride carboxylic acid (Kühling, *B.* 22, 2370). Prisms (from hot water), almost insol. alcohol.

OXY-METHYL-QUINAZOLINE $C_6H_4{<}\begin{smallmatrix}C(OH):N\\N\!=\!=\!=CMe\end{smallmatrix}$. *Anhydro-acetyl-o-amido-benzamide.* [233°]. Formed from acetyl-o-amido-benzamide by the action of heat, alkalis, or boiling water (Weddige, *J. pr.* [2] 36, 143). Silky needles (containing aq), v. sol. hot alcohol. MeI and KOH yield the methyl derivative $C_9H_7N_2(OMe)$ [109°].—B′HCl.—$B'_2H_2PtCl_6$.

Oxy-methyl-quinazoline $\begin{smallmatrix}CH\;:CH.C.C(OH):N\\CMe:CH.C.N\!-\!-\!-\!CH\end{smallmatrix}$ [238°]. Formed from *o*-amido-*p*-toluic amide and formic acid (Niementowski, *J. pr.* [2] 40, 12). Crystals, insol. water.

Oxy-di-methyl-quinazoline $C_{10}H_{10}N_2O$ *i.e.* $C_6H_3Me<\begin{smallmatrix}CO.NH\\N:CMe\end{smallmatrix}$. [255°]. Formed by boiling o-amido-*p*-toluic amide with Ac_2O (Niementowski, *B.* 21, 1534; *J. pr.* [2] 40, 13). Needles (from boiling water), sol. acids and alkalis.

Oxy-di-methyl-quinazoline $C_6H_4<\begin{smallmatrix}CO-N\\NMe.CMe\end{smallmatrix}$. [199°]. Formed by heating acetyl-*o*-amido-benzamide above its melting-point (Weddige, *J. pr.* [2] 36, 154). Crystals (containing 3aq), v. e. sol. alcohol.—B'HCl.

Di-oxy-methyl-quinazoline $\begin{smallmatrix}CH:CH\ .C.CO\ .NH\\CH:CMe.C.NH.CO\end{smallmatrix}$ (?) Formed by heating amido-*m*-toluic acid with urea at 180° (Niementowski, *J. pr.* [2] 40, 21). White needles (from amyl alcohol), insol. benzene. Not melted at 300°. HI and P yield *o*-toluidine.

Di-oxy-methyl-quinazoline $C_6H_4<\begin{smallmatrix}CO\ .NMe\\NH.CO\end{smallmatrix}$. [234°]. Formed by heating $C_6H_4(NH_2).CO.NHMe$ with urea at 200° (Abt, *J. pr.* [2] 39, 147). Long white needles, sl. sol. hot water.

Di-oxy-methyl-quinazoline $C_6H_4<\begin{smallmatrix}CO\ .NH\\NMe.CO\end{smallmatrix}$. [148°]. Formed by heating $C_6H_4(NHMe).CO.NHCO_2H$ with urea (Abt).

Di-oxy-di-methyl-quinazoline $C_6H_4<\begin{smallmatrix}CO\ .NMe\\NMe.CO\end{smallmatrix}$. [151°]. Formed by the action of MeI and NaOH on either of the two preceding bodies or on di-oxy-quinazoline (Abt, *J. pr.* [2] 39, 145). White needles (from water), v. sol. alcohol.

Oxy-methyl-quinazoline dihydride $C_6H_4<\begin{smallmatrix}CH_2.NMe\\NH.CO\end{smallmatrix}$. [120°]. Formed by boiling ω-oxy-tolyl-methyl-thio-urea with yellow HgO Söderbaum a. Widman, *B.* 22, 2936). Needles, v. e. sol. methyl alcohol.—$B'_2H_2PtCl_6$. [203°]. $B'HAuCl_4$. [185°]. Yellow prisms.

OXY-METHYL-QUINIZINE *v.* OXY-PHENYL-METHYL-PYRAZOLE.

(*B.* 1, 4)-**OXY-METHYL-QUINOLINE** $\begin{smallmatrix}CH:C(OH)\\CH:CMe\end{smallmatrix}>C_5H_3N$. [263°]. Formed from the amido- compound and HNO_2 (Noelting a. Trautmann, *Bl.* [3] 4, 244), and by fusing (*B.* 4)-methyl-quinoline (*B.* 1)-sulphonic acid with NaOH (Herzfeld, *B.* 17, 905, 1551). Needles (from dilute alcohol). Yields a nitroso- derivative $C_9H_4Me(NOH)(OH)N$ [200°]. By KOH, MeI, and MeOH it is converted into the methyl derivative $C_{10}H_8(OMe)N$ (c. 230°), whence $B'_2H_2PtCl_6$.

(*B.* 4, 1)-**Oxy-methyl-quinoline** $\begin{smallmatrix}CH:CMe\\CH:C(OH)\end{smallmatrix}>C_5H_3N$. [124°]. Formed by heating amido-*p*-cresol (10 g.) with glycerin (24 g.), H_2SO_4 (20 g.), and picric acid (2 g.) (N. a. T.). Needles, v. sl. sol. cold water. Dyes fabrics mordanted with alumina, yellow.

(*B.* 4, 2)-**Oxy-methyl-quinoline** $\begin{smallmatrix}CMe:CH\\CH\ :C(OH)\end{smallmatrix}>C_5H_3N$. [96°]. Formed from the amido- compound by the diazo- reaction (N. a. T.). Formed also by fusing the sulphonic acid with NaOH (O. Fischer a. Willmack, *B.* 17, 441; Herzfeld, *B.* 17, 1552). Needles (from chloroform). Smells like vanilla. Its alcoholic solution is coloured green by $FeCl_3$. Yields a nitroso-derivative [200°]. — $B'_2H_2PtCl_6$ 2aq: orange needles.

Methyl derivative $C_{11}H_{11}NO$. Oil. — $B'_2H_2PtCl_6$ 4aq: brown crystalline pp.

Tetrahydride $C_6H_2Me(OH)<\begin{smallmatrix}CH_2.CH_2\\NH\ .CH_2\end{smallmatrix}$. Formed by reduction with tin and HCl. Needles or plates, sl. sol. water. Yields a nitrosamine $C_{10}H_{12}(NO)NO$ crystallising in small yellow needles.

(*B.* 4, 3)-**Oxy-methyl-quinoline** $\begin{smallmatrix}CH\ :CH\\CMe:C(OH)\end{smallmatrix}>C_5H_3N$. [74°]. Formed from amido-o-cresol hydrochloride (10 g.), glycerin (24 g.), H_2SO_4 (20 g.), and picric acid (2 g.) (Noelting a. Trautmann, *B.* 23, 3663). Needles (from dilute alcohol), volatile with steam. $FeCl_3$ gives a dark-green colour. Mixed with CuO it colours a flame green. Yields a crystalline *p*-nitroso- derivative decomposing at 200° without melting.

(*B.* 2, 4)-**Oxy-methyl-quinoline** $\begin{smallmatrix}C(OH):CH\\CH\ \ :CMe\end{smallmatrix}>C_5H_3N$. [200°]. Formed by soda-fusion from *o*-toluquinoline sulphonic acid (Herzfeld, *B.* 17, 903). Needles. Not volatile with steam. $FeCl_3$ colours its alcoholic solution brownish-red.

(*B.* 1, 2)-**Oxy-methyl-quinoline** $\begin{smallmatrix}CMe:C(OH)\\CH\ :CH\end{smallmatrix}>C_5H_3N$. *Ana-oxy-paratoluquinoline.* [230°]. Formed from the amido- compound, and also from para-toluquinoline by sulphonation (with 25 p.c. SO_3 extra) at 90° and potash-fusion (Noelting a. Trautmann, *B.* 23, 3658). Needles, v. sl. sol. hot water. Not volatile with steam.

(*Py.* 3, 1)-**Oxy-methyl-quinoline** $C_6H_4<\begin{smallmatrix}CMe:CH\\N=C(OH)\end{smallmatrix}$. [224° cor.]. (above 360°). Formed by heating the anilide of acetoacetic acid with H_2SO_4 (Knorr, *A.* 236, 83; *C. J.* 46, 334; Roos, *B.* 21, 624; Reissert, *B.* 24, 855). Small needles (from water). Reduced by sodium-amalgam to $C_{20}H_{20}N_2O_2$ [280°]. Sodium added to its alcoholic solution reduces it to a dihydride $C_{10}H_{11}NO$ [101°] and methyl-quinoline tetrahydride $C_{11}H_{13}N$ (253°). NaOEt and MeI form oxy-di-methyl-quinoline [132°] and the methyl derivative $C_{10}H_8(OMe)N$ [276° cor.], whence $B'_2H_2PtCl_6$. The ethyl derivative $C_{10}H_8(OEt)N$ [51°] (250°) is formed from chloro-lepidine and KOEt.

S a l t s.—B'HCl. [187°].—$B'_2H_2PtCl_6$ aq.—$B'H_2SO_4$: needles.—$B'HNO_3$: prisms.—B'HI.—P i c r a t e: [166°]. Needles.—$Ba(C_{10}H_8NO)_2$ aq.

(*Py.* 3, 4)-**Oxy-methyl-quinoline** $C_6H_4<\begin{smallmatrix}CH\ :CH\\NMe:CO\end{smallmatrix}$. *Methyl-ψ-carbostyril.* [72°]. Formed by digesting carbostyril with MeOH and MeI, adding NaOH as required to neutralise the HI formed (Friedländer a. Müller, *B.* 20, 2010). Slender needles. Weak base. Sodium-amalgam forms $C_{10}H_{10}NO$ [276°]. — $B'_2H_2PtCl_6$ 2aq. — $B'HgCl_2$. [189°]. Small pyramids.

Methylo-iodide B'MeI. Bronzed needles.

(*Py.* 1, 3)-**Oxy-methyl-quinoline** $C_6H_4<\begin{smallmatrix}C(OH):CH\\N=\!=CMe\end{smallmatrix}$. [[231°] (above 360°). S. 1 in the cold; 10 at 100°. Formed by heating

phenylamido-crotonic ether rapidly to 240° (Conrad a. Limpach, *B.* 20, 947). Prisms (containing 2aq), v. sol. alcohol. Tastes bitter. $FeCl_3$ colours its solution yellowish-red. $KMnO_4$ oxidises it to acetyl-anthranilic acid. Yields quinaldine on distillation with zinc-dust.—B′HCl.—$B'_2H_2PtCl_6$. [215°].—$B'H_2CrO_4$. [108°].—$B'C_6H_2(NO_2)_3OH$. [200°]. Yellow needles.

Methyl derivative $C_{10}H_8(OMe)NO$. [82°]. (296°). Formed from chloro-methyl-quinoline, MeOH, and NaOMe at 135°. Needles, sl. sol. water.

Methylo-chloride $C_{10}H_9NOMeCl$ aq. [217°]. Formed from the methylo-iodide and AgCl (Conrad a. Eckhardt, *B.* 22, 74).—$B'_2H_2PtCl_6$. [240°]. Yellow crystalline pp.

Methylo-iodide $C_{10}H_9NOMeI$ aq. [201°]. Formed from the base and MeI at 100°. Satiny needles (from hot water).

Sulphonic acid $C_{10}H_8NO(SO_3H)$. [283°]. Long prisms (containing 2aq).—BaA'_2 4aq.

(*B.* 2)-Oxy-(*Py.* 1)-methyl-quinoline
C(OH):CH.C.CMe:CH
CH══CH.C.N══CH. [218°]. Formed by fusing lepidine sulphonic acid with NaOH (Busch a. Koenigs, *B.* 23, 2684). Obtained also by boiling with HBrAq the methyl derivative which is produced by heating quinine sulphate (40 g.) with KOH (95 g.) and water (45 c.c.) at 220° in a current of superheated steam (Koenigs, *B.* 23, 2674). Groups of slender needles, v. sol. warm alcohol and acetone. Gives no colour with $FeCl_3$.

Methyl derivative $C_{11}H_{11}NO$. [52°]. Formed as above, and also by heating quinene zinc chloride with water at 200°. Slender needles (containing aq). Its solution fluoresces like quinine. Gives a bluish-green colour with ammonia and chlorine-water. — $B'_2H_2PtCl_6$. [237°]. Orange powder.

Oxy-(*Py.* 1)-methyl-quinoline [141°]. Formed from a sulphonic acid of lepidine prepared by mixing lepidine with H_2SO_4 and heating to 300° (Busch a. Koenigs, *B.* 23, 2686). Greenish needles, v. sol. benzene.—$B'_2H_2PtCl_6$ 2aq: orange-yellow needles.

(*B.* 2)-Oxy-(*Py.* 3)-methyl-quinoline
C(OH):CH.C.CH:CH
CH══CH.C. N :CMe. *p-Oxy-quinaldine.* [213°]. Formed by the action of paraldehyde and HCl upon *p*-amido-phenol, and also by fusing (*Py.* 3)-methyl-quinoline sulphonic acid with potash (Doebner a. Miller, *B.* 17, 1708). Crystals, not volatile with steam, v. sl. sol. cold water.—$B'_2H_2PtCl_6$ 2aq: yellow needles.

(*B.* 2 ?)-Oxy-(*Py.* 3)-methyl-quinoline $C_9H_5Me(OH)N$. [234°]. Formed by fusing quinaldine (*β*)-sulphonic acid with potash (D. a. M.). Silvery plates, sol. ether and hot alcohol, nearly insol. hot water.—B′HCl 2aq.—$B'_2H_2PtCl_6$ 2aq: small yellow needles.

(*B.* 4)-Oxy-(*Py.* 3)-methyl-quinoline
CH:CH——C.CH:CH
CH:C(OH).C. N :CMe. *o-Oxy-quinaldine.* [74°]. (266°). Formed by fusing (*Py.* 3)-methyl-quinoline (*B.* 4)-sulphonic acid with potash, and also by the action of paraldehyde and HCl on o-amido-phenol (Doebner a. Miller, *B.* 17, 1705). Trimetric prisms, easily volatile with steam.—$B'_2H_2PtCl_6$ 2aq: yellow needles.

Methyl derivative $C_9H_5Me(OMe)N$ [125°]. (282°). Formed from *o*-anisidine, paraldehyde, and HCl.—$B'_2H_2PtCl_6$: yellow needles.

Tetrahydride $C_9H_9Me(OH)N$. (280°). Formed by reducing *o*-oxy-quinaldine with tin and HCl (Doebner a. Miller, *B.* 17, 1706). Yields $C_9H_9Me(OMe)N$ (270°) whence B′HCl and $C_9H_8Me(OMe)NMe$ (261°), whence $B'_2H_2PtCl_6$: yellow needles.

(*B.* 2)-Oxy-(*Py.* 4)-methyl-quinoline tetrahydride. *Methyl derivative* $C_9H_9NMe(OMe)$. *Methyl-thallin.* (278°). Formed by methylation of thallin (Skraup, *M.* 6, 776). Oil.—$B'H_2SO_4$. — B′MeI aq. [224°]. — $B'_2Me_2PtCl_6$. Orange plates.

(*B.* 4)-Oxy-(*Py.* 4)-methyl-quinoline.

Tetrahydride $C_{10}H_{13}NO$ *i.e.*
CH:CH——C.CH$_2$.CH$_2$
CH:C(OH).C.NMe.CH$_2$. [114°]. Formed from (*B.* 4)-oxy-quinoline tetrahydride and MeI (O. Fischer, *B.* 16, 714). Trimetric tables (from ether) $a:b:c$ = ·631:1:1·538. Its alcoholic solution is coloured brown by $FeCl_3$.—B′HCl aq. *Kairine*, a febrifuge.—B′MeI. [216°]. Prisms (from MeOH).—$B'C_7H_7Cl$. (312°). Oil (Fischer a. Kohn, *B.* 19, 1040; *C. J.* 49, 503).

Methyl derivative $C_9H_9(OMe)NMe$. (257°). Formed by means of MeI and MeOH. Pale-yellow oil. Gives a crimson colour with $NaNO_2$ and a little acid.—$B'_2H_2PtCl_6$. [199°].—$B'H_2SO_4$: prisms, v. sol. water.

Methyl derivative of the methylo-iodide $C_9H_9(OMe)NMe_2I$. [175°]. Prisms (from MeOH). Moist Ag_2O converts it into strongly alkaline crystalline $C_9H_9(OMe)NMe_2OH$, whence $\{C_9H_9(OMe)NMe_2Cl\}_2PtCl_4$ [200°].

Ethyl derivative $C_9H_9(OEt)NMe$. (270°) at 716 mm. Oil.

(*Py.* 3)-Oxy-(*B.* 2)-methyl-quinoline
CMe:CH.C.CH:CH
CH :CH.C.NH.CO. *Methyl-carbostyril.* [228°]. Formed by boiling chloro-methyl-carbostyril with NaOHAq (Einhorn a. Lauch, *A.* 243, 359). Crystalline, v. sol. alcohol.

(*B.* 1,2,4)-Oxy-di-methyl-quinoline
CMe:C(OH).C.CH:CH
CH :CMe .C.N :CH. [198°]. Formed by the action of nitrous acid on (*B.* 1,2,4)-amido-di-methyl-quinoline (Noelting a. Trautmann, *B.* 23, 3683). Plates (from chloroform), v. sol. alcohol.

(*Py.* 3,1,4)-Oxy-di-methyl-quinoline $C_{11}H_{11}NO$ *i.e.* $C_6H_4<^{CMe:CH}_{NMe.CO}$. *Methyl-lepidone. Di-methyl-ψ-carbostyril.* [132°]. (290° at 250 mm.). Formed by heating (*Py.* 3,1)-oxy-methyl-quinoline with KOH and MeI, or by heating the isomeric methoxy-lepidine above its boiling-point (290°). Formed also by heating methylaniline with acetoacetic ether, and treating the product with H_2SO_4 (Knorr, *B.* 17, 2876; 19, 3301; *A.* 236, 104). Needles, sl. sol. water and ether, v. sol. alcohol, insol. alkalis. Sodium-amalgam reduces it to $(C_{11}H_{12}NO)_2$ [268°].—$B'_2H_2PtCl_6$ 3aq. [214°]. Slender needles.

(*Py.* 1,3,4)-Oxy-di-methyl-quinoline
$C_6H_4<^{CO.CH}_{NMe.CMe}$ [175°]. Formed from methoxy-methyl-quinoline by heating at 315° in a sealed tube, or by heating oxy-quinaldine methylo-iodide with $NaHCO_3$ (Conrad, *B.* 20, 956; 22, 75). Needles, v. sol. water.—$B'HHgCl_3$.

[187°]. Needles.—$B'_2H_2PtCl_6$. [240°].—B'MeI. [210°]. Sl. sol. cold water.

(*Py.* 3,2,1)-**Oxy-di-methyl-quinoline** $C_6H_4\left\langle\begin{matrix}\text{CMe:CMe}\\ \text{N=COH}\end{matrix}\right.$. [262°]. Formed from methyl-acetoacetic anilide and H_2SO_4 in the cold (Knorr, *A.* 245, 357). Yields a sulphonic acid, which forms a crystalline Ba salt $Ba(C_{11}H_{10}NSO_4)_2$.—B'HCl. Long silky needles.

(*B.* 2)-**Oxy-(*Py.* 1,3)-di-methyl-quinoline** $\begin{matrix}\text{C(OH):CH.C.CMe:CH}\\ \text{CH=CH.C.N=CMe}\end{matrix}$. [214°]. (above 360°). Formed by heating *p*-amido-phenol hydrochloride (1 vol.) with acetone (3 vols.) for some days at 175° (Engler a. Bauer, *B.* 22, 213). Prisms or tables, v. sl. sol. water. $FeCl_3$ colours its alcoholic solution brown.—B'HCl.—$B'_2H_2PtCl_6$ 2aq. — $B'_2H_2SO_4$. — $B'_2H_2Cr_2O_7$. — $B'C_6H_2(NO_2)_3OH$. [225°]. Yellow plates or prisms.

(*B.* 4)-**Oxy-(*Py.* 1,3)-di-methyl-quinoline** $\begin{matrix}\text{CH:CH — C.CMe:CH}\\ \text{CH:C(OH).C.N=CMe}\end{matrix}$. [65°]. (281° uncor.). Formed in like manner from o-amido-phenol. Prepared by saturating a mixture of acetone (3 mols.) and paraldehyde (3 mols.) with dry HCl, adding, after 3 days, o-amido-phenol (2 mols.) dissolved in conc. HClAq, and heating on the water-bath. Crystals, v. sol. alcohol, ether, and benzene. $FeCl_3$ colours its alcoholic solution green.—$B'H_2SO_4$.—B'HCl.—$B'_2H_2PtCl_6$ 2aq. —$B'_2H_2Cr_2O_7$.—$B'C_6H_3N_3O_7$. [207°]. Plates or prisms, sl. sol. hot alcohol.

(*Py.* 3)-**Oxy-(*B.* 2 *Py.* 1)-di-methyl-quinoline** $\begin{matrix}\text{CMe:CH.C.CMe:CH}\\ \text{CH :CH.C.N=C.OH}\end{matrix}$. [250°]. Formed from acetoacetic ether by successive treatment with *p*-toluidine and H_2SO_4 (Knorr, *A.* 245, 365). Flat prisms, sl. sol. hot water, dilute acids, and alkalis. Yields (*B.* 2; *Py.* 1)-di-methyl-quinoline on distillation with zinc-dust.

(*Py.* 3)-**Oxy-(*B.* 3; *Py.* 1)-di-methyl-quinoline** $\begin{matrix}\text{CH :CH.C.CMe:CH}\\ \text{CMe:CH.C.N=C.OH}\end{matrix}$. [220°]. Formed in like manner from *m*-toluidine (K.). V. sl. sol. hot water. Yields (*B.* 3, *Py.* 1)-di-methyl-quinoline on distillation with zinc-dust.—Platinochloride. [234°]. The hydrochloride is crystalline, and is decomposed by water.

(*Py.* 3)-**Oxy-(*B.* 4; *Py.* 1)-dimethyl-quinoline** $\begin{matrix}\text{CH:CH .C.CMe.CH}\\ \text{CH:CMe.C.N—C.OH}\end{matrix}$. Formed in like manner from *o*-toluidine (Knorr, *A.* 245, 368). Slender needles (from water). Yields (*B.* 4, *Py.* 1)-di-methyl-quinoline on distillation.—$B'_2H_2PtCl_6$2aq. [220°].—$NaC_{11}H_{10}NO$. Plates.

(*Py.* 1)-**Oxy-(*B.* 2; *Py.* 3)-di-methyl-quinoline** $\begin{matrix}\text{CMe:CH.C.C(OH):CH}\\ \text{CH=CH.C.N=CMe}\end{matrix}$. [275°]. Formed by heating *p*-tolyl-amido-crotonic ether $C_7H_7NH.CMe:CH.CO_2Et$ at 250° (Conrad a. Limpach, *B.* 21, 525; *cf.* Knorr, *B.* 17, 542). Needles (containing aq).—B'HCl. Needles (from hot water).—$B'_2H_2PtCl_6$. [228°]. Prisms (from hot water).

(*Py.* 1)-**Oxy-(*B.* 4, *Py.* 3)-di-methyl-quinoline** $\begin{matrix}\text{CH:CH—C.C(OH):CH}\\ \text{CH:CMe. C.N— CMe}\end{matrix}$. [261°]. Formed by distilling *o*-tolyl-amido-crotonic ether (C. a. L.). Plates (containing aq).—$B'_2H_2PtCl_6$. Needles.

Oxy-(*Py.* 1, 3)-di-methyl-quinoline $C_{11}H_{10}N(OH)$. [44°]. Made from (*Py.* 1, 3)-di-methyl-quinoline by conversion into the sulphonic acid and fusing this with NaOH (Beyer, *J. pr.* [2] 33, 409).—$(B'HCl)_2PtCl_4$ 2aq.

Oxy-tri-methyl-quinoline $\begin{matrix}\text{CMe:CH .C.C(OH):CH}\\ \text{CH :CMe.C.N=CMe}\end{matrix}$. [264°]. Formed by heating *m*-xylyl-β-amido-crotonic ether (Conrad a. Limpach, *B.* 21, 526). Needles (containing aq).—Platinochloride. [282°]. Needles.

Oxy-tetra-methyl-quinoline $C_{13}H_{15}NO$ *i.e.* $C_6HMe_3\left\langle\begin{matrix}\text{C(OH):CH}\\ \text{N=CMe}\end{matrix}\right.$. Formed by quickly heating ψ-cumyl-amido-crotonic ether at 250° (Conrad a. Limpach, *B.* 21, 529). Prisms (from alcohol). Sublimes at 285°, without previous fusion.—$B'_2H_2PtCl_6$. Prisms (from alcohol).

(*Py.* 1, 3, 4)-**Di-oxy-methyl-quinoline** $C_6H_4\left\langle\begin{matrix}\text{C(OH):CH}\\ \text{NMe . CO}\end{matrix}\right.$. [260°]. Formed by heating its methyl derivative with HClAq at 120°. Small needles, sol. alkalis. Yields a nitrosamine $C_{10}H_8NO_2(NO)$ crystallising in red needles [c. 188°].

Methyl derivative $C_6H_4\left\langle\begin{matrix}\text{C(OMe):CH}\\ \text{NMe . CO}\end{matrix}\right.$. [68°]. Formed by heating (*Py.* 1, 3, 4)-chloro-oxy-methyl-quinoline with NaOMe (Friedländer a. Müller, *B.* 20, 2014). Slender white needles, v. sol. alcohol.—$B'_2H_2PtCl_6$: pyramids.

Ethyl derivative $C_{10}H_8(OEt)NO$. [87·5°]. Slender white needles.

(*B.* 4; *Py.* 1)-**Di-oxy-(*Py.* 3)-methyl-quinoline.** *Methyl derivative* $\begin{matrix}\text{CH:CH — C.C(OH):CH}\\ \text{CH:C(OMe).C.N=CMe}\end{matrix}$. [229°]. Formed by heating *o*-methoxy-phenyl-amido-crotonic ether at 260° (Conrad a. Limpach, *B.* 21, 1654). Long silky needles (containing aq). — $B'_2H_2PtCl_6$ [239°]. Tables.

(*B.* 2; *Py.* 1)-**Di-oxy-(*Py.* 3)-methyl-quinoline.** *Methyl derivative* $\begin{matrix}\text{C(OMe):CH.C.C(OH):CH}\\ \text{CH=CH.C.N=CMe}\end{matrix}$. [290°]. Formed by the action of heat on *p*-methoxy-phenyl-amido-crotonic ether which is made from *p*-anisidine and acetoacetic ether (C. a. L.).—B'HCl.—$B'_2H_2PtCl_6$.—$B'_2H_2SO_4$. S. ·6 in the cold.—B'MeCl. [251°]. Needles.—$B'_2Me_2PtCl_6$4aq.—B'MeI. Converted by moist Ag_2O into $C_{12}H_{13}NO_2$ [149°].

Di-methyl derivative $C_9H_4Me(OMe)_2N$. [94°]. Formed from the methyl derivative, NaOMe, and MeI. Needles or prisms.

(*B.* 2, 3)-**Di-oxy-(*Py.* 3)-methyl-quinoline.** *Methylene derivative* $CH_2\left\langle\begin{matrix}\text{O.C:CH.C.CH:CH}\\ \text{O.C:CH.C. N :CMe}\end{matrix}\right.$. [152°]. Formed on reduction of $CH_2O_2{:}C_6H_2(NO_2).CH{:}CH.CMe{:}N_2HPh$ (Haber, *B.* 24, 623). Silvery needles, m. sol. ether.—$B'_2H_2PtCl_6$.—$B'H_2CrO_4$. Detonates at 210°.—Picrate. [175°]. Yellow crystals.

(*Py.* 1, 2, 3, 4)-**Tri-oxy-methyl-quinoline** $C_6H_4\left\langle\begin{matrix}\text{C(OH).C(OH)}\\ \text{NMe .CO}\end{matrix}\right.$. *Di-oxy-methyl-pseudo-carbostyril.* Formed by warming the nitroso-derivative of (*Py.* 1, 3, 4)-di-oxy-methyl-quinoline with $SnCl_2$. White needles, sl. sol. water, benzene, and $CHCl_3$. By Fe_2Cl_6 it is oxidised to methyl-pseudo-quinisatin

$C_6H_4\left\langle\begin{matrix}CO.CO\\ |\\ NMe.CO\end{matrix}\right.$ [122°] (Friedländer a. Müller, *B.* 20, 2015).

References. — Bromo-, Chloro-, and Di-chloro-di-nitro- oxy-methyl-quinolines.

(*B.* 4)-**OXY-**(*Py.* 4)-**METHYL-QUINOLINE CARBOXYLIC ACID.** *Tetrahydride* $C_9H_8Me(OH)(CO_2H)N$. [211°] (S. a. E.); [216°] (K. a. N.). Formed by heating oxy-quinoline carboxylic acid tetrahydride with MeI and MeOH at 120° (Schmitt a. Engelmann, *B.* 20, 1219; Krolikovsky a. Nencki, *M.* 9, 208). Prisms (containing 2aq), v. sol. hot water and alcohol. Has no toxic action. After administration to dogs the urine contains the acid $C_9H_5Me(OH)_2(CO_2H)N$ [255], insol. water.

(*B.* 4)-**Oxy-**(*Py.* 3)-**methyl-quinoline carboxylic acid** $NC_9H_4Me(OH)(CO_2H)$. [207°]. Formed by heating potassium oxy-quinaldine with liquid CO_2 at 190° (König, *B.* 21, 883). Yellow needles (containing aq), sl. sol. cold water. Gives a cherry-red colour with $FeCl_3$.

(*Py.* 1)-**Oxy-**(*Py.* 3)-**methyl-quinoline** (*Py.* 2)-**carboxylic acid** $C_6H_4\left\langle\begin{matrix}C(OH).C(CO_2H)\\ N{=\!=\!=}CMe\end{matrix}\right.$. [245°]. Formed by oxidising the corresponding aldehyde with alkaline $KMnO_4$ (Conrad a. Limpach, *B.* 21, 1975). Crystals (from alcohol).—MgA'_2 (dried at 100°). Crystalline pp.

(*Py.* 3, 1)-**Oxy-methyl-quinoline** (*B.* 4)-**carboxylic acid.** [312°]. Formed by oxidising (α)-oxy-(γ)-methyl-julole dihydride with $KMnO_4$ in acid solution (Reissert, *B.* 24, 853). Needles, m. sol. alcohol, sl. sol. hot water.

(*Py.* 1)-**OXY-**(*Py.* 3)-**METHYL-QUINOLINE** (*Py.* 2)-**CARBOXYLIC ALDEHYDE** $C_6H_4\left\langle\begin{matrix}C(OH).C.CHO\\ N{=\!=\!=}CMe\end{matrix}\right.$. [273°]. Formed, together with $C_{31}H_{25}N_3O_3$ [192°], by boiling (*Py.* 1, 3)-oxy-methyl-quinoline with chloroform and KOHAq (Conrad a. Limpach, *B.* 21, 1972). Yellow plates (from alcohol), sol. acids and alkalis.—B'HCl.—$B'_2H_2PtCl_6$. [215°–220°].

Phenyl-hydrazide $C_{17}H_{15}N_3O$.—B'HCl: yellow needles, sl. sol. hot water.

(*Py.* 1)-**Oxy-**(*B.* 1, 2, 4; *Py.* 3)-**tetra-methyl-quinoline** (*Py.* 2)-**carboxylic aldehyde** $\begin{matrix}CMe{:}CMe\ .\ C.C(OH){:}C.CHO\\ CH\ {:}CMe{-}C.N{=\!=\!=}CMe\end{matrix}$. Formed by the action of caustic soda and chloroform on the corresponding oxy-tri-methyl-quinoline (C. a. L.). Yields, with phenyl-hydrazine hydrochloride, crystalline $C_{20}H_{22}N_3OHCl$.

OXY-METHYL-QUINOXALINE $\begin{matrix}CH\ {:}CH.C.N{:}CH\\ CMe{:}CH.C.N{:}C.OH\end{matrix}$. *Oxytoluquinoxaline.* Formed by oxidation of its dihydride by the air or by ammoniacal $AgNO_3$ (Hinsberg, *B.* 19, 483; *A.* 248, 75). Feebly basic plates. PCl_5 yields chloro-methyl-quinoxaline [77°]. — NaA' aq: plates, sol. water.

Methyl derivative [71°].

Ethyl derivative [67°]. From the chloro-methyl-quinoxaline and NaOEt. Satiny needles.

Dihydride $C_9H_{10}N_2O$. [95°–124°]. Formed by reducing *o*-nitro-tolyl-amido-acetic acid with tin and HCl (Plöchl, *B.* 19, 10; Leuckart a. Hermann, *B.* 20, 27). Formed also from chloro-acetic ether and tolylene-*o*-diamine (Hinsberg, *B.* 18, 2870). Very oxidisable.

Oxy-di-methyl-quinoxaline $C_6H_3Me\left\langle\begin{matrix}N{:}CMe\\ N{:}C.OH\end{matrix}\right.$. [238°]. Formed by passing air through an alkaline solution of the dihydride, which is obtained by condensing tolylene-*o*-diamine with α-bromo-propionic or pyruvic acid (Hinsberg, *A.* 237, 351; 248, 78). Thin crystals (from alcohol), v. sl. sol. water. Is perhaps a mixture of isomerides.

Dihydride $C_6H_3Me\left\langle\begin{matrix}NH.CHMe\\ NH.CO\end{matrix}\right.$. [c. 135°]. Crystallises from alcohol.

Oxy-tri-methyl-quinoxaline. *Dihydride* $C_6H_3Me\left\langle\begin{matrix}NH.CMe_2\\ NH.CO\end{matrix}\right.$. [227°]. Formed by heating tolylene *o*-diamine with bromo-isobutyric ether (Hinsberg, *A.* 248, 79). Plates, v. sl. sol. water. Yields an acetyl derivative [206°], a nitrosamine [154°], and a di-nitro- compound [above 280°].

Di-oxy-di-methyl-quinoxaline. *Di-ethyl derivative* $\begin{matrix}CH{:}C(OEt).C.N{:}CMe\\ CH{:}C(OEt).C.N{:}CMe\end{matrix}$. [127°]. Formed by the action of di-methyl-diketone (diacetyl) on the hydrochloride of the di-ethyl derivative of (α)-di-amido-hydroquinone (Nietzki a. Rechberg, *B.* 23, 1212). Long yellow needles.

Di-oxy-di-methyl-diquinoxaline, so-called, $\begin{matrix}CMe\ {:}N.C.CH{:}C.N{:}CMe\\ C(OH){:}N.C.CH{:}C.N{:}COH\end{matrix}$. Formed by the action of NaOAc and pyruvic acid in excess on a solution of the hydrochloride of tetra-amido-benzene (Nietzki a. Müller, *B.* 22, 445). Dissolves in alkalis with greenish-yellow fluorescence.

OXY-METHYL-QUINOXALINE CARBOXYLIC ACID $C_{10}H_8N_2O_3$ *i.e.* $C_6H_3(CO_2H)\left\langle\begin{matrix}N{:}CMe\\ N{:}C.OH\end{matrix}\right.$. Formed by adding pyruvic acid in slight excess to an aqueous solution of di-amido-benzoic acid (Zehra, *B.* 23, 3629). Pale-yellow needles, m. sol. hot alcohol. Blackens above 300° without melting.—BaA'_2 3aq: yellowish-white needles.

Oxy-methyl-quinoxaline carboxylic acid $C_6H_3Me\left\langle\begin{matrix}N{:}C.CO_2H\\ N{:}C.OH\end{matrix}\right.$. Formed by the action of boiling potash on $C_{11}H_{10}N_4O_3$ [258°], which is made by mixing aqueous solutions of alloxan and tolylene *o*-diamine (Hinsberg, *A.* 237, 356). Yellow needles (from dilute alcohol). Gives off CO_2 at 214°.

OXY-METHYL-SUCCINIC ACID *v.* Oxypyrotartaric acid.

Oxy-di-methyl-succinic acid *v.* Oxy-adipic acid.

Di-oxy-di-methyl-succinic acid $CO_2H.CMe(OH).CMe(OH).CO_2H$. *Di-methyl-racemic acid.* [179°]. Formed by saponifying its nitrile with HClAq. Crystals (containing aq). —KHA″. Plates, m. sol. hot water.—CaA″$1\frac{1}{2}$aq. —BaA″2aq: small needles.

Nitrile CN.CMe(OH).CMe(OH).CN. [c. 110°]. Formed from di-methyl-di-ketone (diacetyl) and HCy (Fittig, *A.* 249, 208). Very hygroscopic needles, sl. sol. chloroform.

Isomeride.—Di-methyl-tartaric acid.

OXY-METHYL-TEREPHTHALIC ACID $C_6H_2Me(OH)(CO_2H)_2$ [2:5:4:1]. [285°–290°]. Formed by fusing $C_6H_2Me(SO_2NH_2)(CO_2H)_2$ with potash (Jacobsen a. H. Meyer, *B.* 16, 191). Minute prisms (from very dilute alcohol), decomposed on fusion.

OXY-METHYL-THIAZOLE $\begin{matrix}S.C(OH)\\CH:CMe\end{matrix}\!\!>\!N$. *Thiocyanacetone.* [102°]. Formed by heating the carboxylic acid (Wohmann, *A.* 259, 298), or by heating with dilute HClAq the compound $CH_3CO.CH_2SCy$, formed from chloro-acetone and a sulphocyanide (Tscherniak a. Norton, *C. J.* 44, 568; Hantzsch, *B.* 20, 3127, 3337; 21, 941; *A.* 249, 20). Needles. Yields methyl-thiazole on distilling with zinc-dust. With phenylene *m*-diamine it forms $C_6H_4(NH.C_4H_4SN)_2$ [152°]. Reacts with hydroxylamine.

Di-oxy-methyl-thiazole $\begin{matrix}S-CO\\CH_2.CO\end{matrix}\!\!>\!NMe$. Formed from di-oxy-thiazole, NaOMe, and MeI (Arapides, *A.* 249, 28). Liquid, v. e. sol. water. Decomposed by boiling NaOHAq into methylamine and thioglycollic acid. PCl_5 yields $C_3H_3Cl_2NOS$ [161°].

OXY-METHYL-THIAZOLE CARBOXYLIC ACID $\begin{matrix}S.C(OH):N\\C(CO_2H):CMe\end{matrix}$. [222°]. Formed from its ether, and also by heating chloro-methyl-thiazole carboxylic acid with conc. KOHAq (Zürcher, *A.* 250, 286; Wohmann, *A.* 259, 296). Plates or needles (containing *x*aq), v. sol. water. — $NH_4A'5aq$. Prisms, decomposing at 138°.

Ethyl ether EtA'. [129°]. Formed together with $(SC_3Me(CO_2Et)N)_2O$ [142°] from chloro-acetoacetic ether and ammonium or barium sulphocyanide (Hantzsch a. Weber, *B.* 20, 3132). Silky plates. Hydroxylamine forms $C_{10}H_{10}O_5N_4S_2$ [c. 217°].

OXY-METHYL-THIOPHENE $S\!<\!\begin{matrix}CMe\ \ :CH\\C(OH):CH\end{matrix}$. Formed from levulic acid and P_2S_5 (Kues, *B.* 19, 555). Oil, sl. sol. water.—B'HOAc. (210°). Yellow oil.

OXY-METHYL-UREA. *Di-ethyl derivative of the glycollyl derivative* $CH_2(OEt).NH.CO.NH.CO.CH_2.OEt$. [80°]. Formed from $CH_2(OEt).CONH_2$, bromine, and potash (Hofmann, *B.* 18, 2736). Needles (from water).

OXY-METHYL-XANTHINE $C_6H_8N_4O_3$. S. ·16 at 16°. Formed by the action of potassium cyanate on the hydrochloride of di-oxy-amido-methyl-pyrimidine $CO\!<\!\begin{matrix}NMe.CH\\NH\ \ .CO\end{matrix}\!\!>\!C.NH_2$ (Behrend, *A.* 231, 252; Lehmann, *A.* 253, 80). Needles or prisms (containing 2aq), sl. sol. water. Does not reduce alkaline $AgNO_3$.

OXY-MYRISTIC ACID $C_{14}H_{28}O_3$. [51°]. Occurs in the essential oil from the fruit of *Angelica archangelica* (Müller, *B.* 14, 2480). Pearly plates (from alcohol).—KA' aq.—CuA'_2.—AgA': bulky pp. *Benzoyl derivative* [68°].—AgA'.

(1,2)-DI-OXY-NAPHTHALENE $C_{10}H_6(OH)_2$ [1:2]. [60°]. *v.* (β)-Hydronaphthoquinone, vol. ii. p. 728.

(1,4)-Di-oxy-naphthalene [176°] *v.* (α)-Hydronaphthoquinone.

(1,4')-Di-oxy-naphthalene. [260°]. Formed by potash-fusion from (α)-naphthol sulphonic acid and from naphthalene (1,4')-disulphonic acid (Erdmann, *A.* 247, 356; Bernthsen, *B.* 20, 938; Armstrong a. Wynne, *C. J. Proc.* 3, 43). Scales, v. sol. hot alcohol, sl. sol. water. Yields crystalline $C_{10}H_6(OAc)_2$ [160°].

Peri-**di-oxy-naphthalene** $C_{10}H_6(OH)_2$ [1:1']. [140°]. Formed by potash-fusion from the anhydride got by boiling naphthylamine *peri*-sulphonic acid with water (Erdmann, *A.* 247, 357). Needles or plates, sl. sol. water. Yields $C_{10}H_6(OAc)_2$ [148°] crystallising in white plates.

Di-oxy-naphthalene. Made by reducing peri-naphthoquinone with HOAc and zinc-dust (Meldola a. Hughes, *C. J.* 57, 631). Minute needles which blacken at 205°. Yields $C_{10}H_6(OAc)_2$ [227°]. According to theory, this body should be identical with the preceding.

(1,2')-Dioxynaphthalene [178°]. Formed by fusing (β)-naphthol (α)-sulphonic acid (Bayer, *B.* 15, 1351) with potash (Emmert, *A.* 241, 371). Needles, v. e. sol. alcohol, m. sol. water. Its alkaline solution blackens quickly. $FeCl_3$ gives a blue pp. Yields $C_{10}H_6(OAc)_2$ [108°] and $C_{10}H_6(OEt)_2$ [67°].

(1,3')-Di-oxy-naphthalene [135°]. Made by potash-fusion from naphthalene (1,3')-di-sulphonic acid (Ewer a. Pick, *G. P.* 45,229 [1887]) or (β)-naphthal (α)-sulphonic acid (Claus, *J. pr.* [2] 39, 315). White prisms (from benzene). Turns red in air. $FeCl_3$ gives a blue colour. Yields $C_{10}H_6(OAc)_2$ [73°].

(2,3')-Di-oxy-naphthalene [216°]. Formed by potash-fusion from naphthalene (2,3')-di-sulphonic acid (Dusart, *Bl.* [2] 8, 200; Darmstädter a. Wichelhaus, *A.* 152, 306) and from (β)-naphthol (β)-sulphonic acid (Schäffer, *A.* 152, 298; Armstrong a. Graham, *C. J.* 39, 140; Emmert, *A.* 241, 369). Thin plates, v. sol. alcohol, sl. sol. cold water. Gives a yellowish-white pp. with $FeCl_3$. Yields $C_{10}H_6(OAc)_2$ [175°] and $C_{10}H_6(OEt)_2$ [162°]. Forms a disulphonic acid which gives $BaC_{10}H_6S_2O_8$ 2aq (Griess, *B.* 13, 1959).

(2, 2')-Di-oxy-naphthalene. [190°]. Formed by potash-fusion from naphthalene (2,2')-di-sulphonic acid (Ebert a. Merz, *B.* 9, 609; Weber, *B.* 10, 1233; 14, 2206; Clausius, *B.* 23, 519). Needles (from hot water). Its alkaline solution blackens in air. Yields $C_{10}H_6(OAc)_2$ [136°], $C_{10}H_6(OBz)_2$ [139°], $C_{10}H_6(OMe)_2$ [134], and $C_{10}H_6(OEt)_2$ [104°] (Liebermann, *B.* 15, 1428).

Dioxynaphthalene [161°]. Got by fusing (β)-naphthol (*R*)-disulphonic acid (1 pt.) with NaOH (4 pts.) at 310°, or by heating with dilute (25 p. c.) H_2SO_4 at 200° (*E. P.* 15,803). Crystals (from water). $FeCl_3$ gives an intense blue colour. Combines with diazo- compounds.

Tri-oxy-naphthalene $C_{10}H_8O_3$. Got by reducing oxy-(α)-naphthoquinone (Graebe, *A.* 154, 324). Yellow needles (from ether). Very readily oxidised.

DI-OXY-NAPHTHALENE DICARBOXYLIC ACID $C_{10}H_4(OH)_2(CO_2H)_2$. [162°]. Formed by heating narceïc acid (Claus a. Meixner, *J. pr.* [2] 37, 1). White needles, v. sol. ether. Yields $C_{10}H_6(CO_2H)_2$ [253°] on reduction.—Na_2A'' 6aq.—$NaHA''5\frac{1}{2}$aq; small needles.—BaA'' 2aq.—Ag_2A''.

DIOXYNAPHTHALIC ACID $C_{10}H_8O_6$. [126°]. Made by boiling chloro-oxy-naphthalic acid (*v.* Naphthalene) with baryta (Hermann, *A.* 151, 67). Prisms.—KHA'' aq.—BaA'' 3aq.—$Ba(HA'')_2$.—$Ba(NH_4A'')_2$ 2aq.—$Ca(NH_4A'')_2$.—$Cu(NH_4A'')_2$: blue prisms.

DI-OXY-NAPHTHAZINE $C_{16}H_{10}N_2O_2$. [c. 300°]. Formed from di-oxy-naphthoquinone and naphthylene-(1, 2)-diamine in alcohol (Nietzki

a. Hasterlik, *B.* 24, 1339). Reddish-brown needles, sl. sol. alcohol.

(α)-**OXY-(β)-NAPHTHOIC ACID** $C_{10}H_6(OH)CO_2H$ [1:2]. *Naphthol carboxylic acid.* [187°]. S. ·058 at 17°. Formed by passing CO_2 over sodium-α-naphthol at 100° (Eller, *A.* 152, 277; Schäffer, *A.* 152, 291; Nietzki a. Goetermann, *B.* 20, 1274), or by heating sodium-(α)-naphthol with liquid CO_2 at 130° (Schmitt a. Burkard, *B.* 20, 2699). Stellate groups of needles (from alcohol). $FeCl_3$ colours its solution blue. PCl_5 forms $C_{10}H_6(OPOCl_2).CCl_3$ [115°], whence moist air forms $C_{10}H_6(O.PO(OH)_2).CO_2H$, while alcohol yields $C_{10}H_6(O.P(OEt)_2).CO_2H$ [63°] (Wolffenstein, *B.* 21, 1186).—NaA′ 3aq.—NaA′.—NH_4A'.—PhA′. [96°].

Acetyl derivative $C_{10}H_6(OAc).CO_2H$. [158°].

Methyl ether MeA′. [78°]. Converted by hydroxylamine into $C_{10}H_6(OH).CO.NH(OH)$ [174°].

Ethyl ether EtA′. [49°].

Phenyl ether PhA′. [96°].

Methyl derivative of the anilide $C_{10}H_6(OMe).CONHPh$. [218°]. Made from methyl (α)-naphthol, phenyl cyanate, and $AlCl_3$ (Leuchart a. Schmitt, *B.* 20, 2340). Prisms.

(β)-**Oxy-(α)-naphthoic acid** $C_{10}H_6(OH)(CO_2H)$ [2:1]. [157°]. Formed, in like manner, from (β)-naphthol (S. a. B.; *cf.* Kauffmann, *B.* 15, 804). Slender needles, decomposing at 125° when slowly heated. Completely decomposed by boiling water into CO_2 and (β)-naphthol. $FeCl_3$ gives a blue colour. PCl_5 yields $C_{10}H_6(OPOCl_2)COCl$ [38°], whence moist air forms $C_{10}H_6(OPO(OH)_2).CO_2H$ [156°], while dilute alcohol produces $C_{10}H_6(OPO(OEt)_2).CO_2H$ [113°] (Rabe, *B.* 22, 392).—NH_4A': yellow needles, m. sol. cold water.

Methyl ether MeA′. [76°]. Converted by hydroxylamine into amorphous $C_{10}H_6(OH).CO.NH(OH)$ [178°] (Jeaurenaud, *B.* 22, 1277).

Ethyl ether EtA′. [55°].

Methyl derivative of the amide $C_{10}H_6(OMe).CONH_2$. [186°]. Form from methyl (β)-naphthol, $AlCl_3$, and $ClCONH_2$ (Gattermann, *A.* 244, 75). Crystals (from alcohol).

Ethyl derivative of the amide $C_{10}H_6(OEt).CONH_2$. [161°]. Plates (from alcohol).

Methyl derivative of the anilide $C_{10}H_6(OMe).CONHPh$. [169°]. Made from methyl (β)-naphthol and phenyl cyanate in presence of $AlCl_3$ (L. a. S.). Needles.

(β)-**Oxy-naphthoic acid** $C_{10}H_6(OH)CO_2H$ [? 2:3′]. [216°]. Formed in small quantity from sodium (β)-naphthol and CO_2 at 290° (Schmitt a. Burkard, *B.* 20, 2702). Plates, v. sol. alcohol. Very stable. $FeCl_3$ colours its solution blue. Its methyl ether does not react with hydroxylamine.

Peri-**Oxy-naphthoic acid** $C_{10}H_6(OH)CO_2H$ [1:1′]. [169°]. Made by heating its internal anhydride for a long time with dilute KOHAq (Ekstrand, *B.* 19, 1138; *J. pr.* [2] 38, 278). Small needles (from ether), v. sol. water. Solutions of its salts are coloured violet by $FeCl_3$.—$CaA'_2\,3\frac{1}{2}aq$: decomposed on boiling.

Anhydride $C_{10}H_6{<}^{CO}_{O}{>}$. *Naphtholactone.* [108°]. Made from amido-(α)-naphthoic acid by the diazo- reaction. Needles (from alcohol) or tables (from ether), insol. cold aqueous alkalis.

(α)-**Oxy-naphthoic acid** $C_{10}H_6(OH).CO_2H$ [1:4 ?].

Ethyl derivative $C_{10}H_6(OEt)CO_2H$. [214°]. Formed by the action of alcoholic potash on the amide $C_{10}H_6(OEt)CONH_2$ [244°], which is made from $C_{10}H_7OEt$ and $ClCONH_2$ in presence of $AlCl_3$ (Gattermann, *B.* 23, 1198; *A.* 244, 73). Needles, m. sol. alcohol.—NaA′3aq: plates.—CaA'_2 3aq: needles, sl. sol. water.

Methyl derivative $C_{10}H_6(OMe).CO_2H$. [232°]. Formed, in like manner, from $C_{10}H_6(OMe).CONH_2$ [234°] which is prepared from $C_{10}H_7OMe$.

(α)-**Oxy-(α)-naphthoic acid.** [234°–237°]. Formed by fusing (α)-sulpho-(α)-naphthoic acid [235°] with potash (Battershall, *A.* 168, 114). Needles (from water), v. sol. alcohol. Aqueous solutions of its salts blacken on boiling. $FeCl_3$ gives a dirty violet pp.

(α)-**Oxy-(β)-naphthoic acid.** [213°]. Made by potash-fusion from sulpho-(β)-naphthoic acid. Needles (from boiling water). Its salts are unstable. $FeCl_3$ gives a dirty red pp.

(β)-**Oxy-(α)-naphthoic acid.** [247°]. Made by potash-fusion from the sulpho-naphthoic acid [218°–222°] (Stumpf, *A.* 188, 6). Mass of needles (from water). $FeCl_3$ has no effect in the cold, but gives a brown pp. on warming.

(β)-**Oxy-(α)-naphthoic acid.** [187°]. Made by potash-fusion from sulpho-naphthoic acid [182°–185°] (Stumpf). Branching needles (from water). Gives a chocolate colour with $FeCl_3$. Yields (β)-naphthol on distilling with lime.

(β)-**OXY-NAPHTHOIC ALDEHYDE** $C_{10}H_6(OH)CHO$. *Aldehydo-naphthol.* [76°]. Formed from (β)-naphthol, chloroform, and aqueous NaOH (Kauffmann, *B.* 15, 805; 16, 683). Prisms (from alcohol), almost insol. water. $FeCl_3$ colours its solution brown. Reduces warm ammoniacal $AgNO_3$, forming a mirror. With Ac_2O and NaOAc it forms $C_{10}H_6(OAc).CH(OAc)_2$ [124°]. Yields, on oxidation, oxy-naphthoic acid [150°].—$C_{10}H_6(ONa).CHO$: yellow plates.

(α)**OXY-(α)-NAPHTHOPHENAZINE** $C_{16}H_{10}N_2O$ *i.e.* $C_6H_4{:}N_2{:}C_{10}H_5OH$ [4:3:1]. Formed by heating (α)-amido- or diethylamido-(α)-naphthophenazine with conc. HClAq for 5 hours at 180° (Fischer a. Hepp, *B.* 23, 845; Eicker, *B.* 23, 3805). Reddish-yellow needles (from alcohol). The hydrochloride forms red prisms with green lustre.

OXY-(β)-NAPHTHOQUINOLINE $C_{13}H_9NO$. Formed by fusing (β)-naphthoquinoline sulphonic acid with potash (Gentil, *B.* 18, 202). Does not melt below 250°.

(α)-**OXY-(α)-NAPHTHOQUINONE** *v.* Juglone.

(β)-**Oxy-(α)-naphthoquinone** $C_{10}H_5(OH)O_2$. *Naphthalic acid.* [190°]. Formed by heating amido- or oxy- naphthoquinonimide or oximido-naphthol with HClAq or alkalis (Martius a. Griess, *A.* 134, 377; Graebe a. Ludwig, *A.* 154, 321; *B.* 4, 970; Merz a. Diehl, *B.* 11, 1314; Kehrmann, *B.* 23, 2453). Formed also in like manner from phenyl-amido-(α)-naphthoquinone and from phenyl-amido-(β)-naphthoquinone (Baltzer, *B.* 14, 1900; Zincke, *B.* 14, 1496; Lie-

bermann a. Jacobson, *A.* 211, 80). Yellow needles, v. sl. sol. cold water. May be sublimed.

Reactions.—1. Reduced by *tin* and HCl to tri-oxy-naphthalene.—2. The Na salt heated with o-*phenylene-diamine* forms (α)-naphtho-eurhodol (Kehrmann, *B.* 23, 2453).—3. *Benzoic aldehyde* forms $CHPh(C_{10}H_4(OH)O_2)_2$ [211°–214°] (Zincke, *B.* 21, 2203).—4. *Phenyl-hydrazine* yields $C_{10}H_5(OH)O(N_2HPh)$ [230°] which forms the salts CaA'_2 4aq and BaA'_2 10aq, the ethers MeA′ [175°] and EtA′ [173°], and the acetyl- derivative $C_{16}H_{11}AcN_2O_2$ [179°]. It reacts with aldehyde, benzoic aldehyde, and acetone, forming $C_{34}H_{28}N_4O_4$ [c. 258°], $C_{39}H_{28}N_4O_4$, and $C_{35}H_{40}N_4O_4$ [245°–250°] respectively (Zincke a. Thelen, *B.* 17, 1812; 21, 2205).—$AgC_{10}H_5O_3$: scarlet needles (from hot water).

Ethyl ether $EtC_{10}H_5O_3$. [127°]. Needles.

Imide v. AMIDO-NAPHTHOQUINONE.

Anilide v. PHENYL-AMIDO-NAPHTHOQUINONE.

Oxim $C_{10}H_5(NOH)(OH)O$ [1:2:4]. *Nitroso-naphtharesorcin.* Formed from oxy-naphthoquinone and hydroxylamine (Kostanecki, *B.* 22, 1343). Needles, decomposing at 180°. Gives with ferrous salts a green, and with ferric salts a dark-brown lake. The hydrochloride forms yellow needles. Nitrous acid forms $C_{10}H_4(NOH)_2O_2$ crystallising in plates (containing aq), decomposing at 165°.

Oxy-(β)-naphthoquinone $C_{10}H_5(OH)O_2$[2′:1:2]. Formed by oxidising its oxim with $FeCl_3$. Reddish-brown, amorphous pp., v. sol. alcohol.

Oxim $C_{10}H_5(OH)(NOH)O$ [2′:1:2]. [235°]. Formed from (2,2′)-di-oxy-naphthalene and nitrous acid (Clausius, *B.* 23, 521). Brownish-yellow needles.

Di-oxy-naphthoquinone $C_{10}H_4(OH)_2O_2$. *Naphthazarin.* Formed by heating di-nitro-naphthalene [214°] with zinc and H_2SO_4 at 200° (Roussin; De Aguiar a. Baeyer, *B.* 4, 251, 438; Liebermann, *B.* 3, 905; *A.* 162, 330). Reddish-brown needles with green lustre, v. sl. sol. boiling water, v. sol. alcohol. Its alkaline solution is blue. Its solution in H_2SO_4 is crimson. Baryta- and lime- waters give violet-blue pps.

Isomeride *v.* OXY-JUGLONE, p. 101.

Di-oxy-naphthoquinone $C_{10}H_4(OH)_2O_2$. Formed by heating oxy-amido-naphthoquinone with HClAq at 175° (Merz a. Diehl, *B.* 11, 1322). Reddish-brown needles (from alcohol). Its alkaline solution is brownish-violet. Dyes violet with alumina mordants and dark-blue with iron-mordants. Dyes silk brownish-violet with metallic lustre. It forms a crystalline di-acetyl derivative.—BaA″.—PbA″.—Ag_2A'': greenish-blue pp.

Tri-oxy-naphthoquinone. A black by-product in preparing naphthazarin (Aguiar, *B.* 4, 439).

References.—BROMO- and CHLORO- OXY-NAPHTHOQUINONE.

OXY - NAPHTHOQUINONE SULPHONIC ACID $C_{10}H_3(OH)O_2SO_3H$. Formed by the action of alkalis on the acid $C_{10}H_4(OH)(SO_3H)(OSO_3H)_2$ got by dissolving dichloro-naphthoquinone in aqueous $KHSO_3$ (Graebe, *A.* 149, 9).—K_2A'' (dried at 140°): orange crystals.

References.—BROMO- and CHLORO- OXY-NAPHTHOQUINONE SULPHONIC ACID.

(β)-OXY-o-NAPHTHOYL-BENZOIC ACID $C_{10}H_6(OH).CO.C_6H_4.CO_2H$. *Phenyl-oxy-naphthoyl-ketone-o-carboxylic acid.* [256°]. Prepared by oxidising an alkaline solution of ($\beta\beta$)-dioxy-dinaphthyl with $KMnO_4$ (Walder, *B.* 16, 299). Silky prisms. Sol. alcohol, ether, and acetic acid, nearly insol. water.

Reactions.—1. On fusion with KOH it gives (β)-naphthol and phthalic acid.—2. Heated with HI it is reduced to (β)-oxy-ω-naphthyl-o-toluic acid ($C_{10}H_6(OH).CH_2.C_6H_4.CO_2H$).—3. Heated with $ZnCl_2$ to 220° it yields a substance $C_{36}H_{22}O_7$ which forms colourless crystals [146°], easily soluble in alcohol.—4. Heated with resorcin it gives a red colouring-matter, and with dimethyl-aniline and $ZnCl_2$ a green.

Salts.—A′Na: white crystalline powder, sl. sol. cold water and alcohol.—A′Ag: insoluble pp.—A'_2Ba 2aq: slightly soluble white pp.

Methyl ether A′Me: [199°]; prisms.

Ethyl ether A′Et: [206°]; needles.

Acetyl derivative $C_{18}H_{11}O_3(OAc)$. [170°].

DI-(α)-OXY-DINAPHTHYL $C_{10}H_6(OH).C_{10}H_6(OH)$. *Dinaphthol.* [300°]. Formed by adding $FeCl_3$ to a conc. solution of (α)-naphthol (Dianin, *B.* 6, 1252; 7, 125, 487; Julius, *Chem. Ind.* 10, 97). Silvery plates (from alcohol), insol. water. Its alcoholic solution is coloured red by $FeCl_3$.

Benzoyl derivative $C_{20}H_{12}(OBz)_2$. [253°].

Di-methyl ether $C_{20}H_{12}(OMe)_2$. [251°].

Di-ethyl ether $C_{20}H_{12}(OEt)_2$. [211°]. Pearly plates (Ostermayer a. Rosenhek, *B.* 17, 2453).

Di-(β)-oxy-($\alpha\alpha$)-dinaphthyl. [218° cor.]. V.D. 9·52 (obs.). Prepared by oxidation of an ethereal solution of (β)-naphthol with $FeCl_3$, the yield being 60 p.c. of the theoretical amount (Dianin; Walder, *B.* 15, 2166). Needles or plates. Gives with $FeCl_3$ a greenish colour, becoming red on heating. On heating with $ZnCl_2$ it gives (β)-dinaphthylene oxide. H_2SO_4 forms $C_{20}H_{10}(OH)_2(SO_3H)_2$, whence BaA″ 6aq; $C_{20}H_8(OH)_2(SO_3H)_4$ is also formed. $ZnCl_2$ and NH_3 at 330° form $C_{20}H_{13}N$ [157°], which forms a picrate [217°] and an acetyl derivative [144°].—Picrate $C_{20}H_{14}O_2 2C_6H_2(NO_2)_3OH$. [174°]. White crystals, sol. alcohol.

Benzoyl derivative $C_{20}H_{12}(OH)(OBz)$. [204°].

Di-benzoyl derivative $C_{20}H_{12}(OBz)_2$. [160°].

Di-methyl ether $C_{20}H_{12}(OMe)_2$. [190°].

Di-ethyl ether $C_{20}H_{12}(OEt)_2$. [90°].

Di-oxy-dinaphthyl. [195°]. A product of the action of melted potash on (β)-naphthoic aldehyde (Kauffmann, *B.* 15, 807). Silky needles (from alcohol).

Tetra-oxy-dinaphthyl $C_{20}H_{10}(OH)_4$. '*Dinaphthyl dihydroquinone.*' [178°]. Formed by reduction of the quinone $C_{20}H_{10}O_4$ (Stenhouse a. Groves, *C. J.* 33, 415), and by the action of tin and HCl on (β)-naphthoquinone (Korn, *B.* 17, 3024). Colourless needles, darkening by oxidation in air, insol. water, v. sol. HOAc. The quinone $C_{20}H_{10}O_4$ is oxidised in alkaline solution by the air to [4:3:2:1] $C_{10}H_4O_2(OH).C_{10}H_4O_2(OH)$ [1:4:3:2] [245°–250°].

Acetyl derivative $C_{20}H_{10}(OAc)_4$. [166°].

α-OXY-(α)-NAPHTHYL-ACETIC ACID $C_{12}H_{10}O_3$ *i.e.* $C_{10}H_7.CH(OH).CO_2H$. (α)-*Naphthyl-glycollic acid.* [93°]. Formed by reducing (α)-naphthyl-glyoxylic acid with sodium-amalgam (Boessneck, *B.* 16, 640). Formed also by saponifying its nitrile (Brandis, *B.* 22, 2153), and

from (α)-naphthyl methyl ketone by successive treatment with bromine and potash (Schweizer, *B.* 24, 549). Rosettes of needles (from water). Yields (α)-naphthoic aldehyde on oxidation with dilute HNO_3.—BaA'_2.—AgA′: pulverulent pp.

Methyl ether MeA′. [79°]. Needles.

Nitrile $C_{10}H_7.CH(OH).CN$. Formed from (α)-naphthoic aldehyde, KCy, and cold HClAq. Oil, v. sol. alcohol.

α-Oxy-(β)-naphthyl-acetic acid. [158°] (S.); [c. 176°] (C. a. T.). Prepared in the same way as its isomeride (Claus a. Tersteegen, *J. pr.* [2] 42, 518; Schweizer, *B.* 24, 547). Small needles (from water). Reduced by HIAq to $C_{10}H_7CH_2CO_2H$ [c. 142°].

Methyl ether MeA′. [75°]. Needles.

Ethyl ether EtA′. [87°]. Needles.

Acetyl derivative $C_{10}H_7.CH(OAc).CO_2H$. [150°].

Amide $C_{10}H_7.CH(OH).CONH_2$. [228°].

Oxy-di-naphthyl-acetic acid $C_{22}H_{14}O_3$ *i.e.* $(C_{10}H_7)_2C(OH).CO_2H$. Yellowish-green tables, decomposing about 100°.

Anhydride $C_{22}H_{12}O_2$. Formed by heating (α)-naphthol with oxalic acid and H_2SO_4 (Hoenig, *M.* 1, 251). Pale-red plates, sl. sol. chloroform.

(β)-OXY-NAPHTHYL-ACRYLIC ACID $C_{10}H_6(OH).CH:CH.CO_2H$. [170°]. Formed by heating its anhydride with aqueous potash at 170°. Crystalline powder, sol. alcohol.

Anhydride $C_{10}H_6\!<\!\begin{matrix}CH:CH\\ O-CO\end{matrix}$. (β)-*Naphthocoumarin.* [118°]. Prepared by heating (β)-oxy-naphthoic aldehyde (2 pts.) with Ac_2O (10 pts.) and NaOAc (2 pts.) at 180° (Kauffmann, *B.* 16, 685). Needles, v. sol. alcohol, sl. sol. hot water.

An isomeride of this anhydride [141°] is got by heating (β)-naphthol with malic acid and H_2SO_4 (Pechmann a. Welsh, *B.* 17, 1651).

OXY-DINAPHTHYLAMINE *v.* IMIDO-DI-NAPHTHYL OXIDE.

Tri-oxy-(β)-naphthylamine $C_{10}H_4(OH)_3(NH_2)$[1:3:4:2]. Formed from nitro-oxy-quinone, $SnCl_2$, and HCl (Kehrmann a. Weichardt, *J. pr.* [2] 40, 181). Brownish-violet needles.—B′HCl: monoclinic prisms.

Tetra-acetyl derivative. [145°].

(β)-OXY-NAPHTHYL-CROTONIC ACID. *Anhydride* $C_{10}H_6\!<\!\begin{matrix}CMe:CH\\ O-CO\end{matrix}$. [162°]. Formed by the action of H_2SO_4 on a mixture of aceto-acetic ether and (β)-naphthol (Pechmann a. Cohen, *B.* 17, 2190). Needles, sol. alcohol. Its solution in H_2SO_4 exhibits green fluorescence.

DI-OXY-NAPHTHYLENE-DIAMINE $C_{10}H_4(OH)_2(NH_2)_2$[1:3:2:4]. Formed by the action of $SnCl_2$ and HCl on the oxim of oxy-amido-naphthoquinone (Kehrmann a. Weichardt, *J. pr.* [2] 40, 186). Its alkaline solutions become crimson on oxidation, and then blue on boiling. —B′HCl: white needles.

TRI-OXY-TRI-NAPHTHYL-ETHANE $C_{10}H_6(OH).CH_2.CH(C_{10}H_6.OH)_2$. Formed from di-chloro-di-ethyl oxide and (α)-naphthol (Wislicenus, *A.* 243, 165). White amorphous powder, insol. water, sol. alcohol.

(α)-OXY-NAPHTHYL ETHYL KETONE $C_{10}H_6(OH).CO.C_2H_5$. [81°]. Formed by heating (α)-naphthol with propionic acid and $ZnCl_2$ at 173°. Pale-yellow plates (from ether or alcohol).

Phenyl hydrazide [128°].

Methyl ether [58°]. Formed from propionyl chloride, $C_{10}H_7OMe$, and $AlCl_3$ (Gattermann, *B.* 23, 1209). Prisms (from ether). Yields an oxim $C_{10}H_6(OMe).C(NOH).C_2H_5$ [172°].

OXY-NAPHTHYL METHYL KETONE [1:3]$C_{10}H_6(OH).CO.CH_3$. '*Ketonaphthol*' [168°]. Formed by the rapid distillation of phenyl-aceto-isocrotonic acid (Erdmann, *A.* 254, 197). Crystals (from dilute alcohol).

Acetyl derivative $C_{14}H_{12}O_3$. [109°].

Oxim $C_{12}H_{11}NO_2$. [174°].

Oxy-naphthyl methyl ketone [103°]. Formed by heating (α)-naphthol with HOAc and $ZnCl_2$ (Witt, *B.* 21, 321). Pale-green six-sided prisms (from benzene). Its alkaline salts are yellow. Alcoholic NH_3 at 200° forms $C_{10}H_6(OH).C(NH_2).CH_3$. [203°].

Oxim $C_{10}H_6(OH).C(NOH).CH_3$. [170°].

(α)-Oxy-naphthyl methyl ketone. Probably identical with the preceding isomeride. *Methyl ether* $C_{10}H_6(OMe).CO.CH_3$. [72°]. (above 350°). Formed from $C_{10}H_7(OMe)$, AcCl, and $AlCl_3$ (Gattermann, *B.* 23, 1208). Six-sided tables.

Ethyl ether $C_{10}H_6(OMe)Ac$. [79°].

(β)-Oxy-naphthyl methyl ketone. *Methyl ether* $C_{10}H_6(OMe).CO.CH_3$. [58°]. Formed from $C_{10}H_7OMe$, AcCl, and $AlCl_3$ (G.). Slender needles.

Ethyl ether. [63°]. Compact tables.

OXY-(α)-NAPHTHYL-METHYL-PYRAZOLE $C_{14}H_{12}N_2O$ *i.e.* $C_{10}H_7.N\!<\!\begin{matrix}C(OH):CH\\ N\text{———}CMe\end{matrix}$. [c. 190°]. Formed by heating (α)-naphthyl-hydrazine with acetoacetic ether at 130° (Knorr, *B.* 17, 551). Yields a methyl derivative [129°]. (α)-Naphthyl-hydrazine and thio-acetoacetic ether form $C_{24}H_{18}N_4O$ [220°] (Sprague, *C. J.* 59, 343).

Oxy-(β)-naphthyl-methyl-pyrazole. [190°]. Formed in the same way. Yields a methyl derivative [129°].

(α)-OXY-NAPHTHYL PROPYL KETONE $C_{10}H_6(OH).CO.C_3H_7$. [78°]. Formed by heating butyric acid with (α)-naphthol and $ZnCl_2$ (Goldzweig, *J. pr.* [2] 43, 97). Silky needles (from ether), m. sol. hot water.

DI-OXY-DI-(α)-NAPHTHYL-PYRAZINE HEXAHYDRIDE

$C_{10}H_7N\!<\!\begin{matrix}C(OH).CH\\ CH\ \ \ .C(OH)\end{matrix}\!>\!NC_{10}H_7$. [275°].

Formed by boiling the acetyl derivative of chloro-(α)-naphthylamine with alcoholic potash (Abenius, *J. pr.* [2] 40, 437). Formed also by heating (α)-naphthylamido-acetic acid with Ac_2O at 200° (Bischoff, *B.* 22, 1807; 23, 2003). Plates (from HOAc), insol. alkalis.

Di-oxy-di-(β)-naphthyl-pyrazine hexahydride [above 360°]. Formed by heating (β)-naphthyl-amido-acetic acid at 220° in hydrogen, and by the action of chloro-acetic ether on the naphthalide of (β)-naphthylamido-acetic acid (Bischoff). Plates, sol. aniline. Converted by boiling alcoholic potash into $C_{10}H_7NH.CH_2CO.N(C_{10}H_7)CH_2CO_2H$ [105°].

DI-OXY-DI-(β)-NAPHTHYL SULPHIDE $S(C_{10}H_6.OH)_2$. *Naphthol sulphide.* [215°]. Formed, together with the di- and tri-sulphides, by the action of sulphur at 180° in presence of PbO, or of S_2Cl_2 in benzene, upon (β)-naphthol (Tassinari, *G.* 17, 94; Onufrovitch, *B.* 21, 3559; 23, 3355). Prisms, insol. water, ether, and

benzene, m. sol. hot alcohol. Yields di-oxy-di-naphthyl on heating with powdered copper. NH_3Aq forms, on heating, (β)-naphthylamine. Alcoholic and ammoniacal $AgNO_3$ forms $C_{20}H_{12}SO_2$. [164°].—Na_2A'' 6aq: needles.

Acetyl derivative $SC_{20}H_{12}(OAc)_2$. [154°].

Benzoyl derivative [208°]. Plates.

Ethyl ether $SC_{20}H_{12}(OEt)_2$. [189°]. Yields a di-nitro- derivative [235°].

Di-oxy-di-(β)-naphthyl disulphide $S_2(C_{10}H_6OH)_2$. [169°]. Formed as above. Thin yellow needles, m. sol. benzene. Yields di-oxy-dinaphthyl on heating with Cu at 240°.

Di-acetyl derivative $S_2C_{20}H_{12}(OAc)_2$. [c. 140°]. Yellowish crystalline mass.

Di-benzoyl derivative [187°]. Prisms.

Di-ethyl ether [158·5°]. Needles.

Di-oxy-di-naphthyl disulphide $S_2(C_{10}H_6OH)_2$. [210°]. Formed by heating (β)-naphthol with NaOHAq and S (Lange, *B.* 21, 260). Needles, insol. water, v. sol. HOAc. It is accompanied by the preceding isomeride [170°].

Di-oxy-di-(β)-naphthyl trisulphide $S_3(C_{10}H_6OH)_2$. Formed as above (Onufrovitch). Powder. Yields a dibenzoyl derivative [194°].

ν-OXY-(α)-NAPHTHYL-THIO-UREA $C_{10}H_7NH.CS.NH(OH)$. [116°]. Formed from (α)-naphthyl thiocarbimide and hydroxylamine (Tiemann, *B.* 22, 1939; Voltmer, *B.* 24, 382). Pearly plates (from alcohol), insol. water. Hot alcohol converts it into (α)-naphthyl-cyanamide.

Benzyl ether $C_{10}H_7NH.CS.NH(OCH_2Ph)$. [133°]. Formed by using benzyl-hydroxylamine.

(β)-OXY-ω-NAPHTHYL-o-TOLUIC ACID $C_{10}H_6(OH)—CH_2—C_6H_4.CO_2H$. [261°]. Formed by reduction of oxy-naphthoyl-benzoic acid by heating with HI and P to 200° (Walder, *B.* 16, 304). Small colourless prisms. Nearly insol. water, sl. sol. alcohol and ether.—A'Ag: flocculent pp.

OXY-NITRO- *v.* NITRO-OXY-.

DI-OXY-OCTANE $C_8H_{18}O_2$ *i.e.* CPrH(OH).CPrH(OH). Mol. w. 146. [51·5°]. (223°). Formed by the action of alcoholic potash on isobutyric aldehyde (Fossek, *M.* 4, 664; 11, 397). Monoclinic tables, v. sol. alcohol. Combines with $CaCl_2$. Yields isobutyric and oxalic acids on oxidation by HNO_3. Boiling dilute H_2SO_4 forms a (β)-pinacolin $C_{16}H_{32}O_2$ (162°). Conc. H_2SO_4 in the cold forms an (α)-pinacolin $C_8H_{16}O$ (122°) smelling like camphor.

Acetyl derivative $C_8H_{16}(OAc)_2$. (235°).

Di-oxy-octane $C_8H_{16}(OH)_2$. *Octylene glycol.* (235°–240°). S.G. $\frac{0}{0}$ ·932. Obtained from octylene bromide by successive treatment with AgOAc and solid KOH (De Clermont, *C. R.* 59, 80). Oil, sol. alcohol.

Acetyl derivative $C_8H_{16}(OAc)_2$. (245°–250°).

Di-oxy-octane CMeEt(OH).CMeEt(OH). *Methyl-ethyl-pinacone.* [c. 28°]. (200°–205°). A product of the action of sodium-amalgam on methyl ethyl ketone (Lavrinovitch, *A.* 185, 124). Crystalline mass, m. sol. water.

Tri-oxy-octane $CMePr(OH).CH_2.CH(OH).CH_2OH$. (210° at 60 mm.). Formed by the action of HOCl followed by KOH upon methyl-allyl-propyl-carbinol (Reformatzky, *J. pr.* [2] 40, 412). Thick liquid, v. sol. water and alcohol, sl. sol. alcohol. Yields a liquid tri-acetyl derivative.

Tetra-oxy-octane $C_8H_{14}(OH)_4$ *i.e.* $CH_2(OH).CMe(OH).CH_2.CH_2.CMe(OH).CH_2OH$. [154°]. Formed by the action of water on the liquid $C_8H_{14}O_2$ (170°–180° at 125 mm.) which is produced by the action of potash on $C_8H_{14}ClO(OH)$, a body formed by the addition of oxygen and HOCl to $CH_2:CMe.CH_2.CH_2.CMe:CH_2$ (Przybytek, *B.* 20, 3242).

DI-OXY-OCTENOIC LACTONE $CH_2:CH.CH_2.C(OH)<\begin{matrix}CH_2.CHMe\\ CO\ .O\end{matrix}$. Formed by the action of conc. H_2SO_4 on $(C_3H_5)_2C(OH).CO_2H$ [48°] (Bulitsch, *J. pr.* [2] 39, 94). Yellow syrup. Yields amorphous $Ba(C_8H_{13}O_4)_2$.

OXY-OCTINOIC ACID $C_8H_{12}O_3$ *i.e.* $C(C_3H_5)_2(OH).CO_2H$. '*Diallyloxalic acid.*' [48°]. Formed by saponifying its ether, which is made by the action of zinc and allyl iodide on oxalic ether (Saytzeff, *A.* 185, 183; Schatzky, *J. pr.* [2] 34, 485; *Bl.* [2] 45, 183). Needles, m. sol. water, v. sol. alcohol and ether.—NaA' 2aq.—LiA'aq.—BaA'_2.—CaA'_2 2aq.—ZnA'_2 $1\frac{1}{2}$aq. S. (of ZnA'_2) ·28 at 22°.—CdA'_2aq.—PbA'_2 2aq.—CuA'_2: minute green needles.

Ethyl ether EtA'. (213·6° cor.). S.G. $\frac{0}{0}$ ·9873; $\frac{18}{0}$ ·9718.

Methyl derivative $C(C_3H_5)_2(OMe)CO_2H$. Yields the salts BaA'_2 2aq.—PbA'_2 $6\frac{1}{2}$aq.—CuA'_2aq and the ether EtA' (216°). S.G. $\frac{20}{4}$ ·9607. $\mu_\beta = 1·4556$. $R_\infty = 89·52$ (Barataeff, *J. pr.* [2] 35, 1).

Heptic acid [151°], obtained by the action of bromine and potash on isobutyl-acetoacetic ether (Demarçay, *A. Ch.* [5] 20, 472), is perhaps an oxyoctinoic acid. It yields CaA'_2 5aq, crystallising in needles.

α-OXY-OCTOIC ACID $C_8H_{16}O_3$ *i.e.* $CPr_2(OH).CO_2H$. [73°] (K. a. S.); [81°] (R.). Formed by the action of zinc and propyl iodide on oxalic ether (Rafalsky, *B.* 14, 2068; *Bn.* 1, 527). Formed also by heating butyroïn with conc. KOHAq (Klinger a. Schmitz, *B.* 24, 1273). Needles.—KA'.—BaA'_2: scales.

Ethyl ether EtA'. (209° cor.). Oil.

α-Oxy-octoic acid $CPr_2(OH).CO_2H$. [111°]. Formed from its ether, which is made from oxalic acid, isopropyl iodide, and zinc (Markownikoff, *Z.* [2] 6, 516). Needles (from water), volatile with steam.—BaA'_2 3aq; small efflorescent needles.

Ethyl ether EtA'. (203° cor.). Oil.

α-Oxy-octoic acid $CH_2Pr.CH_2.CH_2.CH(OH).CO_2H$. [69·5°]. Formed from œnanthol and HCy, followed by boiling HClAq (Erlenmeyer a. Sigel, *B.* 7, 697, 1108; *A.* 177, 102). Plates, v. sl. sol. water. Split up by HClAq at 120° into œnanthol and formic acid.—AgA'.

Ethyl ether EtA'. (230°) at 715 mm.

Amide [150°]. Satiny plates.

Nitrile $C_6H_{13}.CH(OH).CN$. S.G.^{11} ·905. Formed from œnanthol and anhydrous HCy in the cold. Liquid, sl. sol. water.

α-Oxy-octoic acid $CMe_3.CH_2.CMe(OH).CO_2H$. [107°]. A product of the oxidation of 'isodibutylene' with $KMnO_4$ (Butleroff, *J. R.* 1882, 190; *C. J.* 42, 936; *Bl.* [2] 38, 554). Needles or prisms, v. sol. hot water.—AgA': needles.

β-Oxy-octoic acid $CH_3.CH(OH).CEt_2.CO_2H$. Formed by reducing di-ethyl-acetoacetic ether with sodium-amalgam and water (Schnapp, *A.* 201, 62). Hygroscopic syrup, v. sol. alcohol, m. sol. water. Decomposed on distillation into aldehyde and di-ethyl-acetic acid.—$NaA'_2$6aq.—$CuC_8H_{14}O_3$.—AgA': flocculent pp.

β-Oxy-octoic acid $CH_3.CH(OH).CMePr.CO_2H$. Formed by reducing methyl-propyl-acetoacetic ether (Jones, *A.* 226, 288). Split up on distillation into aldehyde and methyl-propyl-acetic acid.—ZnA'_2: crusts.

β-Oxy-octoic acid $CPrH(OH).CMe_2.CO_2H$. [108°]. Formed by reducing isobutyryl-isobutyric ether (Wohlbrück, *B.* 20, 2334; Hantzsch, *A.* 249, 54). Prisms, v. sol. ether.—$BaA'_2$3aq.

γ-Oxy-octoic acid $CEt_2(OH).CH_2.CH_2.CO_2H$. Formed from succinyl chloride and $ZnEt_2$ (Wischin, *A.* 143, 262).—CaA'_2 *x*aq.—BaA'_2.

Lactone $C_8H_{14}O_2$. (228°-233°) (Emmert, *B.* 15, 1852). Oil, v. sol. alcohol and ether.

γ-Oxy-octoic acid $CH_3.CH(OH).CMeH.CEtH.CO_2H$. Formed by reducing acetyl-hexoic acid (Young, *C. J.* 43, 177; *A.* 216, 43).—BaA'_2: amorphous.

Lactone $C_8H_{14}O_2$. (227°).

γ-Oxy-octoic acid. *Lactone* $C_8H_{14}O_2$. (134° at 36 mm.). A product of the action of iodoform or iodine on $NaOCH_2Pr$ (Gorboff, *J. pr.* [2] 41, 236, 261). Liquid.

Oxy-octoic acid [92°]. A product of the action of alcoholic potash on isobutyric aldehyde (Fossek, *M.* 4, 676). Crystals.—CaA'_2: sol. water.

Di-oxy-octoic acid $CHMe(OH).C(CH_2Pr)(OH).CO_2H$. A product of the action of alcoholic potash on bromo-iso-butyl-acetoacetic ether (Demarçay, *C. R.* 86, 1135). Liquid, m. sol. water.—BaA'_2: needles.—CaA'_2.

Di-oxy-octoic acid $(CHMe(OH).CH_2)_2CH.CO_2H$. Formed by boiling barium di-oxy-di-propyl malonate with water (Hjelt, *A.* 216, 70). *Anhydride* $C_8H_{14}O_3$. Liquid, v. e. sol. water.

Tri-oxy-octoic acid. *Lactone*

$$CH_3.CH(OH).CH_2.C(OH)<{CH_2.CHMe \atop CO\ .O}$$

Formed by the action of H_2SO_4 on α-oxy-octoic acid [47°] (Bulitsch, *J. pr.* [2] 39, 89). Syrup, sol. alcohol.—$Ba(C_8H_{15}O_5)_2$.

Tetra-oxy-octoic acid $C_8H_{16}O_6$ *i.e.* $(CH_2(OH).CH(OH).CH_2)_2CH.CO_2H$. Formed by boiling tetra-oxy-di-propyl-malonic acid with baryta-water (H.). Readily changes to the oily anhydride $C_8H_{14}O_5$.

Penta-oxy-octoic acid. $(CH_2(OH).CH(OH).CH_2)_2C(OH).CO_2H$. *Lactone* $C_8H_{14}O_6$. Formed by heating α-oxy-octoic ('diallyl-oxalic') acid with nitric acid on a water-bath (Bulitsch, *J. pr.* [2] 39, 65). Yellow liquid, v. sol. water and alcohol, insol. ether.

References.—Bromo- and Di-chloro- oxy-octoic acid.

DI-OXY-OCTYLENE $C_8H_{14}(OH)_2$. *Conylene-glycol. Acetyl derivative* $C_8H_{14}(OAc)_2$. (225°). S.G. $\frac{18.2}{}$ ·9887. Formed by conylene bromide and AgOAc (Wertheim, *A.* 130, 298). Oil.

OXY-OLEÏC ACID $C_{18}H_{34}O_3$. An oily product of the action of Ag_2O on dibromostearic acid (Burg a. Overbeck, *A.* 140, 69). An isomeric acid [58°] is formed by the action of H_2SO_4 on oleïc acid (Liechti a. Suida, *B.* 16, 2455).

OXY-OXALACETIC ETHER. *Ethyl derivative* $CO_2Et.CH(OEt).CO.CO_2Et$. (155° at 17mm.). Formed by the action of sodium ethylate on a mixture of oxalic ether and $CH_2(OEt).CO_2Et$ in ether (Wislicenus a. Scheidt, *B.* 24, 432). Thick liquid, miscible with alcohol and ether.

α-OXY-PALMITIC ACID $C_{16}H_{32}O_3$. [83°]. Formed by boiling α-bromo-palmitic acid with alcoholic potash (Hell a. Jordanoff, *B.* 24, 939). Small crystals (from alcohol).

Acetyl derivative [62·5°]. Scales.

OXYPARACONIC ACID $C_5H_6O_5$. An acid formed by boiling calcium chloroitamalate with water (Morawski, *J. pr.* [2] 11, 450). Thick liquid.—$CaA'_2$2aq: rhombohedra.

TETRA-OXY-PENTAMETHENYL HYDRIDE

$$CH(OH)<{CO.CH(OH) \atop CO.CH_2}$$

Formed by the action of HOAc on the Ba salt of its carboxylic acid (Hantzsch, *B.* 20, 2792). Oil.—$BaA''3\frac{1}{2}aq$: amorphous powder, almost insol. water.

Carboxylic acid $CH(OH)<{CO.CH(OH) \atop CO.CH.CO_2H}$. Formed from ammonium tri-chloro-di-oxy-hexenoic acid and baryta-water at 60°. — $BaA'_2$4aq: bulky pp., insol. water.

OXY-PENTANE *v.* Amyl alcohol.

Di-oxy-pentane $CH_2(CH_2.CH_2OH)_2$. Mol. w. 104. (260°). Formed from pentamethylene-diamine by HNO_2 (Gustavson, *J. pr.* [2] 39, 542).

Di-oxy-pentane $CHMe(OH).CH_2.CH_2.CH_2(OH)$. (220°) at 713 mm. S.G. $\frac{0}{0}$ 1·0003. Formed by reducing aceto-propyl alcohol by sodium-amalgam (Freer a. Perkin, *C. J.* 51, 836; *B.* 19, 2568; Lipp, *B.* 22, 2567). Liquid, miscible with water, decomposing at 236°. HBrAq at 100° forms an anhydride (78° at 716 mm.), and finally $C_5H_{10}Br_2$ (201°).

Di-oxy-pentane $CHEt(OH).CHMe(OH)$. (187·5°). S.G. $\frac{0}{0}$ ·9945; $\frac{19}{0}$ ·9800. Formed from the corresponding di-bromo-pentane by successive treatment with AgOAc and baryta-water (Wagner a. Saytzeff, *A.* 179, 308). Formed also by heating the oxide $O<{CHEt \atop CHMe}$ with water at 100° (Eltekoff, *J. R.* 1882, 355). Yields α-oxy-butyric acid on oxidation.

Di-oxy-pentane $CHPr(OH).CH_2(OH)$. (206°). S.G. $\frac{0}{}$ ·999. Formed from the corresponding di-bromo-pentane (Flavitzky, *B.* 10, 230, 2240; *A.* 179, 351). Yields oxy-valeric acid on oxidation. P_2O_5 forms valeric aldehyde and methyl iso-propyl ketone.

Di-oxy-pentane $CMe_2(OH).CHMe(OH)$. (177°). S.G. $\frac{0}{}$ ·987. Made from the corresponding di-bromo-pentane (Würtz, *A. Ch.* [3] 51, 458). Formed also by heating methyl-iso-propenyl-carbinol with dilute H_2SO_4 (Kondakoff, *J. R.* 20, 32). Syrup, with bitter taste. Miscible with water, alcohol, and ether. Yields oxy-iso-butyric acid on oxidation. Yields methyl-iso-propyl ketone when heated at 220°.

Acetyl derivative $C_5H_{10}(OAc)_2$. (above 200°). Oil, readily saponified.

Benzoyl derivative $C_5H_{10}(OBz)_2$. [123°]. Laminæ, sol. alcohol and ether (Meyer, *C. R.* 59, 444).

Di-oxy-pentane $CH_3.CH(OH).CH_2.CH(OH).CH_3$. (177°). Formed by reducing methylene-di-methyl-diketone (acetyl-acetone) with sodium-amalgam (Combes, *A. Ch.* [6] 12, 229). Liquid, sol. water.

Tri-oxy-pentane $CHMe(OH).CH_2.CH(OH).CH_2(OH)$. (180° at 27 mm.). S.G. $\frac{0}{0}$ 1·135; $\frac{22}{0}$ 1·120. Got by oxidising $CH_2{:}CH.CH_2.CHMe(OH)$ with $KMnO_4$. The yield is 82 p.c. (Wagner, *B.* 21, 3351). Syrup not volatile with steam.

Tri-acetyl derivative $C_5H_9(OAc)_3$. (270°) at 740 mm. S.G. $\frac{0}{0}$ 1·120; $\frac{20}{0}$ 1·101.

Tri-oxy-pentane $CHEt(OH).CH(OH).CH_2(OH)$. (192° at 63 mm.). S.G. $\frac{34}{0}$ 1·0851. Made by oxidising $CHEt(OH).CH{:}CH_2$ (114°) with $KMnO_4$ (Wagner, *B.* 21, 3349). The yield is 63 p.c. Thick, sweet syrup, miscible with water, alcohol, and ether.

Tri-acetyl derivative. (265°). S.G. $\frac{0}{0}$ 1·122; $\frac{18}{0}$ 1·103. Smells like onions.

Tri-oxy-pentane $CHMe(OH).CMe(OH).CH_2(OH)$. '*Pentenyl glycerin.*' (158° at 24 mm.). Formed from tiglic alcohol by addition of bromine and subsequent distillation (Lieben a. Zeisel, *M.* 7, 68). Thick liquid.

Tri-acetyl derivative. (149° at 18 mm.).

Tetra-oxy-pentane $C_5H_{12}O_4$. [253°]. S. 6 at 15°. Formed by the action of lime on a solution of formic and acetic aldehydes (Tollens a. Wigand, *A.* 265, 316). Prisms. Inactive to light. HI and P form $C_5H_8I_2(OH)_2$ [130°] and $C_5H_8I_3(OH)$ [62°].

Tetra-acetyl derivative. [84°].

Penta-oxy-pentane $\{CH_2(OH).CH(OH)\}_2CH(OH)$. [102°]. Formed by reducing arabinose with sodium-amalgam, the liquid being kept neutral with H_2SO_4 (Kiliani, *B.* 20, 1233). Prisms or needles, v. e. sol. water, v. sl. sol. cold alcohol.

OXY-PENTANE TRICARBOXYLIC ACID $C_3H_6(OH).C(CO_2H)_2.CH_2CO_2H$. Formed from $C_3H_5.C(CO_2H)_2.CH_2CO_2H$ by successive treatment with HBr and KOH (Hjelt, *B.* 16, 1258).

Anhydride $C_8H_{10}O_6$. *Dicarbocaprolactonic acid.* [153°]. Triclinic crystals (from water).—$BaC_8H_8O_6$.—$Ag_2C_8H_8O_6$: pulverulent pp.

OXY-PENTANE PHOSPHONIC ACID $C_4H_9.CH(OH).PO(OH)_2$. [184°]. Formed from isovaleric aldehyde and PCl_3 followed by water (Fossek, *M.* 5, 627; 7, 20). Monoclinic scales. Yields isovaleric aldehyde on distillation and on treatment with $KMnO_4$. PCl_5 forms $C_5H_{10}Cl.POCl_2$ (134°–140° at 22 mm.). Reduced by HI and P to isopentane phosphonic acid $C_5H_{13}PO_3$ [161°].—$BaA''2aq$.—$Ba(HA'')_2$.—Ag_2A'': amorphous pp.

OXY-PENTANE SULPHONIC ACID $C_5H_{10}(OH)SO_3H$. *Amylene isethionic acid.* Formed from chloro-amyl alcohol (amylene chlorhydrin) and Na_2SO_3 (Falk, *J. pr.* [2] 2, 272). Decomposed on evaporation of its solution.—NaA'.—CaA'_2.—$CuA'_2 2aq$: pale-blue laminæ.

An isomeric acid is formed by the action of SO_3 on isoamyl alcohol (Schwarz, *B.* 3, 691).—BaA'_2: crystalline.

OXYPENTIC ACID $C_5H_6O_3\frac{1}{3}aq$ or $C_6H_8O_4$. [193°]. Formed from ethyl-acetoacetic ether, bromine, and alcoholic potash (Demarçay, *C. R.* 88, 289). Crystals, m. sol. cold water. Ammonia converts its ether into a substance [77°], and its chloride into another body [204°]. Zn and H_2SO_4 yield $C_6H_{10}O_4$ [95°]. Oxypentic acid is perhaps $\Delta^{\beta\gamma}$ hydromuconic acid (Gorboff, *J. R.* 1887, 605; this vol. p. 443).

OXYPENTINOIC ACID $C_5H_6O_3$ *i.e.* $CH_3.CO.CH{:}CH.CO_2H$. *Aceto-acrylic acid.* [125°]. Prepared by boiling an aqueous solution sodium β-bromo-lævulate for a few minutes, neutralising with Na_2CO_3, again boiling, neutralising again, and so on till the solution finally remains alkaline after boiling (Wolff, *B.* 20, 426). Glistening plates. V. sol. alcohol and ether, less sol. cold water and chloroform.

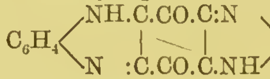
Salts.—CaA'_2.—ZnA'_2: amorphous.—AgA': needles.

OXY-PHENANTHRAQUINONE *v.* PHENANTHRAQUINONE.

DI-OXY-PHENAZINE $C_{12}H_8N_2O_2$. Formed by heating di-amido-phenazine with conc. HClAq at 200° (Fischer a. Hepp, *B.* 23, 843; Nietzki a. Hasterlik, 24, 1337). Reddish-yellow needles (containing $\frac{1}{2}$aq).—$B'_2H_2SO_4 2aq$.

Di-acetyl derivative [230°] (F. a. H.); [226°] (N. a. H.). Pale-yellow tables.

Dioxytriphenazine



Quinone homo-fluorindin. Formed by heating di-*o*-nitro-diphenyl-quinone with alcoholic ammonium sulphide at 100°, the product being oxidised by exposure to air (Leicester, *B.* 23, 2794). Dark-green crystals, yielding a violet powder. Its solution in HOAc exhibits brownish-red fluorescence.

OXYDIPHENYLS. All these compounds yield diphenyl when distilled with zinc-dust.

p-**Oxy-diphenyl** $C_6H_5.C_6H_4.OH$. [165°]. (c. 307°). Formed by fusing diphenyl sulphonic acid with potash (Latschinoff, *B.* 6, 194; Osten, *B.* 7, 170), by warming diazobenzene chloride with phenol, and in small quantity in the decomposition of diazobenzene chloride by water (Hirsch, *B.* 23, 3705). Plates, volatile with steam. Yields a mono-nitro- derivative [67°] and a di-nitro- derivative [154°].

Acetyl derivative. [89°]. Plates, v. sol. alcohol and ether (Kaiser, *A.* 257, 101).

Benzoyl derivative. [152°]. Tables.

An isomeric or identical oxydiphenyl [152°] is obtained from *p*-amido-diphenyl by the diazo-reaction (Hübner, *A.* 209, 348).

oo-**Di-oxy-diphenyl** $C_6H_4(OH).C_6H_4(OH)$. [99°]. Formed by potash-fusion from diphenyl disulphonic acid (Limpricht, *A.* 261, 331), and by dropping fluorene into fused KOH at 400° (Hodgkinson a. Matthews, *C. J.* 43, 168). Crystals (from benzene-ligroïn).

pp-**Di-oxy-diphenyl.** [272°]. (above 360°). Formed from benzidine by the diazo- reaction (Griess, *J.* 1866, 461; Hirsch, *B.* 22, 336), and by potash-fusion from diphenyl di-*p*-sulphonic acid (Engelhardt a. Latschinoff, *Z.* 1871, 261; Doebner, *B.* 9, 130). Got also by distilling di-oxy-phenyl-benzoic acid with lime (Schmidt a. Schultz, *A.* 207, 334; *B.* 12, 490). Obtained also by passing a rapidly alternating electric current through a solution of phenol (Drechsel, *J. pr.* [2] 29, 237). Laminæ (from alcohol).

Di-acetyl derivative [160°].

Ethyl ether [176°] (Hirsch).

op-**Di-oxy-diphenyl** [161°]. (342°). Formed in small quantity by potash-fusion from phenol o- and *p*- sulphonic acids (Lincke, *J. pr.* [2] 8, 43; Herzig, *B.* 13, 2234), and by the action of nitrous acid on *op*-di-amido-diphenyl (Schmidt, *A.* 207, 357; *B.* 12, 497). Yields a di-acetyl derivative [94°].

By fusing phenol with potash two more **di-oxy-diphenyls** [123°] and [190°] have been obtained (Barth a. Schreder, *A.* 156, 93; *B.* 11, 1336). The one melting at 123° yields $C_{12}H_8(OMe)_2$ (310°–320°) and $C_{12}H_8O_2(SO_3H)_2$, whence Na_2A'' 2aq and KA′aq.

Tri-oxy-diphenyl $C_6H_4(OH).C_6H_3(OH)_2$. Two isomerides of this formula [180°] and [205°] are formed by fusing fluorene sulphonic acid with potash at a little above 400° (Hodgkinson a. Matthews, *C. J.* 43, 167). Neither gives any colour with $FeCl_3$. The compound [180°] forms an acetyl derivative [100°].

Tetra-oxy-diphenyl $C_6H_3(OH)_2.C_6H_3(OH)_2$. *Dipyrocatechin.* [84°]. Formed from diphenyl (α)-disulphonic acid by potash-fusion (Barth, *B.* 11, 1336). Needles. $FeCl_3$ colours its solution green.

Tetra-oxy-diphenyl $C_{12}H_{10}O_4$. *Diresorcin.* [310°]. Formed in small quantity by fusing resorcin or phenol with NaOH (Barth, *B.* 12, 503; Benedikt, *M.* 1, 355; 5, 177; Herzig, *M.* 11, 419). Needles (containing 2aq). Gives a blue colour with $FeCl_3$. Phthalic anhydride and H_2SO_4 at 120° form $C_{32}H_{20}O_9$ 4aq, which gives blue solutions with alkalis.

Acetyl derivative $C_{12}H_6(OAc)_4$. [159°].

Benzoyl derivative $C_{12}H_6(OBz)_4$. [199°]. Formed from phloroglucin, BzCl, and NaOH (Skraup, *M.* 10, 721; Pukall, *B.* 20, 1143).

Ethyl ether $C_{12}H_6(OEt)_4$. [114°]. Plates.

Tetra-oxy-diphenyl $C_6H_3(OH)_2.C_6H_3(OH)_2$. *Dihydroquinone.* [237°]. Formed by fusing hydroquinone with NaOH (Barth, *M.* 5, 600). Plates. Tastes sweet. $FeCl_3$ colours it red, and then forms diquinhydrone $C_{12}H_8O_4$ and diquinone $C_{12}H_6O_4$ [187°].

Hexa-oxy-diphenyl $C_6H_2(OH)_3.C_6H_2(OH)_3$. Formed by heating hydrocœrulignone with HClAq at 200° (Liebermann, *A.* 169, 239; *B.* 9, 1887). Plates, m. sol. water. $FeCl_3$ gives a bluish-grey pp. Iodine yields $C_{12}H_8O_6$, crystallising in blue needles.

Tri-methyl ether $C_{12}H_4(OMe)_3(OH)_3$. Formed from cœrulignone and H_2SO_4 (Fischer, *B.* 8, 158).

Tetra-methyl ether $C_{12}H_4(OMe)_4(OH)_2$. *Hydrocœrulignone.* [190°]. Formed by reduction of cœrulignone (Liebermann, *A.* 169, 226). Monoclinic prisms (from alcohol). $FeCl_3$ oxidises it to cœrulignone. Yields $C_{12}H_4(OMe)_4(OAc)_2$ [217°–225°].—$Na_2C_{16}H_{16}O_6$.—K_2A'' 4aq (Ewald, *B.* 11, 1623).

Hexa-methyl ether $C_{12}H_4(OMe)_6$. [126°].

Tetra-ethyl ether $C_{12}H_4(OH)_2(OEt)_4$. [176°]. Crystals (from alcohol) (Hofmann, *B.* 11, 802).

Hexa-acetyl derivative $C_{12}H_4(OAc)_6$. [145°].

Hexa-propionyl derivative. Needles.

Di-bromo-hexa-oxy-diphenyl. *Tetra-methyl derivative* $C_{12}H_2Br_2(OH)_2(OMe)_4$. [262°]. Formed from $C_{12}H_2Br_2(OAc)_2(OMe)_4$ [178°], which is got from di-acetyl-cœrulignone, HOAc, and bromine (Hayduck, *B.* 9, 929). It yields $C_{12}H_2Br_2(OMe)_6$ [140°].

References.—Di-bromo- and Di-chloro-hexa-oxy-diphenyl.

(β)-**Hexa-oxy-diphenyl.** Formed by fusing ellagic acid with potash (Barth a. Goldschmidt, *B.* 12, 1244). Needles, blackening at 250°, and melting at a higher temperature. Its alkaline solution is blue, changing in air to red.

(γ)-**Hexa-oxy-diphenyl.** Formed from ellagic acid by fusion with NaOH (B. a. G.), or by treatment with sodium-amalgam (Cobenzl, *M.* 1, 672). Needles, blackening at 230°. Its alkaline solution is red, changing in air to green.

(δ)-**Hexa-oxy-diphenyl.** Formed by fusing hydroquinone with NaOH (Barth a. Schreder, *M.* 5, 597). Plates, blackening and melting near 290°. Its alkaline solution is red.

Acetyl derivative [172°]. Needles.

OXY-PHENYL-ACETAMIDINE $C_8H_{10}N_2O$ *i.e.* $CHPh(OH).C(NH)(NH_2)$. [110°]. Formed from mandelic imido-ether and alcoholic NH_3 (Beyer, *J. pr.* [2] 28, 191). Needles (from ether). —B′HCl. [214°]. Prisms (from water).

Di-acetyl derivative CHPh(OAc).C(NH).NHAc. [210°] (Pinner, *B.* 23, 2948).

OXY-PHENYL-ACETAMIDOXIM $C_6H_5.CH(OH).C(NH_2)(NOH)$. [159°]. Formed from the nitrile of mandelic acid and alcoholic hydroxylamine (Tiemann, *B.* 17, 126; Gross, *B.* 18, 1074). Crystals (from alcohol). Yields the derivatives $C_8H_9NaN_2O_2$, B′HCl, $C_8H_9EtN_2O_2$ [89°], and $C_8H_9(CH_2Ph)N_2O_2$ [103°].

Reactions.—1. $COCl_2$ forms the compound $(CHPh(OH).C(NH_2).NO)_2CO$ [121°].—2. Its hydrochloride reacts with *potassium cyanate*, forming $CHPh(OH).C(NOH).NH.CO.NH_2$ [127°].—3. *Phenyl cyanate* forms the compound CHPh(OH).C(NOH).NH.CO.NHPh [155°].—4. $ClCO_2Et$ yields $CHPh(OH).C(NH_2):NOCO_2Et$ [107°].

Acetyl derivative $CHPh(OH).C(NH_2):NOAc$. [140°]. Crystals (from alcohol).

Di-acetyl derivative [113°]. Plates.

Benzoyl derivative $C_{15}H_{14}N_2O_3$. [149°].

Acetyl-benzoyl derivative [165°].

o-**OXY-PHENYL-ACETIC ACID** $[2:1]C_6H_4(OH).CH_2.CO_2H$. [137°]. Formed from o-oxy-phenyl-glyoxylic acid by reduction with sodium-amalgam to $C_6H_4(OH).CH(OH).CO_2H$, and further reduction of this acid with HI (Baeyer a. Fritsch, *B.* 17, 975). Needles, v. sol. water. Gives a violet colour with $FeCl_3$. On heating it yields the *lactone* $C_6H_4{<}{\scriptstyle\begin{matrix}CH_2\\O\end{matrix}}{>}CO$, crystallising in tables [49°] (237°).

m-**Oxy-phenyl-acetic acid** [129°]. Formed by saponification of its nitrile and from *m*-amido-phenyl-acetic acid by the diazo- reaction (H. Salkowski, *B.* 17, 507). Needles, v. sol. water. Coloured violet by $FeCl_3$.

Nitrile $[3:1]C_6H_4(OH).CH_2.CN$. [53°]. Formed from $C_6H_4(NH_2).CH_2.CN$ and nitrous acid. Trimetric tables, v. sol. alcohol and hot water.

p-**Oxy-phenyl-acetic acid.** [148°]. Formed by the action of nitrous acid on *p*-amido-phenyl-acetic acid (Salkowski, *B.* 12, 1438), and by

saponifying its nitrile, which is a product of the action of $AgNO_3$ on sinalbin (Will a. Laubenheimer, *A.* 199, 156; Salkowski, *B.* 22, 2137). Occurs in human urine (Baumann, *B.* 13, 280). Prismatic needles, sol. water and alcohol. $FeCl_3$ gives a dark colouration.—NH_4A'.—CaA'_2 4aq.—PbA'_2.—AgA′: minute needles.

Methyl ether $C_6H_4(OH).CH_2.CO_2Me$. (310° i.V.). S.G. $\frac{0}{4}$ 1·1948; $\frac{20}{4}$ 1·1786. Oil.

Ethyl ether EtA′. (314° i.V.) S.G. $\frac{0}{4}$ 1·1386; $\frac{18.5}{4}$ 1·1226.

Nitrile. [70°]. (330·5° i.V.). Made like its *m*-isomeride (Salkowski, *B.* 22, 2137). Triclinic crystals. Yields $C_6H_4(OMe).CH_2CN$ (287° i.V.). S.G. $\frac{0}{4}$ 1·1001.

Methyl derivative $C_6H_4(OMe).CH_2.CO_2H$. [86°]. Formed from $C_6H_4(OMe).CH_2Cl$ and KCy, the product being saponified (Cannizzaro, *A.* 117, 243). Pearly plates.—AgA′.

Ethyl derivative. [88°]. Plates.

Amide $C_6H_4(OH).CH_2.CONH_2$. [175°].

Methyl derivative of the amide $C_6H_4(OMe).CH_2.CONH_2$. [189°]. Scales.

α-Oxy-phenyl-acetic acid *v.* MANDELIC ACID.

ao-Di-oxy-phenyl-acetic acid $C_6H_4(OH).CH(OH).CO_2H$. Formed from salicylic aldehyde, HCy, and HCl (Plöschl, *B.* 14, 1317), and also by reducing oxy-phenyl-glyoxylic acid (Bayer a. Fritsch, *B.* 17, 974). Syrup. Yields a crystalline anhydride.

Methyl derivative of the nitrile $C_6H_4(OMe).CH(OH).CN$. [71°]. Formed from methyl-salicylic aldehyde and HCy (Voswinckel, *B.* 15, 2025). Colourless crystals.

Di-oxy-phenyl-acetic acid $[1:3:5]C_6H_3(OH)_2.CH_2.CO_2H$. [54°]. Formed from $C_6H(OH)_2(CO_2Et)_2.CH_2.CO_2Et$ and alcoholic potash (Pechmann, *B.* 19, 1449). Crystals (containing aq).—PbA'_2 2aq: needles (from water).

ap-Di-oxy-phenyl-acetic acid. *Methyl derivative* $C_6H_4(OMe).CH(OH).CO_2H$. [93°]. Formed from anisic aldehyde, HCy, and HCl (Tiemann a. Köhler, *B.* 14, 1976). Needles.—CaA'_2.—AgA′: amorphous pp.

Amide $C_6H_4(OMe).CH(OH).CONH_2$. [159°].

Nitrile $C_6H_4(OMe).CH(OH).CN$. [63°].

Di-oxy-phenyl-acetic acid $C_6H_3(OH)_2.CH_2.CO_2H$ [4:3:1]. *Homoprotocatechuic acid.* [127°]. Formed by heating its methyl derivative with HClAq at 175° (Tiemann a. Nagai, *B.* 10, 207). Slender needles (from benzene). $FeCl_3$ gives a green colour.

Di-acetyl derivative $C_6H_3(OAc)_2.CH_2.CO_2H$. [90°] (Nagai, *B.* 11, 658).

Methyl derivative $C_6H_3(OMe)(OH).CH_2.CO_2H$ [3:4:1]. *Homovanillic acid.* [143°]. Made from its acetyl derivative [140°], which is got by oxidising acetyl-eugenol.

Di-methyl derivative $C_6H_3(OMe)_2.CH_2.CO_2H$. *Homoveratric acid.* [99°] (Tiemann a. Matsmoto, *B.* 11, 143). Needles (containing aq).

Methylene derivative $C_6H_3(O_2CH_2).CH_2.CO_2H$. [128°]. Got from safrol, $KMnO_4$, and dilute HOAc (Tiemann, *B.* 24, 2882). Yields MeA′ (279°), EtA′ (291°), and an amide [173°].

A di-oxy-phenyl-acetic acid [168°] occurs in urine after poisoning by phosphorus (Baumann, *H.* 6, 192). It crystallises in small needles.

Tri-oxy-phenyl-acetic acid. *Methylene derivative* $[4:3:1]C_6H_3(O_2CH_2).CH(OH).CO_2H$. [153°]. Made from piperonal by treatment with HCy and saponification (Lorenz, *B.* 14, 793).

Hexa-oxy-di-phenyl-acetic acid. *Hexa-methyl derivative* $(C_6H_2(OMe)_3)_2C(OH).CO_2H$. [175°]. Formed by boiling the hexa-methyl derivative of hexa-oxy-benzil with potash (Marx, *A.* 263, 255). Prisms, v. sol. alcohol, sl. sol. water.

α-Oxy-di-phenyl-acetic acid *v.* BENZILIC ACID.

Tri-oxy-di-phenyl-acetic acid. Di-methyl derivative *v.* ANISILIC ACID.

(*B.* 2)-OXY-(*A.*)-PHENYL-ACRIDINE

$C_6H_4<{N \atop C\,Ph}>C_6H_3(OH)$. [c. 275°–280°]. Formed by heating *p*-oxy-di-phenylamine with benzoic acid and $ZnCl_2$. Formed also by heating (*B.* 2)-amido-(*A.*)-phenyl-acridine with HCl at 200°–220° (Hess a. Bernthsen, *B.* 18, 695). Thin yellow crystals. V. sol. alcohol and acetic acid; less sol. ether. Dissolves in caustic alkalis and in acids. The ethereal and alcoholic solutions have a slight bluish-violet fluorescence. The salts are all rather sparingly soluble, and have a tendency to separate in a gelatinous form.

Acetyl derivative $C_{19}H_{13}N(OAc)$ [174°]; glistening four-sided prisms.

OXY-PHENYL-ACRYLIC ACID *v.* OXY-CINNAMIC ACID and COUMARIC ACID.

Oxy-di-phenyl-acrylic acid. *Methyl derivative* $C_6H_4(OMe).CH:CPh.CO_2H$. [189°]. Made from anisic aldehyde, sodium phenyl-acetate, and Ac_2O at 160° (Oglialoro, *G.* 9, 533). Prisms, yielding $C_6H_4(OMe).CH:CHPh$ when heated.

Methyl derivative of the nitrile $C_6H_4(OMe).CH:CPh.CN$. [93°]. Formed from anisic aldehyde, benzyl cyanide, and alcoholic NaOEt (Frost, *A.* 250, 159). White needles.

Reference.—PHENYL-COUMARIN.

TRI-OXY-PHENYL ALLYL KETONE. According to Schiff (*A.* 253, 336), filicic acid (vol. ii. p. 548) is the isobutyryl derivative of this ketone $[5:3:1:2]\ C_6H_2(OH)_2(O.COPr).CO.C_3H_5$.

OXY-TRI-PHENYL-ALLYL-PYRROLE

$N(C_3H_5)<{CPh:CH \atop CO\ .CPh_2}$. [112°]. Formed by heating anhydracetophenone-benzil PhCBz:CHBz with alcoholic allylamine at 100° (Japp a. Klingemann, *C. J.* 57, 707). Monoclinic prisms (from alcohol); $a:b:c = 1·665:1:1·844$; $\beta = 88° 53'$.

o-OXY-PHENYL-ALLYL-THIO-UREA $C_6H_4(OH).NH.CS.NHC_3H_5$. [99°]. Formed from o-amido-phenol and allyl thiocarbimide in alcoholic solution (Von Chelmicki, *J. pr.* [2] 42, 442). V. sl. sol. cold, v. sol. hot, water.

o-OXY-PHENYL-AMIDO-ACETIC ACID $C_6H_4(OH).CH_2.CO_2H$. *Oxy-phenyl-glycocoll.* Formed by boiling chloro-acetic acid (1 mol.) with *o*-amido-phenol (2 mols.) and water (Vater, *J. pr.* [2] 29, 289). Plates (containing aq), sl. sol. water, v. sol. alcohol. $FeCl_3$ colours its solutions red. At 105° it yields an *anhydride* which crystallises from alcohol in cubes.

Methyl derivative $C_6H_4(OMe).NH.CH_2.CO_2H$. [142°]. Formed from *o*-anisidine and chloro-acetic acid. Rectangular plates.—$PbH_2A'_4$.—B′HCl: crystals.

Ethyl derivative $C_6H_4(OEt).NH.CH_2.CO_2H$ [120°]. Formed from chloro-acetic acid and

$C_6H_4(OEt)NH_2$.—EtA′: long waxy needles.—EtA′HCl.

p-Oxy-phenyl-amido-acetic acid $C_6H_4(OH).NH.CH_2.CO_2H$. Formed from chloro-acetic acid and *p*-amido-phenol (V.). Plates, sl. sol. water and alcohol. $FeCl_3$ colours its solutions red.—NaA′.

Methyl derivative $C_6H_4(OMe).NH.CH_2.CO_2H$. Formed in like manner from *p*-anisidine (V.), and also by saponifying its nitrile, which is got by heating anisaldehyde-cyanhydrin with alcoholic NH_3 (Tiemann a. Köhler, *B.* 14, 1976).—Needles, sol. hot water.—CuA'_2.—HA′HCl.

Ethyl derivative $C_6H_4(OEt).NH.CH_2.CO_2H$. [163°]. Crystals (containing *x*aq). Yields, on heating, $C_6H_4(OEt).NH.CH_2.CO.NHC_6H_4(OEt)$ [140°] and other bodies (Bischoff a. Nastvogel, *B.* 22, 1788).

p-**OXY-PHENYL-AMIDO-BENZENE SULPHONIC ACID** $C_6H_3(OH)(NHPh).SO_3H$. Formed from $C_6H_4(OH)NHPh$ [1:4] and conc. H_2SO_4 at 100° (Limpricht, *B.* 22, 2910). Small grey prisms. Does not melt below 260°.

OXY-PHENYL-AMIDO-CROTONIC ETHER. *Methyl derivative* $C_{13}H_{17}NO_3$. [46°]. Formed from *p*-anisidine and acetoacetic ether (Conrad a. Limpach, *B.* 21, 1649).

DI-OXY-PHENYLAMIDOETHYL-BENZOIC ACID. *Methylene derivative of the anhydride* $C_{16}H_{13}NO_3$ *i.e.* $CH_2<{}^{O}_{O}>C_6H_2<{}^{CO\ .NPh}_{CH_2.CH_2}$ [157°]. Formed from $CH_2O_2{:}C_6H_2(C_2H_4Cl).CO_2Me$ and alcoholic aniline (Perkin, jun., *C. J.* 57, 1036). Prisms, v. sl. sol. hot alcohol.

OXY-PHENYL-AMIDO-NAPHTHOQUINONE $C_{10}H_4O_2(OH)(NHPh)$. *Oxy-naphthoquinone anilide.* [210°]. Formed from $C_{10}H_4ClO_2(NPh.NO)$ and boiling KOHAq (Plagemann, *B.* 16, 896). Deep-blue needles with metallic lustre; sol. alkalis.

o-**OXY-PHENYLAMIDO-PHENYL-ACETONITRILE.** *Methyl derivative* $C_6H_4(OMe).CH(NHPh).CN$. [61°]. Formed by the action of aniline on $C_6H_4(OMe).CH(OH).CN$ (Voswinckel, *B.* 15, 2027). Six-sided tables, sol. alcohol.

OXY-PHENYL-AMIDO-QUINONE ANILIDE $C_6H_2(OH)(NHPh)O(NPh)$. Formed by heating its ethers with alcoholic potash (Zincke a. Hagen, *B.* 18, 788). Small scales, sl. sol. alcohol. Cold, very dilute potash, converts it into the quinone $C_6H_2(OH)(NHPh)O_2$, a blue crystalline pp. decomposing above 200°.

Methyl ether $C_6H_2(OMe)(NHPh)<{}^{O}_{NPh}$. [194°]. Formed by warming the compound $C_6H_2(NHPh)_2O(NPh)$ with MeOH and H_2SO_4 (Z. a. H.), and also from azophenine, MeOH, and H_2SO_4 (Fischer a. Hepp, *B.* 21, 677; *A.* 262, 253). Brownish-red plates, forming blue salts with acids, $C_6H_2(OMe)(NHPh)O_2$ [189°].

Ethyl ether $C_6H_2(OEt)(NHPh)O(NPh)$. [137°]. Formed in like manner, using EtOH.

Isobutyl ether [138°]. Needles.

OXY-PHENYL-AMIDO-THYMOQUINONE $C_6Me(C_3H_7)(OH)(NHPh)O_2$. [135°]. Formed by boiling oxy-thymoquinone with aniline and alcohol (Schulz, *B.* 16, 902). Lustrous, dark-violet needles (from alcohol), forming a violet solution in NH_3Aq.

OXY-PHENYL-AMIDO-TOLUQUINONE $C_6HMeO_2(OH)(NHPh)$. Formed from di-phenyl-di-amido-toluquinone by boiling with alcoholic H_2SO_4 (Hagen a. Zincke, *B.* 16, 1560). Deep-blue needles (from alcohol), decomposing at 250°.

Anilide $C_6HMe(OH)(NHPh)<{}^{O}_{NPh}$. Formed by treating its ethers with acids or alkalis. Brown needles (from HOAc). The ethers $C_{19}H_{15}MeN_2O_2$ [131°], $C_{19}H_{15}EtN_2O_2$ [116°] and $C_{19}H_{15}(C_4H_9)N_2O_2$ [117°] are crystalline.

ω-**OXY-PHENYL-ω-AMIDO-TOLYL GLYCOLLIC ACID** $NHPh.CH(OH).C_6H_4.O.CH_2.CO_2H$. Formed from *o*-aldehydo-phenoxy-acetic acid and aniline (Rossing, *B.* 17, 2992). Very unstable in alkaline solution.—HA′HCl. [191°].—$HA'H_2SO_4$. [186°]. Yellow needles, v. sol. hot water.

m-**OXY-DIPHENYLAMINE** $C_6H_5NH.C_6H_4(OH)$. *Phenyl-amido-phenol.* [82°]. (c. 340°). Formed by heating resorcin (1 mol.) with aniline (4 mols.) and $CaCl_2$ (2 mols.) for eight hours at 280°; the yield being 85 p.c. of the theoretical (Calm, *B.* 16, 2786; Kohler, *B.* 21, 908). White pearly plates, v. sol. alcohol. Yields a crystalline nitrosamine $NPh(NO).C_6H_4.OH$ [115°].—HA′HCl: needles.—$H_2A'_2H_2SO_4$: needles.—BaA'_2 5aq: colourless plates, sol. water.

p-Oxy-diphenylamine $C_6H_5NH.C_6H_4OH$. [70°]. (330°). Prepared by heating hydroquinone (1 mol.) with aniline (4 mols.) and $CaCl_2$ (2 mols.) for ten hours at 260°; the yield being 90 p.c. (Calm, *B.* 16, 2799; 17, 2431). Formed also by heating hydroquinone with aniline for sixteen hours at 300° (the yield being 85 p.c.), and by the action of aniline on quinone phenylimide (Bandrowski, *M.* 9, 133, 416). Plates, v. sol. aqueous alkalis and acids; sl. sol. water. Yields a nitrosamine [95°]. On oxidation with HgO in benzene it yields $C_{12}H_9NO$ [97°] (B.).—HA′HCl: slender needles, decomposed by water.—HA′HBr: needles.

Isobutyl ether C_4H_9A'. [68°].

Formyl derivative $C_{12}H_{10}NO(CHO)$. [178°]. White needles, sol. alcohol.

Di-acetyl derivative $NPhAc.C_6H_4OAc$. [120°]. Monoclinic prisms.

Di-benzoyl derivative [175°]. Prisms.

Di-oxy-diphenylamine $NH(C_6H_4OH)_2$. Formed by heating resorcin with ammoniacal $CaCl_2$ at 200° (Seyevitch, *C. R.* 109, 946). Minute crystals (from dilute alcohol).

o-**OXY-PHENYL-ANGELIC ACID** $C_{11}H_{12}O_3$ *i.e.* $C_6H_4(OH).CH{:}CMe.CH_2.CO_2H$? [73°]. Formed from salicylic aldehyde, sodium pyrotartrate, and Ac_2O (Fittig a. Brown, *A.* 255, 290). Large plates, v. sol. chloroform.—BaA'_2 4aq.—AgA′: flocculent pp.

o-Oxy-phenyl-angelic acid $C_6H_4(OH).CH{:}CEt.CO_2H$. [174°]. Formed by boiling its anhydride with potash (Perkin, *A.* 150, 84; *C. J.* 21, 472). Flat prisms (from dilute alcohol), sl. sol. water and chloroform.—AgA′: yellowish pp.

Anhydride $C_6H_4<{}^{CH:CEt}_{O-CO}$. [71°]. (299°). Formed by boiling sodium salicylic aldehyde

with butyric anhydride (Perkin, *A.* 147, 233; *C. J.* 21, 53, 472; Fletcher, *C. J.* 39, 447). Formed also by distilling coumaryl-propionic acid (Fittig, *A.* 255, 288). Monoclinic crystals, $a:b:c = 1{\cdot}192:1:{\cdot}694$; $\beta = 67° 18'$.

(α) *Methyl derivative* $C_6H_4(OMe).CH:CHEt.CO_2H$. [88°]. Formed from the anhydride NaOH, and MeI, the resulting $C_6H_4(OMe).CH:CHEt.CO_2Me$ (282°) being saponified (Perkin, *C. J.* 39, 435). Monoclinic crystals.

(β)-*Methyl derivative* $C_6H_4(OMe).CH:CEt.CO_2H$. [105°]. Formed from methyl-salicylic aldehyde, butyric anhydride, and sodium butyrate. Needles (from alcohol). Yields $C_6H_2Br_2(OMe).C_4H_6Br_2.CO_2H$ [159°] and $C_6H_4(OMe).CH:CEt.CO_2Me$ (292°). HI forms a compound whence Na_2CO_3 produces o-butenyl-phenol.

p-**Oxy-phenyl-angelic acid** $C_6H_4(OH).CH:CEt.CO_2H$. *Methyl derivative.* [124°]. Formed from anisic aldehyde, butyric anhydride, and sodium butyrate (Perkin). Needles (from alcohol).

γ-**Oxy-phenyl-angelic acid.** *Anhydride* $C_6H_5CH\Big\langle{CH:CMe \atop CO-O}$. [53°]. Made by distilling α-phenyl-levulic acid (Erdmann, *A.* 254, 219). Plates (from CS_2 and ligroïn).

Di-oxy-phenyl-angelic acid. *Methylene derivative* $CH_2\Big\langle{O \atop O}\Big\rangle C_6H_3.CH_2.CH:CH.CH_2.CO_2H$. *Hydro-piperic acid.* [78°]. Formed by reducing piperic acid with sodium-amalgam (Foster, *A.* 124, 117; Buri, *A.* 216, 172; Weinstein, *A.* 227, 32). Needles (from hot water). Changes on heating with NaOHAq into a less soluble isomeric acid [131°]. Both acids combine with bromine.—NH_4A'.—KHA_2.—BaA'_2.—AgA′: crystalline pp.

Di-oxy-phenyl-angelic acid. *Methylene derivative* $CH_2\Big\langle{O \atop O}\Big\rangle C_6H_3.C_4H_6.CO_2H$. [c. 160°]. Prepared by heating piperonal with butyric anhydride and NaOAc (Lorenz, *B.* 14, 786). Long felted needles (from dilute alcohol), sl. sol. water.—AgA′: curdy pp.

Di-*p*-oxy-di-phenyl-angelic acid. *Di-methyl derivative* $C_6H_4(OMe).CH:CH.CH(CO_2H).CH_2.C_6H_4(OMe)$. [111°]. Made by reducing $(C_6H_4(OMe).CH)_2C_2H.CO_2H$ with sodium-amalgam (Fittig a. Politis, *A.* 255, 302). Hard needles (from CS_2), sl. sol. water, v. sol. alcohol. Yields a dibromide $C_{19}H_{20}Br_2O_4$.—CaA'_2 2aq.—AgA′: flocculent pp.

DI-OXY-DI-PHENYL-ANTETRAZINE DI-HYDRIDE ${N=C(OH).\overset{|}{C}.CH_2.\overset{|}{C}\text{——}N:\overset{|}{C}Ph \atop CPh:N\text{——}C.CH_2.C.C(OH):N}$. Formed from dioxyterephthalic ether, benzamidine hydrochloride, and dilute (10 p.c.) NaOHAq (Pinner, *B.* 22, 2624). Crystalline powder, insol. water and alcohol.—$C_{22}H_{14}Na_2N_4O_2$ 4aq: white needles.

OXY-PHENYL-ANTHRANOL $C_{20}H_{14}O_2$ *i.e.* $C_6H_4\Big\langle{C(OH)\text{——} \atop C(C_6H_4OH)}\Big\rangle C_6H_4$. Formed by the action of H_2SO_4 on oxy-triphenyl-methane carboxylic acid (Pechmann, *B.* 13, 1610). Exhibits green fluorescence in ethereal solution.

Di-oxy-phenyl-anthranol $C_{20}H_{14}O_3$ *i.e.* $C_6H_4\Big\langle{C(C_6H_4OH) \atop C(OH)\text{——}}\Big\rangle C_6H_4$. *Phenolphthalidin.* A sticky mass got by dissolving phenol-phthalin in H_2SO_4 and pouring into water (Baeyer, *A.* 202, 91). Its ethereal solution fluoresces green. Water at 170° converts it into phenol-phthalin. Potash-fusion gives di-oxy-benzophenone.

OXY-PHENYL-ARSINE *v.* ARSINE.

DI-OXY-PHENYL-TRIAZOLE $C_8H_7N_3O_2$ *i.e.* ${C_6H_5.N-C(OH) \atop N=C(OH)}\Big\rangle N$ or ${C_6H_5.N.CO \atop HN.CO}\Big\rangle N$. *Phenyl-urazol.* [263°].

Formation.—1. By heating phenyl-hydrazine hydrochloride (1 pt.) with urea (2 pts.) for 4 or 5 hours at 160°, the yield is 70–80 p.c. of the hydrazine hydrochloride used.—2. By heating phenyl-semicarbazide (1 pt.) with urea (2 pts.) for 4 hours at about 160°.

Properties.—Colourless glistening plates. M. sol. hot water, sl. sol. cold water, v. sol. hot alcohol, sl. sol. ether. Dissolves in cold aqueous alkalis and ammonia, and is reppd. by acids unaltered. It does not reduce alkaline solutions of Ag or Cu. It is not affected by boiling with alkalis or acids (Pinner, *B.* 20, 2358).

TETRA-OXY-PHENYL-BENZOPYRAZOLE $NPh\Big\langle{CO.\overset{|}{C}:C(OH).\overset{|}{C}=N \atop N=C.C(OH):C\ .\ CO}\Big\rangle NPh$. [c. 150°]. Formed by the action of HClAq on the phenyl-hydrazide which is made by warming di-oxy-quinone dicarboxylic ether with alcohol and phenyl-hydrazine (Böniger, *B.* 22, 1291). Begins to decompose at 125°.—$(NH_4)_2A''$: ochre-yellow powder, sol. water.

OXY-DI-PHENYL-BENZYLIDENE-PYRAZOLE ${NPh.CO \atop N=CPh}\Big\rangle C:CHPh$. [147°]. Formed from oxy-di-phenyl-pyrazole and benzoic aldehyde (Knorr a. Klotz, *B.* 20, 2548). Needles.

Di-oxy-tetra-phenyl-benzylidene-dipyrazole $\Big({NPh.CO \atop N=CPh}\Big\rangle CH\Big)_2:CHPh$. [c. 220°]. Formed from benzoic aldehyde and excess of oxy-di-phenyl-pyrazole.

Exo-**OXY-PHENYL-BENZYL-KETONE** *v.* BENZOÏN.

Tri-oxy-phenyl-benzyl-ketone. *Di-methyl-derivative v.* ANISOÏN.

Hexa-oxy-phenyl-benzyl-ketone. *Hexa-methyl derivative* $C_6H_2(OMe)_3.CO.CH_2.C_6H_2(OMe)_3$. [162°]. Formed from hexamethoxy-benzil, HOAc, and zinc-dust (Marx, *A.* 263, 255). Needles, insol. cold water.

OXY-PHENYL-BENZYL-METHYL-PYRIMIDINE $CPh\Big\langle{N.CMe \atop N:C(OH)}\Big\rangle C.CH_2Ph$. [243°]. Formed from benzamidine hydrochloride, benzyl-acetoacetic ether, and dilute (10 p.c.) NaOHAq (Pinner, *B.* 22, 1626). Needles, insol. water, v. sl. sol. alcohol.

Di-oxy-phenyl-benzyl-methyl-pyrimidine. *Ethyl derivative* $C_6H_4(OEt).C\Big\langle{N.CMe \atop N:C(OH)}\Big\rangle C(OH)$. [242°]. Formed from *p*-ethoxy-benzamidine hydrochloride, benzyl-acetoacetic ether, and NaOHAq (Pinner, *B.* 23, 2955). Needles, v. sl. sol. hot alcohol.

OXY-PHENYL-BENZYL-PYRIMIDINE
$CH_2Ph.C\left\langle\begin{matrix}N.CPh\\N:C(OH)\end{matrix}\right\rangle CH$. [233°]. Made from phenylacetamidine hydrochloride, benzyl-aceto-acetic ether and dilute (10 p.c.) NaOHAq (Pinner, *B.* 22, 1623). Needles, v. sl. sol. water.

Oxy-phenyl-di-benzyl-pyrimidine
$CH_2Ph.C\left\langle\begin{matrix}N.C(CH_2Ph)\\N:C(OH)\end{matrix}\right\rangle CPh$. [180°]. Formed by heating 'cyanbenzyline' (derived from benzyl cyanide) with HClAq (Wache, *J. pr.* [2] 39, 258).

Di-oxy-phenyl-benzyl-pyrimidine
$CHPh(OH).C\left\langle\begin{matrix}N.CPh\\N:C(OH)\end{matrix}\right\rangle CH$. [218°]. Formed from α-oxy-phenyl-acetamidine and benzoyl-acetic ether (Pinner, *B.* 23, 2951). Felted needles, v. sl. sol. water, sol. alkalis and acids.

ν-OXY-PHENYL-BIURET
$(NHPh.CO)_2N(OH)$. [178°]. Formed by the action of an aqueous solution of hydroxylamine on phenyl cyanate (von der Kall, *A.* 263, 263). Needles, sl. sol. hot water. Does not reduce Fehling's solution.

p-OXY-PHENYL-BROMO-p-TOLYL-THIO-UREA $C_6H_4(OH).NH.CS.NH.C_7H_6Br$.
Acetyl derivative. [156°]. Formed by the action of acetyl-oxy-phenyl-thiocarbimide on bromo-p-toluidine (Kalckhoff, *B.* 16, 1832). V. sol. acetic acid, sl. sol. alcohol and ether, insol. water.

OXY-PHENYL-BUTANE *v.* BUTYL-PHENOL.

Di-oxy-phenyl-butane
$CHPh(OH).C_2H_4.CH_2OH$. (c. 200°). A thick syrup formed by reduction of $C_6H_5.CO.C_2H_4.CHO$ (Burcker, *A. Ch.* [5] 26, 469).

Di-oxy-di-phenyl-butane
$CPhMe(OH).CPhMe(OH)$. [120°]. Formed by adding sodium-amalgam to a solution of aceto-phenone in dilute alcohol (Emmerling a. Engler, *B.* 4, 147; 6, 1005; Buchka, *B.* 10, 1714). Long prisms, insol. water, v. sol. alcohol. Split up by long boiling in acetophenone and phenyl-methyl-carbinol (Zincke a. Thörner, *B.* 13, 641).

Di-oxy-tetra-phenyl-butane
$CH_2Ph.CPh(OH).CPh(OH).CH_2Ph$. [213°]. Formed, together with an isomeride [172°], by reducing benzoïn with zinc (Limpricht a. Schwanert, *A.* 155, 60; Zagoumenny, *B.* 7, 1651; Wislicenus, *A.* 248, 5). The compound [213°] is formed, together with an isomeride (?) [61°], by reducing benzoïn with Na and alcohol (Limpricht, *A.* 155, 98). The compounds [172°] and [213°] are both converted by heat into phenyl benzyl ketone and phenyl-benzyl-carbinol.

OXY-DI-PHENYL-BUTANE CARBOXYLIC ACID $C_6H_5.CH(CO_2H).CH_2.CH(OH).CH_2.C_6H_5$. *Tetrahydrocornicularic acid.* Formed by reducing hydro-cornicularic acid with sodium-amalgam (Spiegel, *A.* 219, 35). Thick oil, decomposed by boiling with water, yielding the lactone.
Lactone $C_{17}H_{16}O_2$. [71°].

Oxy-phenyl-butane dicarboxylic acid *v.* OXY-BENZYL-PYROTARTARIC ACID.

Di-oxy-di-phenyl-butane dicarboxylic acid $C_6H_4(OH).CH_2.CH(CO_2H).CH(CO_2H).CH_2.C_6H_4.OH$. Formed by heating salicylic aldehyde with sodium succinate and Ac_2O, saponifying the resulting 'dicoumarin,' and reducing the product with sodium amalgam (Fittig a. Dyson, *A.* 255, 281). Colourless crystals, v. sol. alcohol.—$CaC_{18}H_{16}O_6$ 6aq.—Ag_2A'': bulky white pp.
Lactone
$C_6H_4\left\langle\begin{matrix}O.CO\\CH_2\end{matrix}\right\rangle CH.CH\left\langle\begin{matrix}CO.O\\CH_2\end{matrix}\right\rangle C_6H_4$. *Dicoumarin tetrahydride.* [224°]. Formed by heating the acid above 100°. Needles (from chloroform-alcohol).

Di-oxy-di-phenyl-butane dicarboxylic acid.
Lactone $C_6H_4\left\langle\begin{matrix}CH.CH_2.CH_2.CH\\ \diagdown\quad\diagup \\ CO.\;O\quad O.CO\end{matrix}\right\rangle C_6H_4$.
[210°]. Formed by treating $C_2H_4(CO.C_6H_4.CO_2H)_2$ with sodium-amalgam (Gabriel a. Michael, *B.* 10, 2209). Needles (from alcohol), insol. water. The corresponding acid is unstable.

DI-p-OXY-DI-PHENYL-BUTINENE. *Di-methyl ether*
$C_6H_4(OMe).CH:CH.CH:CH.C_6H_4(OMe)$. [225°]. A body formed on heating anisic aldehyde with sodium succinate and Ac_2O at 120° (Fittig a. Politis, *A.* 255, 307). Crystals, insol. water, m. sol. HOAc.

DI-OXY-DI-PHENYL-BUTINENE DI-CARBOXYLIC LACTONE
$C_6H_4\left\langle\begin{matrix}O-CO\;\;CO.O\\CH:C-C\;\;:CH\end{matrix}\right\rangle C_6H_4$. *Dicoumarin* [above 330°]. Made by heating salicylic aldehyde with sodium succinate and Ac_2O at 140° (Fittig a. Dyson, *A.* 255, 275). Needles (from HOAc). Not attacked by cold alkalis.

o-OXY-PHENYL-BUTYLENE DICARBOXYLIC ACID. *Lactone* $C_6H_4\left\langle\begin{matrix}O-CO\\CH:C.CHMe.CO_2H\end{matrix}\right.$.
[171°]. Made by heating salicylic aldehyde with sodium pyrotartrate and Ac_2O for 30 hours at 120° (Fittig a. Brown, *A.* 255, 285). Plates (from water). Yields $Ba(C_{12}H_9O_4)_2$ 3aq, CaA'_2 5aq, and AgA'.

Di-oxy-di-phenyl-butylene dicarboxylic acid.
Lactonic acid
$C_6H_4\left\langle\begin{matrix}O-CO\\CH:C.CH(CO_2H).CH_2.C_6H_4(OH)\end{matrix}\right.$? Formed by boiling dicoumarin with NaOHAq and adding sodium-amalgam (Fittig a. Dyson, *A.* 255, 277). Needles, sl. sol. hot water. — BaA'_2 $x$aq. — $AgC_{18}H_{13}O_5$: curdy pp.
Lactone $C_6H_4\left\langle\begin{matrix}O-CO\;CO.O\\CH:C-CH.CH_2\end{matrix}\right\rangle C_6H_4$.
[256°]. Obtained by heating the lactonic acid at 130°. Crystals, insol. water, Na_2CO_3Aq, and NaOHAq. Yields an unstable dibromide.

α-OXY-β-PHENYL-*iso*-BUTYRIC ACID
$CH_2Ph.CMe(OH).CO_2H$. [99°]. Made by the action of KCy on the bisulphite compound of benzyl methyl ketone, the product being saponified (Gabriel a. Michael, *B.* 12, 814). Long prisms, sol. water and alcohol.

β-Oxy-β-phenyl-isobutyric acid
$CHPh(OH).CHMe.CO_2H$. [125°]. Formed by reducing α-benzoyl-propionic acid with sodium-amalgam (Perkin, jun., a. Calman, *C. J.* 49, 161). Needles, v. e. sol. hot water.—AgA': crystals.

β-Oxy-γ-phenyl-butyric acid
$CH_2Ph.CH(OH).CH_2.CO_2H$. [98°]. Formed by boiling phenyl-isocrotonic acid with NaOHAq (Fittig, *B.* 24, 84). Flat needles.

γ-Oxy-γ-phenyl-butyric acid
$CHPh(OH).CH_2.CH_2.CO_2H$. '*Benzhydrylpropionic acid.*' [75°]. Formed by reducing benzoyl-propionic acid with sodium-amalgam (Burcker,

Bl. [2] 37, 5; *A. Ch.* [5] 26, 455); and also by boiling its lactone with baryta. Flat crystals (from CS_2), splitting up at 70° into water and lactone. Chromic acid mixture oxidises it to benzoyl-propionic acid.—BaA'_2.—CuA'_2.—AgA': crystalline pp.

Lactone $CHPh<\begin{matrix}O-CO\\CH_2.CH_2\end{matrix}>$. [37°]. (306°). Formed from γ-bromo-γ-phenyl-butyric acid by treatment with Na_2CO_3 or boiling with water (Jayne, *A.* 216, 103). Formed also by boiling phenyl-paraconic acid with diluted (1:1) H_2SO_4 (Erdmann, *A.* 228, 178). Six-sided trimetric tables (from CS_2); $a:b:c = \cdot611:1:\cdot426$. It has a pleasant odour, and is volatile with steam.

Amide $CHPh(OH).CH_2.CH_2.CO.NH_2$. [86°]. Formed by heating the lactone with alcoholic NH_3 at 100° (Fittig, *A.* 256, 155). Monoclinic prisms, v. sol. hot water. Forms unstable $C_{10}H_{13}NO_2HCl$, crystallising in needles.

o-Oxy-phenyl-butyric acid. *Methyl derivative.* $C_6H_4(OMe).C_3H_6.CO_2H$. [56°]. Obtained by reducing either (α)- or (β)-methoxy-phenyl-crotonic acid with sodium amalgam (Perkin, *C. J.* 39, 433). Transparent prisms (from light petroleum). May be distilled.—BaA'_2 (dried at 100°).

α-Oxy-di-phenyl-isobutyric acid *v.* DI-BENZYL-GLYCOLLIC ACID.

γ-Oxy-di-γ-phenyl-butyric acid $CPh_2(OH).C_2H_4.CO_2H$. [145°]. Made from its lactone (Auger, *A. Ch.* [6] 22, 316). Thin leaflets (from alcohol). Changes to lactone on melting, but is stable at 100°.—BaA'_2: micaceous plates, sol. water.

Lactone $CPh_2<\begin{matrix}O-CO\\CH_2CH_2\end{matrix}$. [90°]. Formed by the action of succinyl chloride on benzene in presence of $AlCl_3$. Leaflets; insol. water, sl. sol. cold alcohol.

Oxy-tri-phenyl-butyric acid $CHPh(OH).CH_2.CPh_2.CO_2H$. Formed by reducing di-phenyl-benzoyl-propionic acid in alkaline solution with sodium-amalgam (Japp a. Klingemann, *C. J.* 57, 680; *B.* 22, 2882). White solid, sol. Na_2CO_3Aq.

Lactone $C_{22}H_{18}O_2$ [153°]. Small needles, sol. hot alcohol.

βγ-Di-oxy-γ-phenyl-butyric acid $CHPh(OH).CH(OH).CH_2.CO_2H$. [118°]. Made from its lactone, which is got by oxidising phenyl-isocrotonic acid with $KMnO_4$ (Fittig, *B.* 21, 920). Crystals, forming the lactone on melting.

Lactone $CHPh<\begin{matrix}O.CO\\CH(OH)\end{matrix}>CH_2$. [87°]. Melts when hydrated (with ½ aq) at 77°.

Di-oxy-phenyl-butyric acid.

Methyl derivative [4:1] $C_6H_4(OMe).CH(OH).CH_2.CH_2.CO_2H$. Got from its lactone [53·5°], which is made by the action of sodium-amalgam on bromo-*p*-methoxy-phenyl-butyrolactone (Fittig a. Politis, *A.* 255, 299). The free acid is solid, and yields the lactone when heated to 80°.—BaA'_2: amorphous mass.

Di-oxy-phenyl-isobutyric acid.

Methyl derivative [4:3:1] $C_6H_3(OH)(OMe).CH_2.CHMe.CO_2H$. *Hydrohomo-ferulic acid.* [115°]. Obtained by reducing $C_6H_3(OH)(OMe).CH:CMe.CO_2H$ (Tiemann a. Kraaz, *B.* 15, 2070). Sol. water, alcohol, and ether.

Di-methyl derivative $C_6H_3(OMe)_2.CH_2.CHMe.CO_2H$. *Methyl-hydro-homoferulic acid.* [59°]. Got in like manner. Crystals.

Methylene derivative $C_6H_3(O_2CH_2).CH_2.CHMe.CO_2H$. *Hydrohomo-caffeïc acid.* [77°]. Formed by reduction of the methylene derivative of di-oxy-phenyl-methacrylic acid (Lorenz, *B.* 13, 760). Thick prisms, sl. sol. water, v. sol. alcohol and ether.

Di-oxy-di-phenyl-butyric acid? $CH_3.CPh(OH).CPh(OH).CO_2H$. Formed from its nitrile, which is made from acetophenone, KOH, and aqueous K_3FeCy_6 (Buchka, *B.* 20, 389).—BaA'_2 3½aq.

***o*-OXY-PHENYL-CARBAMIC ACID.** *Ethyl ether* $C_9H_{11}NO_3$ *i.e.* $C_6H_4(OH).NH.CO_2Et$. [85°]. Formed from o-amido-phenol and $ClCO_2Et$ (Groenvik, *Bl.* [2] 25, 177). Triclinic prisms (from ether-alcohol), almost insol. cold water. Yields, on distillation, alcohol and the anhydride.

Anhydride $C_6H_4<\begin{matrix}NH\\O\end{matrix}>CO$ or $C_6H_4<\begin{matrix}N\\O\end{matrix}>C.OH$. *Oxycarbanil. Oxymethenyl-amidophenol. Anhydro-o-amido-phenyl-carbonic acid. Carbonyl-amido-phenol.* [138°]. (above 360°).

Formation.—1. As above.—2. By heating oxy-phenyl-urea (Kalckhoff, *B.* 16, 1828).—3. By distilling o-amido-phenyl ethyl carbonate (Bender, *B.* 19, 2269, 2950).—4. By heating a mixture of urea and o-amido-phenol (Sandmeyer, *B.* 19, 2655).—5. By the action of phosgene on o-amido-phenol in benzene (Chetmicki, *B.* 20, 177; Jacoby, *J. pr.* [2] 37, 29).—6. By heating o-amido-phenyl di-phenyl-carbamate (Lellmann a. Bonhöffer, *B.* 20, 2126).

Properties.—Needles (from water), sol. alcohol, ether, and alkalis. Decomposed by heating with HClAq above 150° into CO_2 and *o*-amido-phenol. Bleaching-powder and HCl yield crystalline $C_6H_3Cl<\begin{matrix}NCl\\O\end{matrix}>CO$, whence further action of HClAq forms $C_6H_3Cl<\begin{matrix}NH\\O\end{matrix}>CO$ [196°]. Br forms $C_7H_3BrO_2(NH)$ [196°]. HNO_3 produces $C_7H_3(NO_2)O_2NH$ [256°]. Injected into rabbits, it becomes $C_6H_3(OSO_3H)<\begin{matrix}NH\\O\end{matrix}>CO$ (Nencki, *M.* 11, 253).—$AgC_7H_4NO_2$: curdy pp.

Acetyl derivative $C_7H_4O_2NAc$. [98°]. Crystallises from water.

Phenyl-hydrazide $C_6H_4<\begin{matrix}NH\\O\end{matrix}>C:N_2HPh$. [208°]. Yellow needles.

Ethyl derivative $C_6H_4<\begin{matrix}NEt\\O\end{matrix}>CO$. [29°]. (300°). Formed from the silver salt and EtI. Crystalline. Converted into ethyl-amido-phenol by heating with fuming HClAq at 180°.

Ethyl ether $C_6H_4<\begin{matrix}N\\O\end{matrix}>C.OEt$. (225°-230°). Formed from amido-phenol hydrochloride and $NH:C(OEt)_2$ (Sandmeyer). Liquid, converted by HClAq into EtCl and $C_6H_4<\begin{matrix}NH\\O\end{matrix}>CO$.

p-**Oxy-phenyl-carbamic acid.** *Ethyl ether* $C_9H_{11}NO_3$ *i.e.* $C_6H_4(OH).NHCO_2Et$. [120°]. Formed from *p*-amido-phenol and $ClCO_2Et$ (Groenvik, *Bl.* [2] 25, 179). Monoclinic tables, v. sol. alkalis. The ethyl derivative $C_6H_4(OEt).NHCO_2Et$, formed from $ClCO_2Et$ and $C_6H_4(NH_2)(OEt)$ (Köhler, *J. pr.* [2] 29, 257), crystallises in needles [94°], insol. water.

Reference. — Chloro-oxy-phenyl-carbamic acid.

p-**OXY-DI-PHENYL-CARBINOL** $C_{13}H_{12}O_2$ *i.e.* $C_6H_5.CH(OH).C_6H_4(OH)$. [161°]. Formed by reducing oxy-benzophenone with sodium-amalgam (Doebner, *A.* 210, 253). Silky needles (from water). Coloured red by $FeCl_3$.

op-**Di-oxy-di-phenyl-carbinol** $CH(OH)(C_6H_4.OH)_2$. [160°–165°]. Made by reducing di-oxy-benzophenone (salicyl-phenol) with sodium-amalgam (Michael, *B.* 14, 657). Amorphous powder, sol. hot alcohol.

Di-oxy-tri-phenyl-carbinol $C_6H_5.C(OH)(C_6H_4OH)_2$. [c. 100°]. Made by warming $PhCCl_3$ with dry phenol, and treating the product with water (Doebner, *A.* 217, 227). Formed also by warming phenyl-glyoxylic acid with phenol and H_2SO_4 at 120° (Homolka, *B.* 18, 988). Brick-red powder, insol. cold water; melts under hot water. Its alcoholic solution dyes silk feebly yellow. In alkalis it dissolves with deep violet-red colour, and is reppd. by acids.

Di-acetyl derivative $C_6H_5.C(OH)(C_6H_4OAc)_2$. [119°]. Colourless prisms (from dilute alcohol).

Tri-oxy-tri-phenyl-carbinol. *Anhydride* $C_{19}H_{14}O_3$ *i.e.* $(C_6H_4(OH))_2C\langle{}^{C_6H_4}_{O}\rangle$. *Aurin. Rosolic acid.*

Formation. — 1. By heating phenol with oxalic acid and H_2SO_4 (Kolbe a. Schmitt, *A.* 119, 169; Dale a. Schorlemmer, *A.* 196, 79).—2. By heating phenol with formic acid and $ZnCl_2$ at 120° (Nencki a. Schmid, *J. pr.* [2] 23, 549; 25, 273).—3. By the action of $AlCl_3$ on a mixture of phenol and tri-chloro-nitro-methane (Elbs, *B.* 16, 1275).—4. From para-rosaniline by the diazo- reaction (Fischer, *A.* 194, 268).—5. From di-*p*-oxy-benzophenone by treatment with PCl_5, and heating the product with phenol and H_2SO_4 (Caro a. Graebe, *B.* 11, 1350).

Preparation.—Phenol (10 pts.) is heated with dried oxalic acid (7 pts.) and H_2SO_4 (5 pts.) at 120°-130° about 24 hours, until gas no longer comes off rapidly. The product is poured into water, the pp. dissolved in NaOHAq, saturated with SO_2, and mixed with much water. The filtrate from ψ-rosolic acid (which amounts to 70 p.c. of crude product) is saturated at 70° with HCl, and on cooling it deposits aurin sulphite. This is recrystallised from dilute alcohol, which deposits methyl-aurin on cooling, while the mother-liquor, saturated with SO_2, deposits aurin sulphite, which is freed from SO_2 by heat (Zulkowsky, *A.* 194, 119; 202, 184).

Properties. — Dark-red trimetric crystals (from alcohol-HOAc) or red needles with green lustre (from alcohol). Not melted below 220°. Its alkaline solution is crimson.

Reactions.—1. Reduced by *zinc-dust* and HOAc to tri-oxy-tri-phenyl-methane.—2. Aqueous NH_3 at 120° yields para-rosaniline.—3. *Water* at 250° yields phenol and di-*p*-oxy-benzophenone.—4. On warming with KOHAq and KCy and adding HCl, a product is got which, when heated with Ac_2O, yields tri-acetyl-hydrocyanaurin [194°].

Salts.—$(NH_4)_2C_{19}H_{12}O_3$: dark-red needles with steely lustre.—$C_{19}H_{14}O_3HCl1\frac{1}{2}HOEt$: red crystals.—$(C_{19}H_{14}O_3HCl)HOAc$: red needles.—$(C_{19}H_{14}O_3)_2H_2SO_3 4aq$: brick-red cubes, sl. sol. cold alcohol.—$C_{19}H_{14}O_3(NH_4)HSO_3$.—$C_{19}H_{14}O_3NaHSO_3$. — $C_{19}H_{14}O_3KHSO_3$: minute colourless tables.—$C_{19}H_{14}O_3H_2SO_4$.—$(C_{19}H_{14}O_3)_2H_2SO_4$: bluish-violet needles.

Di-acetyl-derivative $(C_6H_4(OH))_2C(OAc).C_6H_4OAc$. [168°]. Formed from aurin and Ac_2O at 100°. Colourless tables (from alcohol).

Tetra-oxy-tri-phenyl-carbinol $C_{19}H_{16}O_5$ *i.e.* $C_6H_5C(OH)(C_6H_3(OH)_2)_2$.

Anhydride $C_{38}H_{30}O_9$ *Resorcin-benzeïn.* Formed by heating benzo-trichloride with resorcin at 180° (Doebner, *B.* 13, 610; *A.* 217, 234). Large crystals (from alcohol and HOAc). Yellow by transmitted, violet-red by reflected light; at 130° it loses $2H_2O$, and at 200° it is decomposed. Dilute alkaline solutions show yellowish-green fluorescence, but less intense than fluoresceïn; they dye wool yellow. Insol. water, v. sol. alcohol. Zinc-dust and HCl reduce it to tetra-oxy-tri-phenyl-methane. Bromine in alcohol and HOAc forms a fiery-red pp. $C_{38}H_{22}Br_8O_9$, which closely resembles eosin. Its salts dissolve readily in alcohol and dye wool and silk like eosin.

Penta-oxy-tri-phenyl-carbinol $(C_6H_3(OH)_2)_2C(OH).C_6H_4OH$.

Anhydride $C_{19}H_{14}O_6$. Formed by heating resorcin with formic acid and $ZnCl_2$ at 140° (Nencki a. Schmid, *J. pr.* [2] 23, 547). Hygroscopic brick-red powder, v. sol. alcohol.

p-**OXY-DI-PHENYL-CARBINOL o-CARBOXYLIC ACID.**

Methyl derivative of the anhydride $C_6H_4\langle{}^{CH.C_6H_4.OMe}_{CO.O}\rangle$. [117°]. Formed by reducing methoxy-benzophenone carboxylic acid with zinc and alcoholic HCl (Nourrisson, *B.* 19, 2103). Flat white needles, v. sol. warm alcohol, insol. water.

Oxy-tri-phenyl-carbinol carboxylic acid.

Anhydride $C_6H_4(OH)CPh\langle{}^{C_6H_4}_{O}\rangle CO$. *Oxy-di-phenyl-phthalide.* [155°]. Prepared by heating o-benzoyl-benzoic acid with phenol and $SnCl_4$ to 120°; yield 100 p.c. of the benzoyl-benzoic acid (Pechmann, *B.* 13, 1613). Colourless crystals. Sol. all ordinary solvents except water and ligroïn. By fusion with KOH it gives benzoic acid and oxy-benzophenone. With alkalis it forms a deep-red solution. By strong H_2SO_4 it is converted into oxy-phenyl-anthranol $C_6H_4\langle{}^{C(OH)}_{C(C_6H_4.OH)}\rangle C_6H_4$. On reduction it gives oxy-triphenyl-methane carboxylic acid.

Acetyl derivative $C_{20}H_{13}O_2(OAc)$. [136°]. Colourless crystals.

Di-bromo- derivative $C_{20}H_{11}Br_2O_2(OH)$. [196°]. Spikes.

Acetyl di-bromo- derivative $C_{20}H_{11}Br_2O_2(OAc)$ [172°]. Colourless prisms.

ap-di-oxy-di-phenyl-carbinol carboxylic anhydride. *Methyl derivative* $C_6H_4<\begin{smallmatrix}CH(C_6H_4OMe)\\CO\ .\ O\end{smallmatrix}>$. [117°]. Made by reducing '*p*-anisolphthaloylic' acid (Nourrisson, *Bl.* [2] 46, 206). Needles, insol. water, v. e. sol. alcohol.

Di-oxy-tri-phenyl-carbinol carboxylic acid. *Anhydride* $C_6H_3(OH)_2CPh<\begin{smallmatrix}C_6H_4\\O\end{smallmatrix}>CO$. *Benzene-resorcin-phthaleïn.* [176°]. Made by heating benzoyl-benzoic acid with resorcin (Pechmann, *B.* 14, 1859). Prisms (containing $CHCl_3$) melting at 114° (from chloroform). Its alcoholic solution turns greenish-blue on addition of HCl. On heating with H_2SO_4 it yields anthraquinone. H_2SO_4 acting on its solution in HOAc forms $C_{40}H_{26}O_7$ [285°], which yields $C_{40}H_{24}Ac_2O_7$ [245°].

Di-acetyl derivative $C_{20}H_{12}O_2(OAc)_2$. [137°].

Di-bromo- derivative $C_{20}H_{12}Br_2O_4$. [219°].

Tri-oxy-tri-phenyl-carbinol-carboxylic acid. *Anhydride* $(C_6H_2(OH)_3)CPh<\begin{smallmatrix}C_6H_4\\O\end{smallmatrix}>CO$. *Benzene-pyrogallol-phthaleïn.* Prepared by heating benzoyl-benzoic acid with pyrogallol and crystallising the product from acetic acid (Pechmann, *B.* 14, 1864). Four-sided tables (containing AcOH), [190°]. Sol. most solvents except ligroïn, sl. sol. hot water. It dissolves in alkalis with a green colour.

Tri-acetyl derivative $C_{20}H_{11}O_2(OAc)_3$. [231°]. Fine needles. Sol. Ac_2O.

DI-OXY-DI-PHENYL-CARBOLACTONE *v.* *Iso*-EUXANTHIC ACID.

OXY-DI-PHENYL-DI-CARBOXYLIC ACID. *Hexahydride.* $C_{14}H_{16}O_5$. An unstable acid formed by boiling hydro-oxybenzyluric acid with potash (Otto, *A.* 134, 330). Yields Et_2A'' (206°), a heavy oil.

Di-*p*-oxy-diphenyl carboxylic acid $C_{13}H_{10}O_4$ *i.e.* [4:1] $C_6H_4(OH).C_6H_3(OH)(CO_2H)$ [1:4:2]. [270°]. Made by fusing diphenylene-ketone disulphonic acid with potash (Schmidt a. Schultz, *B.* 12, 496). Sl. sol. water, v. sol. hot alcohol.

Di-*p*-oxy-diphenyl dicarboxylic acid $C_6H_3(OH)(CO_2H).C_6H_3(OH).CO_2H$. [151°]. S. ·0052 at 15°. Formed by heating sodium di-oxy-di-phenyl with CO_2 at 200° under high pressure (Schmitt a. Kretzschmer, *B.* 20, 2703). Minute needles, sl. sol. water. $FeCl_3$ colours its solution bluish-violet.

Tetra-oxy-diphenyl dicarboxylic acid $C_6H_2(OH)_2(CO_2H).C_6H_2(OH)_2CO_2H$. *Di-resorcin dicarboxylic acid.* Formed by heating tetra-oxy-diphenyl (diresorcin) with $KHCO_3$ and a little water at 130° (Will a. Albrecht, *B.* 17, 2105). Yellowish powder, decomposing, without melting, above 300°.—K_2A''.—BaA'' 6aq.—Ag_2A'': white pp.

Tetra-oxy-diphenyl dicarboxylic acid $C_6H_2(OH)_2(CO_2H).C_6H_2(OH)_2(CO_2H)$. *Dehydro-diprotocatechnic acid.* [above 300°]. Formed by fusing 'dehydrodivanillin' with potash (Tiemann, *B.* 18, 3495). Amorphous, v. sl. sol. water, sl. sol. alcohol.

Penta-oxy-diphenyl carboxylic acid $C_{14}H_{10}O_9$. Formed by the action of $POCl_3$ on *c*-tri-oxy-benzoic acid (Schiff, *G.* 17, 552; *A.* 245, 37). Yellowish astringent powder.—BaA'_2: greyish-white powder.

Penta-acetyl derivative $C_{14}H_4Ac_5O_9$. White powder, rapidly darkening in air.

Ethyl ether EtA'. [102°].

Penta-oxy-di-phenyl carboxylic acid $C_{14}H_{10}O_9$. Formed by heating phloroglucin carboxylic acid with $POCl_3$ (Schiff). Reddish-brown hygroscopic mass, resembling tannin and the preceding isomeride.

TETRA-OXY-DIPHENYL DICARBOXYLIC ALDEHYDE. *Di-methyl derivative* $C_6H_2(OMe)(OH)(CHO).C_6H_2(OMe)(OH).CHO$. *Divanillin.* [304°]. Formed by boiling vanillin $C_6H_3(OMe)(OH)(CHO)$[3:4:1] with $FeCl_3$ (Tiemann, *B.* 18, 3493). Slender white needles, sl. sol. alcohol, sol. alkalis.

Tetra-methyl derivative. [138°].

***p*-OXY-PHENYL-CINNAMIC ACID.** *Methyl derivative* $C_6H_4(OMe).CH:CPh.CO_2H$. [189°]. Formed from sodium phenyl-acetate, anisic aldehyde, and Ac_2O (Oglialoro, *G.* 9, 533; 10, 481). Prisms (from alcohol), sl. sol. water.

α-OXY-γ-PHENYL-*iso*-CROTONIC ACID $C_6H_5.CH:CH.CH(OH).CO_2H$. [115°]. Formed by boiling cinnamic aldehyde with aqueous HCy and HCl (Matsmoto, *B.* 8, 1144; Peine, *B.* 17, 2114). Formed also by heating the ethyl ether of styryl-ψ-hydantoïn with concentrated baryta-water (Pinner a. Spilker, *B.* 22, 690). Styryl-ψ-hydantoïn $CHPh:CH.CH<\begin{smallmatrix}CO.NH\\O—CNH\end{smallmatrix}$ [198°] is obtained by the action of warm alcoholic potash on styryl-hydantoïn [172°], an isomeric body previously described by Pinner (*B.* 20, 2353) as oxystyryl-pyrazole. Styryl-hydantoïn is got by the action of boiling dilute HClAq on (α)-ur-amido-phenyl-crotonic nitrile $CHPh:CH.CH(NH.CO.NH_2).CN$ [160°], which is made by heating oxy-phenyl-isocrotonic nitrile with urea.

Properties.—Needles, sl. sol. cold water, v. sol. alcohol and ether.

Salts.—PbA'_2 2aq: needles.—AgA': minute needles.

Methyl ether MeA'. (290°). Liquid.

Ethyl ether EtA'. (295°) (Peine).

Nitrile $CHPh:CH.CH(OH).CN$. [81°]. Formed from cinnamic aldehyde, KCy, and HCl. Crystalline grains (from benzene-ligroïn). Converted by hydroxylamine into the crystalline amidoxim $CHPh:CH.CH(OH).C(NH_2):NOH$ (Bornemann, *B.* 19, 1513).

***o*-Oxy-phenyl-crotonic acid** (α)-*Methyl derivative* $C_6H_4(OMe)CH:CMe.CO_2H$. [118°]. Made from its methyl ether by boiling with alcoholic potash (Perkin, *C. J.* 33, 213; 39, 431). Monoclinic crystals (from alcohol); $a:b:c$ = ·863:1:1·252; β = 64° 54′ (Fletcher). Not converted into its (β) isomeride by light. With PCl_5 it gives MeCl, HCl, and the anhydride. Conc. H_2SO_4 also forms propionic coumarin. Sodium-amalgam reduces it to methoxy-phenyl-butyric acid. With Br and with HI it behaves like the (β) acid.

Methyl ether of the (α)-*methyl derivative* $C_6H_4(OMe).CH:CMe.CO_2H$. (275°). S.G. $\frac{15}{15}$ 1·1112; $\frac{30}{30}$ 1·1061. Formed from sodium propionic coumarin and MeI. Liquid.

(β)-*Methyl derivative* $C_6H_4(OMe)CH:CMe.CO_2H$. [107°]. Formed

from methyl-salicylic aldehyde, sodic propionate and propionic acid.

Properties. — Monoclinic crystals; $a:b:c = 1{\cdot}281:1:{\cdot}762$. $\beta = 84°\ 18'$ (Fletcher). With PCl_5 it gives the chloride of the acid. Conc. H_2SO_4 appears to polymerise it. Behaves like the (α)-isomeride with sodium amalgam. With dry bromine vapour it forms the compound $C_6H_2Br_2(OMe)CHBr.CMeBr.CO_2H$ [c. 200°]. With HI (S.G. 1·94) it unites, forming a product whence Na_2CO_3 liberates the methyl derivative of *o*-allyl-phenol.—AgA′: white pp.

Methyl ether of the (β)-methyl derivative MeA′. (c. 286°). S.G. $\frac{15}{15}$ 1·1279; $\frac{30}{30}$ 1·1136.

(β)-*Ethyl derivative* $C_6H_4(OEt)CH:CMe.CO_2H$. [133°]. Formed from ethyl-salicylic aldehyde, sodic propionate, and propionic anhydride. Large tables (from alcohol). Its Ba salt forms satiny needles.

Anhydride $C_6H_4<\begin{matrix}CH:CMe\\O-CO\end{matrix}$. *Propionic coumarin. Methyl-coumarin.* [90°]. (292·5°). Formed by heating sodium-salicylic aldehyde with propionic anhydride (Perkin, *C. J.* 28, 10). Trimetric crystals; $a:b:c = 2{\cdot}1950:1:{\cdot}4001$. Smells like coumarin, m. sol. alcohol, nearly insol. cold KOHAq. Fuming H_2SO_4 forms $C_{10}H_7O_2(SO_3H)$ whence BaA'_2 10aq.

Oxy-phenyl-crotonic acid. *Anhydride* $C_6H_4<\begin{matrix}CMe:CH\\O-CO\end{matrix}$. *$\beta$-Methyl coumarin.* [126°]. Formed by the action of H_2SO_4 on a mixture of acetoacetic ether and phenol (Pechmann a. Duisberg, *B.* 16, 2127).

***p*-Oxy-phenyl-crotonic acid.** *Methyl derivative* $C_6H_4(OMe).CH:CMe.CO_2H$. [154°]. Formed from anisic aldehyde, sodium propionate, and propionic anhydride. Rectangular tables (from alcohol).—AgA′.

***p*-Oxy-phenyl-isocrotonic acid.** *Methyl derivative* $C_6H_4(OMe).CH:CH.CH_2.CO_2H$. [106·5°]. Formed by heating anisic aldehyde with sodium succinate and Ac_2O at 120° (Fittig a. Politis, *A.* 255, 294). Plates, m. sol. hot water.—BaA'_2 3aq.—CaA'_2 2aq.—AgA′: sol. hot water.

γ-Oxy-tri-phenyl-crotonic acid. *Lactone* $C_{22}H_{16}O_2$ *i.e.* $\begin{matrix}CH:CPh\\CPh_2.CO\end{matrix}>O$ (?). [118°]. Mol. w. 329 (by Raoult's method), 312 (calc.). Formed by heating $\alpha\beta$-di-benzoyl-styrene at 310° (Japp a. Klingemann, *C. J.* 57, 679, 702; 59, 148). Lustrous needles or monoclinic prisms. Not attacked by phenyl-hydrazine or Ac_2O at 150°. Bromine forms $C_{22}H_{15}BrO_2$ [109°]. Chromic acid mixture oxidises it to benzophenone. May be reduced to oxy-tri-phenyl-butyric acid. Alcoholic potash at 100° yields $CH_2Bz.CPh_2.CO_2H$, which at 310° changes to the original lactone. Alcoholic methylamine forms $CH_2Bz.CPh_2.CONHMe$. [156°]. Ethylamine acts in like manner.

γ-Oxy-tetra-phenyl-crotonic acid. *Lactone* $\begin{matrix}CPh:CPh\\CPh_2.CO\end{matrix}>O$. *Tabular oxylepiden.* [136°]. S. (alcohol) 7 at 78°. Formed by heating 'acicular oxylepiden' CPhBz:CPhBz at 340° (Zinin, *J. R.* 5, 16; *Bn.* 3, 113; Japp a. Klingemann, *C. J.* 57, 665; Klingemann a. Laycock, *C. J.* 59, 140). Tables (from alcohol): insol. water. Converted by alcoholic potash into $C_{23}H_{21}KO_3$. Methylamine in alcohol at 100° forms $CHPhBz.CPh_2.CONHMe$ [267°] crystallising in triclinic plates.

Di-oxy-phenyl-crotonic acid $C_6H_3(OH)_2.CMe:CH.CO_2H$. ($\beta$)-*methyl-umbellic acid.*

Methyl derivative [4:2:1] $C_6H_2(OH)(OMe).CMe:CH.CO_2H$. [140°]. Formed by boiling the methyl derivative of (β)-methyl-umbelliferon with conc. KOHAq for 5 hours (Pechmann a. Duisberg, *B.* 16, 2125). Four-sided tables, insol. water, v. sol. alcohol. Reconverted into its lactone by boiling with acids or heating with NH_3Aq.

Di-methyl derivative $C_6H_3(OMe)_2.CMe:CH.CO_2H$. [145°]. Formed by saponification of its methyl ether (310°–320°) which is obtained by further methylation of the methyl derivative (Pechmann a. Cohen, *B.* 17, 2132). Small needles, v. sol. alcohol.—AgA′: white powder.

Anhydride $C_6H_3(OH)<\begin{matrix}CMe:CH\\O-CO\end{matrix}$. ($\beta$)-*Methyl-umbelliferone.* [186°]. Formed by the action of H_2SO_4 on a mixture of acetoacetic ether and resorcin (Pechmann a. Duisberg, *B.* 16, 2119; *A.* 261, 169; *cf.* Schmid, *J. pr.* [2] 25, 82). Formed also by warming acetoacetic ether with resorcin and alcoholic potash, and heating the resulting methyl-umbelliferone carboxylic acid [191°] above its melting-point (Michael, *J. pr.* [2] 37, 469). (β)-methyl-umbelliferone is also obtained by heating citric acid with resorcin and H_2SO_4 (Wittenberg, *J. pr.* [2] 24, 125). Plates (by sublimation), sol. alcohol and hot water, sl. sol. ether. Its dilute alkaline solution has blue fluorescence. Potash-fusion forms di-oxy-acetophenone. Yields a nitro-compound, converted by reduction into amido-(β)-methyl-umbelliferone [247°], whence $B'_2H_2SO_4$ 2aq and $C_{10}H_8(NO)NO_3$. Sodium-amalgam reduces (β)-methyl-umbelliferone to $C_{10}H_{10}O_3$ [259°], whence $C_{10}H_9AcO_3$ [222°] (Michael, *Am.* 5, 436).

Acetyl derivative of the anhydride $C_{12}H_{10}O_4$. [150°]. Long white needles, v. sol. alcohol.

Benzoyl derivative of the anhydride $C_{10}H_7BzO_3$. [160°]. Needles (from alcohol).

Methyl derivative $C_6H_3(OMe)<\begin{matrix}CMe:CH\\O-CO\end{matrix}$. [159°]. Needles (from alcohol), insol. water. On reduction with sodium-amalgam it yields $C_6H_3(OMe)<\begin{matrix}CHMe.CH_2\\O\quad CO\end{matrix}$ [244°]. Bromine in chloroform reacts forming $C_6H_3(OMe)<\begin{matrix}CMeBr.CHBr\\O-CO\end{matrix}$ [235°].

(4:3:1)-Di-oxy-phenyl-crotonic acid $C_6H_3(OH)_2.CH:C(CH_3).CO_2H$ [4:3:1]. *Homo-caffeïc acid.*

p-Propionyl-m-methyl derivative $C_6H_3(OCO.C_2H_5)(OMe).CH:C(CH_3).CO_2H$. *Propiohomoferulic acid.* [129°]. Formed by heating vanillin with sodium propionate and propionic anhydride (Tieman a. Kraaz, *B.* 15, 2060). White needles, sol. alcohol, ether, and benzene, insol. water and ligroïn.

m-Methyl derivative $C_6H_3(OH)(OMe).CH:C(CH_3).CO_2H$. *Homoferulic*

acid. [168°]. Large trimetric tables. Sol. alcohol and ether, sl. sol. chloroform, benzene, and hot water, nearly insol. cold water and ligroïn. On heating the acid it splits off CO_2 forming iso-eugenol.—A'_2Ba: yellow needles.

Di-methyl derivative $C_6H_3(OMe)_2.CH:C(CH_3).CO_2H$. *Methyl-homo-ferulic acid.* [141°]. Needles. Sol. alcohol, ether, and hot water.—A'Ag: white crystalline pp.

Di-methyl-derivative-methyl ether $C_6H_3(OMe)_2.CH:C(CH_3).CO_2Me$. [66°]. Colourless plates.

Methylene derivative

$CH_2<\substack{O\\O}>C_6H_3.CH:CMe.CO_2H$. [194°]. Formed by boiling piperonal with propionic anhydride and sodium propionate (Lorenz, *B.* 13, 759). Prisms (from dilute alcohol).—AgA': pp.

Tri-oxy-phenyl-crotonic acid. *Anhydride* $C_6H_2(OH)_2<\substack{CMe:CH\\O\ -\ CO}$. [235°]. Prepared by the action of H_2SO_4 on a mixture of acetoacetic ether and pyrogallol (Wittenberg, *J. pr.* [2] 26, 68; Pechmann a. Duisberg, *B.* 16, 2127). Needles, sol. alcohol and hot water. Coloured green by $FeCl_3$. Yields a di-acetyl derivative [176°]. An isomeride [284°] is formed by using phloroglucin instead of pyrogallol; it yields a di-acetyl derivative [140°] (Pechmann a. Cohen, *B.* 17, 2189).

Tetra-oxy-phenyl-crotonic acid. *Methylene-di-methyl derivative*

$CH_2<\substack{O\\O}>C_6H(OMe)_2.CH:CMe.CO_2H$. [209°]. Formed by heating apionic aldehyde with propionic aldehyde and sodium propionate (Ciamician a. Silber, *B.* 22, 2488). Yellow needles, almost insol. water.—CaA'_2 5aq.—AgA': white gelatinous pp.

OXY-PHENYL-CUMINYLAMINE *v.* CUMINYL-AMIDO-PHENOL.

OXY-PHENYL-CUMYLAMINE *v.* CUMINYL-IDENE-AMIDO-PHENOL.

o-**OXY-PHENYL-CYANAMIDE.** *Ethyl derivative* $C_6H_4(OEt)NH.Cy$. [94°]. Made by passing gaseous ClCy into an ethereal solution of *o*-amido-phenetole (Berlinerblau, *J. pr.* [2] 30, 100). Crystals. Insol. water, v. sol. alcohol and ether. Does not appear to polymerise. With fuming HCl at 120° it gives *o*-amido-phenol.

Salts.—$C_9H_9N_2ONa$. Microscopic needles, got by mixing alcoholic solutions of NaOEt and ethoxy-phenyl-cyanamide. Its aqueous solution does not absorb CO_2.—$C_9H_9N_2OAg$. Curdy pp.

p-Oxy-phenyl-cyanamide. *Ethyl derivative* $C_6H_4(OEt)NHCy$. [78°]. Made in the same way as the *o*- compound. Colourless crystals. Insol. water, v. sol. alcohol and ether.—$C_9H_9N_2OAg$.

OXY-PHENYL-CYANATE. *Ethyl derivative* $C_6H_4(OEt).N:CO$. [219°]. Made by distilling $C_6H_4(OEt).NH.CO_2Et$ (Köhler, *J. pr.* [2] 29, 259). White needles (from HOAc), sol. alcohol and chloroform.

DI-OXY-PHENYL-DI-CYMYL-METHANE $CHPh(C_6H_2MePr.OH)_2$. [146°]. Formed from benzoic aldehyde, thymol, and H_2SO_4 (Russanoff, *B.* 22, 1949). Thin tables (containing EtOH), v. sol. chloroform.

Di-acetyl derivative [126°]. Crystals.

OXY-DIPHENYLENE-ACETIC ACID

$<\substack{C_6H_4\\C_6H_4}>C(OH).CO_2H$. [162°]. Formed by boiling phenanthraquinone with NaOHAq (Baeyer, *B.* 10, 125; Friedländer, *B.* 10, 534). Plates (containing ½aq), v. sl. sol. cold water, v. sol. alcohol. Conc. H_2SO_4 forms a blue solution on warming. Chromic acid mixture yields di-phenylene ketone. NaOHAq at 160° splits it up into fluorene alcohol and CO_2. HIAq and P at 140° reduce it to diphenylene-acetic acid. Bromine forms $C_{14}H_8Br_2O_3$ [225°], whence $C_{14}H_7Br_2EtO_3$ [151°].—CaA'_2 2aq: crystals.

Ethyl ether EtA'. [92°]. Prisms.

DI-OXY-PHENYLENE-DIAMINE $C_6H_2(OH)_2(NH_2)_2$. Got by reducing the dioxim of di-oxy-quinone with $SnCl_2$ and HCl (Nietzki a. Schmidt, *B.* 22, 1656). Yields on oxidation crystalline $C_6H_2(OH)_2(NH)_2$.—$B'H_2SO_4$.

Tetra-acetyl derivative [225°]. Needles.

Isomeride *v.* DI-AMIDO-HYDROQUINONE.

DI-OXY-DIPHENYLENE-DIHYDRAZINE $C_6H_3(OH)(N_2H_3).C_6H_3(OH)(N_2H_3)$. [140°]. Formed by reducing the diazo- compound from di-oxy-di-amido-diphenyl with $SnCl_2$ (Kunze, *B.* 21, 3333). Thin plates, forming with acetone a compound $C_{18}H_{22}N_4O_2$ [200°].

OXY-DIPHENYLENE KETONE $C_{13}H_8O_2$ *i.e.* $CO<\substack{C_6H_4\\C_6H_3.OH}$. [96°] (G.); [91°] (R.). Formed by warming dry sodium salicylate with excess of $POCl_3$ and distilling (R. Richter, *J. pr.* [2] 28, 294). It is also one of the products of the action of phenol on the sulphate of *o*-diazo-benzoic acid (Griess, *B.* 21, 981). Needles, insol. water, v. sol. hot alcohol. Its vapour passed over red-hot lime yields diphenylene ketone and di-phenylene-ketone oxide [82°]. Distilled over red-hot zinc-dust it is reduced to diphenyl. Gives a nitro-derivative [224°], a di-nitro- derivative [c. 235°], and a bromo- derivative [193°].

OXY-DIPHENYLENE-KETONE OXIDE $C_{13}H_8O_3$ *i.e.* $C_6H_4<\substack{O\\CO}>C_6H_3(OH)$. *Oxy-xanthone.* [147°]. Formed by heating resorcin with salicylic acid and $ZnCl_2$ (Michael, *Am.* 5, 91). Formed also by heating salicylic acid with (β)-resorcylic acid and Ac_2O (Graebe, *A.* 254, 290). Yellow needles (from alcohol). Split up by fusion with potash into resorcin and salicylic acid. Gives diphenylene-methane oxide [99°] when distilled with zinc-dust. Yields tri-oxy-benzophenone [133°] when fused with NaOH.—$NaC_{13}H_7O_3$.—$Na_2C_{13}H_8O_4$ (dried at 100°). Lemon-yellow needles.

Acetyl derivative $C_{13}H_7AcO_3$. [168°].

Di-oxy-diphenylene ketone oxide *v.* EUXANTHONE, vol. ii. p. 529. (β)-Iso-euxanthone $C_6H_3(OH)<\substack{O\\CO}>C_6H_3(OH)$, got from di-nitro-diphenylene ketone oxide [260°], yields a crystalline di-acetyl derivative [175°] (Graebe, *A.* 254, 301). An isomeride $C_6H_4<\substack{O\\CO}>C_6H_2(OH)_2$ [247°] is obtained from phloroglucin and salicylic acid (von Kostanecki a. Nessler, *B.* 24, 1896). A second isomeride with the formula $C_6H_4<\substack{O\\CO}>C_6H_2(OH)_2\begin{bmatrix}1&5\\2&6\end{bmatrix}$ [240°], got by heating tetra-oxy-benzophenone with water at 200°, yields a diacetyl derivative [161°] and dyes cotton

mordanted with alumina, yellow, and with iron, greyish-black (Graebe, *B.* 24, 969). Another isomeride $\left[1\begin{smallmatrix}3\\4\end{smallmatrix}\right] C_6H_3(OH)<\begin{smallmatrix}O\\CO\end{smallmatrix}>C_6H_3(OH)\left[\begin{smallmatrix}1\\2\end{smallmatrix}5\right]$ [246° cor.] made by heating resorcylic acid with Ac_2O yields a diacetyl derivative [c. 127°] (G.).

Tetra-oxy-diphenylene ketone oxide *v. Anhydride* of HEXA-OXY-BENZOPHENONE.

DI-OXY-PHENYLENE-DI-METHYL-DIKETONE $C_6H_2(OH)_2(CO.CH_3)_2$. [180°]. Obtained from di-oxy-acetophenone (10g.), $ZnCl_2$ (20g.), HOAc (50g.), and $POCl_3$ (10g.), at 140° (Crepieux, *Bl.* [3] 6, 152). Crystals (from hot water); yields with phenyl-hydrazine the compound $C_6H_2(OH)_2(CMe:N_2HPh)_2$ [c. 231°].

Tri-oxy-phenylene di-methyl diketone $C_6H(OH)_3(CO.CH_3)_2$. [189°]. Formed in like manner from tri-oxy-acetophenone (C.). Yields a di-phenyl-di-hydrazide [246°] and also an acetyl derivative [209°] which yields a di-phenyl-di-hydrazide [265°].

DI-OXY-PHENYLENE DI-PHENYL DIKETONE $C_{20}H_{14}O_4$ *i.e.* $C_6H_2(OH)_2(CO.C_6H_5)_2$. *Dibenzoresorcin.* [149°]. Formed, together with dioxybenzophenone, by heating resorcin with BzCl and $ZnCl_2$ (Doebner a. Stachmann, *B.* 11, 2270; *A.* 210, 259). Leaflets, insol. water.

Di-acetyl derivative. [150°]. Needles.

Di-benzoyl derivative. [151°]. Needles.

Di-oxy-phenylene di-phenyl diketone $C_6H_2(OH)_2(CO.C_6H_5)_2$. *Dibenzohydroquinone.* [207°]. Formed from hydroquinone, BzCl, and $AlCl_3$ (D.). Golden needles (from alcohol).

Di-benzoyl derivative. [146°]. Plates.

TETRA-OXY-DIPHENYLENE-DI-PHENYL-DI-THIO-DI-UREA. *Tetra-methyl derivative* $NHPh.CS.NH.C_6H_2(OMe)_2.C_6H_2(OMe)_2.NH.CS.NHPh$. [184°]. Formed by warming the compound $C_6H_2(OMe)_2(NH_2).C_6H_2(OMe)_2(NH_2)$ with phenyl-thiocarbimide (Bössler, *B.* 17, 2128). Flakes, sol. hot alcohol.

TETRA-OXY-DIPHENYLENEQUINONE. *Tetra-methyl ether v.* CŒRULIGNON.

DI-OXY-DIPHENYLENE-QUINOXALINE. *Di-ethyl ether*

$\left[6{:}3{:}\begin{smallmatrix}2\\1\end{smallmatrix}\right] C_6H_2(OEt)_2<\begin{smallmatrix}N.C.C_6H_4\ [1{:}2]\\N.C.C_6H_4\ [1{:}2]\end{smallmatrix}$. [260°].

Formed by the action of phenanthraquinone on the hydrochloride of the diethyl ether of (α)-diamido-hydroquinone (Nietzki a. Rechberg, *B.* 23, 1212). Yellowish needles, sl. sol. water.

OXY-DI-PHENYL-ETHANE $C_{14}H_{14}O$ *i.e.* $C_6H_5.CH_2.CH_2.C_6H_4(OH)$ or $CH_3.CH(C_6H_5).C_6H_4(OH)$. [58°]. Formed by allowing a mixture of styrene, phenol, H_2SO_4, and HOAc to stand (Koenigs, *B.* 23, 3144). Crystals, sol. dilute NaOHAq.

Benzoyl derivative [83°].

Methyl derivative $CH_2Ph.CH_2.C_6H_4OMe$. [61°]. Formed from α-phenyl-methoxy-cinnamic acid, alcohol, and Na (Freund a. Remse, *B.* 23, 2865). Plates, sol. alcohol.

Sulphonic acid $C_{14}H_{12}(OH)(SO_3H)$. Formed by potash-fusion from *s*-di-phenyl-ethane disulphonic acid (Kade, *B.* 7, 239). Plates, sol. hot water.

Di-*p*-oxy-*s*-di-phenyl-ethane $C_6H_4(OH).CH_2.CH_2.C_6H_4(OH)$. [189°]. Formed from di-phenyl-ethane disulphonic acid by potash-fusion (Kade). Plates or needles, almost insol. cold water. Does not give a dye-stuff on oxidation (Heumann a. Wiernik, *B.* 20, 914).

Di-oxy-di-phenyl-ethane $CH_3.CH(C_6H_4OH)_2$. *Ethylidene diphenol.* [122°] (F.); [125°] (Claus, *B.* 19, 3004). Formed by the action of $SnCl_4$ or HCl on a mixture of phenol and paraldehyde (Fabinyi, *B.* 11, 283). Needles (containing $\frac{1}{2}C_6H_6$). Reduces ammoniacal $AgNO_3$ forming a mirror.

Di-benzoyl derivative. [152°]. Prisms.

Di-methyl derivative. [140°]. Formed from acetyl chloride, anisole, and $AlCl_3$ (Gattermann, *B.* 22, 1129). Micaceous scales.

Di-ethyl derivative [142°]. Scales.

Isomerides *v.* DI-OXY-ETHYL-BENZENE.

Tri-oxy-tri-phenyl-ethane $C_6H_4(OH).CH_2.CH(C_6H_4OH)_2$. *Ethenyl-triphenol.* Formed from $CH_2Cl.CHCl(OEt)$ and phenol (Wislicenus, *A.* 243, 153). Amorphous resin, v. sl. sol. ether. Yields iso-rosolic acid on oxidation with $FeCl_3$. Forms a tri-acetyl derivative.

Tetra-oxy-di-phenyl-ethane $C_6H_4(OH).CH(OH).CH(OH).C_6H_4(OH)$.

Anhydride $C_{14}H_{10}O_2$. Two isomerides [68°] and [117°] are formed by the action of zinc-dust and HOAc on *o*-oxy-benzoic aldehyde (Tiemann, *B.* 24, 3172; Harries, *B.* 24, 3175).

Tetra-oxy-tetra-phenyl-ethane $C_{26}H_{18}(OH)_4$. [248°]. Formed by fusing tetra-phenyl-ethane tetra-sulphonic acid with potash (Engler, *B.* 11, 930). Plates (from dilute alcohol).

Tetra-oxy-tetra-phenyl-ethane $(HO.C_6H_4)_2CH.CH(C_6H_4.OH)_2$. Formed from di-oxy-benzophenone (Baeyer, *A.* 202, 133). Resin, yielding a crystalline tetra-acetyl derivative.

Hexa-oxy-tri-phenyl-ethane $(HO)_2C_6H_3.CH_2.CH(C_6H_3(OH)_2)_2$. Three amorphous isomerides are formed from di-chloro-di-ethyl oxide by the action of pyrocatechin, resorcin, and hydroquinone respectively (Wislicenus, *A.* 243, 181). They are v. sol. alcohol.

OXY-DI-PHENYL-ETHANE CARBOXYLIC ACID $C_6H_4(OH).CH_2.CHPh.CO_2H$. [120°]. Formed from phenyl-coumarin, dilute alcohol, and sodium-amalgam (Sardo, *G.* 13, 273). Small prisms.—AgA': sl. sol. hot water.

Oxy-di-phenyl-ethane dicarboxylic acid $C_6H_4(CO_2H).CH_2.CH(OH).C_6H_4.CO_2H$. *Hydro-oxy-diphthalylic acid.* [c. 170°]. Formed from its anhydride, which is a product of the action of zinc-dust and HOAc on phthalic anhydride (Wislicenus, *B.* 17, 2181). Prisms.—Ag_2A'': decomposes at 225° *in vacuo* (Hasselbach, *A.* 243, 249).

Ethyl ether Et_2A''. Crystalline.

Anhydride $C_{16}H_{12}O_4$. *Hydrodiphthallactonic acid.* [198·5°]. Prisms. Converted by KCy at 215° into $C_6H_4(CO_2H).CH{:}CH.C_6H_4.CO_2H$.—AgA': pp.

Di-oxy-di-phenyl ethane di-*o*-carboxylic acid $C_6H_4(CO_2H).CH(OH).CH(OH).C_6H_4.CO_2H$. Formed by dissolving hydrodiphthalyl in KOHAq (Hasselbach, *A.* 243, 266). Hydrodiphthalyl is a product of the action of zinc-dust and HOAc on diphthalyl. The free acid is unstable, at once yielding the anhydride $C_{16}H_{12}O_5$, which on heating to 190° yields its second anhydride hydrodiphthalyl $C_{16}H_{10}O_4$. [250°].—Ag_2A''. Pp.

Di-oxy-di-phenyl-ethane di-*p*-carboxylic acid $C_6H_4(CO_2H).CH(OH).CH(OH).C_6H_4.CO_2H$. Formed by reducing benzoïn dicarboxylic acid

with sodium-amalgam (Oppenheimer, *B.* 19, 1817). M. sol. water. Infusible.

o-**OXY-PHENYL-ETHYL-AMIDO-ACETIC ACID.** *Ethyl derivative* $C_6H_4(OEt).NEt.CH_2.CO_2H$. Formed from chloro-acetic acid (1 mol.), $C_6H_4(OEt).NHEt$ (2 mols.), and alcohol (Vater, *J. pr.* [2] 29, 296). Oil.—$C_{12}H_{17}NO_3HCl$. Very hygroscopic.—*Ethylo-chloride* $C_{12}H_{17}NO_3EtCl$. Formed from $C_6H_4(OEt).NEt_2$ and chloro-acetic acid. Oil.—$(C_{12}H_{17}NO_3EtCl)_2PtCl_4$: yellow crystals.

p-**OXY-PHENYL-ETHYLAMINE** $C_6H_4(OH).CH_2.CH_2.NH_2$. Formed by heating tyrosine at 270° (Schmitt a. Nasse, *A.* 133, 214). Solid. Yields *p*-oxy-benzoic acid on fusion with potash (Barth, *A.* 152, 101).—B'HCl. Needles.

Oxy-di-phenyl-ethylamine CHPh(OH).CHPh(NH_2). [161°]. Formed by reducing the oxim of hydrobenzoïn or the mono-oxim of benzoïn with sodium-amalgam and alcohol (Goldschmidt a. Polonowska, *B.* 20, 492; 21, 488). Needles (from alcohol).—B'HCl. [210°].—$B'_2H_2PtCl_6$ 2aq.—B'HOAc. [156°]. Prisms.

Di-acetyl derivative [159°].

p-**Oxy-di-phenyl-ethyl-amine.** *Ethyl ether* $EtN(C_6H_5)(C_6H_4.OEt)$. (319°). Formed from *p*-oxy-diphenylamine, EtI, and alcoholic potash. Oil, with an odour between that of geraniums and violets (Philip a. Calm, *B.* 17, 2434).

β-**OXY-*β*-PHENYL-ETHYL-ISOAMYL MALONIC ACID** $CHPh(OH).CH_2.C(CO_2H)_2.C_5H_{11}$. Formed by reducing phenacyl-isoamyl-malonic acid with sodium-amalgam (Paal a. T. Hoffmann, *B.* 23, 1503). Thick oil, almost insol. water, yielding the lactone of *γ*-oxy-*γ*-phenyl-heptoic acid on distillation.

OXY-PHENYL-ETHYL-CARBAMIC ANHYDRIDE $C_6H_4\langle{}^{NEt}_{O}\rangle CO$. [29°]. Formed from $C_6H_4\langle{}^{NH}_{O}\rangle CO$, alcoholic potash, and EtI (Bender, *B.* 19, 2952). Not affected by HCl.

o-**OXY-PHENYL-ETHYL CARBAZIDE.** *Methyl derivative* $C_{10}H_{15}N_3O_2$ *i.e.* $C_6H_4(OMe).N_2H_2.CO.NHEt$. [110°]. Formed from $C_6H_4(OMe).N_2H_3$ and phenyl cyanate (Reisenegger, *A.* 221, 322). Needles (from Aq).

o-**OXY-DI-PHENYL-ETHYLENE** $C_{14}H_{12}O$ *i.e.* $C_6H_5.CH:CH.C_6H_4(OH)$. [136°]. Formed in small quantity by heating salicylic aldehyde with phenyl-acetic acid and NaOAc at 200° (Michael, *Am.* 1, 315). Needles (from alcohol).

p-**Oxy-di-phenyl-ethylene.** *Methyl derivative* $C_{14}H_{11}(OMe)$. [136°]. Formed by heating the methyl derivative of *p*-coumaric acid (Oglialoro, *G.* 9, 536). Plates, sol. alcohol.

Di-o-oxy-di-phenyl-ethylene $C_6H_4(OH).CH:CH.C_6H_4OH$. [95°]. Formed from salicylic aldehyde, zinc-dust, and HOAc (Harries, *B.* 24, 3178; Tiemann, *B.* 24, 3175). Needles. Its alkaline solutions show blue fluorescence. Yields a di-benzoyl derivative [108°] which forms a dibromide [59°].

Di-*p*-oxy-di-phenyl-ethylene $C_6H_4(OH).CH:CH.C_6H_4(OH)$. *Di-oxy-stilbene.* [280°]. Formed by boiling an alcoholic solution of $CCl_3.CH(C_6H_4.OH)_2$ with zinc-dust (E. ter Meer, *B.* 7, 1200; Elbs a. Hoermann, *J. pr.* [2] 39, 498). Small crystals (from HOAc). Yields a di-acetyl derivative [213°].

Di-oxy-di-phenyl-ethylene. *Di-benzoyl derivative* $C_6H_5.C(OBz):C(OBz).C_6H_5$. *Iso-benzil.* [159°]. Formed by the action of sodium on a mixture of benzoic aldehyde and BzCl, or on BzCl alone, in ether (Klinger a. Schmitz, *B.* 24, 1276). Decomposed by HCl into benzil and benzoic acid. Alcoholic potash forms benzoïn.

Di-*p*-oxy-di-phenyl-ethylene. *Di-methyl derivative* $CH_2:C(C_6H_4.OMe)_2$. [140°]. Formed from anisole, AcCl, and $AlCl_3$ (Gattermann, *B.* 22, 1132). Plates, v. sl. sol. cold alcohol. Yields $CO(C_6H_4OMe)_2$ on oxidation by CrO_3.

Di-ethyl derivative $CH_2:C(C_6H_4.OEt)_2$. [142°]. Formed from C_6H_5OEt, AcCl, and $AlCl_3$.

Tetra-oxy-tetra-phenyl-ethylene $C_{26}H_{20}O_4$. Formed by potash-fusion from tetra-phenyl-ethylene tetra-sulphonic acid (Behr, *B.* 5, 278). Plates (from HOAc). Not melted at 300°. $FeCl_3$ in HOAc forms green metallic crystals of $C_{26}H_{18}O_4$ ½aq, sl. sol. alcohol.

DI-OXY-DI-PHENYL-ETHYLENE DIAMINE. *Di-ethyl derivative* $C_2H_4(NH.C_6H_4OEt)_2$. [98°]. Formed by the action of ethylene bromide and Na_2CO_3 on the hydrochloride of $C_6H_4(OEt)NH_2$ (Bischoff, *B.* 23, 1979). Plates (from ether-alcohol).

OXY-DI-PHENYL-ETHYLENE CARBOXYLIC ACID $C_6H_5.CH_2.CH(OH).C_6H_4.CO_2H$. [96°]. Formed from deoxybenzoïn o-carboxylic acid by sodium-amalgam (Gabriel a. Michael, *B.* 11, 1020; 18, 3480). Plates (from dilute alcohol). At 100° it forms an anhydride $C_{15}H_{12}O_2$ [60°].

The isomeric acid $C_6H_5.CH(OH).CH_2.C_6H_4.CO_2H$, [127°], formed by reducing the isomeric deoxybenzoïn o-carboxylic acid, also yields an anhydride $C_{15}H_{12}O_2$ [90°].

p-**OXY-PHENYLETHYLENE-QUINOLINE** $C_9NH_6.CH:CH.C_6H_4OH$. [253°]. Formed from (*Py.* 1)-quinoline (lepidine) by heating with *p*-oxy-benzoic aldehyde and $KHSO_4$ at 160° (Heyman a. Koenigs, *B.* 21, 1424). Crystals, sl. sol. dilute NaOHAq.

p-**OXY-PHENYL ETHYL KETONE** $C_6H_4(OH).CO.C_2H_5$. *Propionyl phenol.* [148°]. S. ·034 at 15°; 3·3 at 100°. Formed by heating phenol with propionic acid and $ZnCl_2$ (Goldzweig, *J. pr.* [2] 43, 86), and also by the action of propionyl chloride on phenol (Perkin, *C. J.* 55, 546). Needles or prisms, v. e. sol. alcohol. Potash-fusion yields phenol and *p*-oxy-benzoic acid. Yields a di-bromo- derivative [100°] and a nitro- derivative [180°].

Methyl derivative $C_6H_4(OMe).CO.C_2H_5$. [27°]. (274°). Formed from anisole (10 g.), propionyl chloride (10 g.), and $AlCl_3$ (12 g.) in CS_2 (Gattermann, *B.* 23, 1203). Yields an oxim [67°] crystallising from alcohol.

Ethyl derivative. [30°]. Prisms. Yields an oxim $C_6H_4(OEt).C(NOH).Et$ [97°].

Di-oxy-phenyl ethyl ketone [1:3:4] $C_6H_3(OH)_2.CO.C_2H_5$. [95°]. Formed from resorcin (1 pt.), propionic acid (1 pt.), and $ZnCl_2$ (Goldzweig). Needles. Gives a red colour with $FeCl_3$. Yields a phenyl-hydrazide [115°].

Di-ethyl derivative $C_6H_3(OEt)_2.CO.C_2H_5$. [76°]. Formed from propionyl chloride, $C_6H_4(OEt)_2$, and $AlCl_3$ (Gattermann). Yields an oxim [133°] crystallising in needles.

Di-oxy-phenyl ethyl ketone [5:2:1] $C_6H_3(OH)_2.CO.C_2H_5$. [92°]. Formed from hydroquinone (1 pt.), propionic acid (1 pt.), and

$ZnCl_2$ (2 pts.) at 190° (Goldzweig). Needles, giving a yellowish-red colour with $FeCl_3$. Yields a phenyl-hydrazide [100°].

OXY-DI-PHENYL-ETHYL NITRITE $C_{14}H_{13}NO_3$ *i.e.* $CPh_2(OH).CH_2.O.NO$. [106°]. Formed from di-phenyl-ethane (1 pt.), HOAc (10 pts.), and HNO_3 (1 pt. of S.G. 1·5) in the cold (Anschütz a. Romig, *A.* 233, 327). Needles, oxidised by CrO_3 to benzophenone and di-phenyl-vinyl nitrite [87°].

DI-OXY-DI-PHENYL-DI-ETHYL-PYRAZINE DIHYDRIDE $NPh\Big<{CHEt.CO \atop CO.CHEt}\Big>NPh$. [260°]. Formed, together with an isomeride [163°], by the action of Ac_2O on α-phenylamido-butyric acid (Nastvogel, *B.* 22, 1795; 23, 2014). Needles (from alcohol).

OXY-PHENYL-ETHYL-PYRIMIDINE $CEt\Big<{N-CPh \atop N:C(OH)}\Big>CH$. [238°]. Formed from propionamidine hydrochloride, benzoyl-aceto-acetic ether, and dilute (10 p.c.) NaOHAq (Pinner, *B.* 22, 1621). Needles, v. sl. sol. water.

OXY-TRI-PHENYL-ETHYL-PYRROLE $CPh_2\Big<{CH:CPh \atop CO.NEt}$. [123°] and [129°]. Formed from $C_6H_5.CBz:CHBz$ and alcoholic ethylamine (Japp a. Klingemann, *C. J.* 57, 705). Formed also by heating the ethylamide of di-phenyl-benzoyl-propionic acid at 340°. Triclinic prisms [123°]; $a:b:c = \cdot 912:1:\cdot 952$; $\alpha = 78°\ 48'$; $\beta = 89°\ 10'$; $\gamma = 68°\ 2'$. From dilute solutions it also crystallises in monoclinic prisms [129°]; $a:b:c = 1\cdot 690:1:1\cdot 958$; $\beta = 86°\ 54'$ (Tutton, *C. J.* 57, 731). Yields a bromo- derivative $C_{24}H_{20}BrNO$ [142°] crystallising in monoclinic prisms.

OXY-PHENYL-(*Py.* 1)-ETHYL-QUINOLINE $C_6H_4\Big<{C(CH_2.CH_2.C_6H_4.OH) \atop N:CH.CH}\Big>$. Formed by condensing o-oxy-benzoic aldehyde with (*Py.* 1)-methyl-quinoline and reducing the product with HI in HOAc and P (Koenigs, *B.* 21, 1428, 2167). The o-compound melts at 181°, the *m*- compound at 200°, and the *p*- compound at 177°. They yield the oxybenzoic acids on fusion with potash.

β-OXY-PHENYL-ETHYL-SUCCINIC ACID $CO_2H.CHPh.CH(CO_2H).CH(OH)Me$. Formed from phenyl-acetosuccinic ether, alcohol, and sodium-amalgam (Weltner, *B.* 18, 791). The free acid splits up at once, yielding the anhydride $C_{12}H_{12}O_4$ [167·5°] whence $Ca(C_{12}H_{11}O_4)_2$.—$AgC_{12}H_{12}O_5$: flocculent pp.

DI-OXY-DI-PHENYL-ETHYL-ψ-THIO-UREA. *Di-methyl derivative* $C_6H_4(OMe).N:C(SEt).NH.C_6H_4OMe$. [83°]. Got from di-anisyl-thio-urea and EtI (Foerster, *B.* 21, 1863). Prisms.—$C_{17}H_{20}N_2SO_2HI$. [163°]. Rhombohedra.—$B'_2H_2PtCl_6$.

o-OXY-PHENYL-GLYCIDIC ACID $C_6H_4(OH).\overset{\;\;O}{CH.CH}.CO_2H$. *Salicylglycidic acid.* Formed by the action of conc. aqueous NaOH upon benzoyl-imido-cumarin $C_6H_4\Big<{\overset{NBz}{CH.CH} \atop O\ .CO}$ (Plöchl a. Wolfrum, *B.* 18, 1185). Flat needles or prisms. V. sol. alcohol and ether, sl. sol. cold water. By boiling with dilute H_2SO_4 it is converted into oxido-cumarin $C_6H_4\Big<{\overset{O}{CH.CH} \atop O\ .CO}$ [153°]. —CaA'_2 6aq: prisms.

o-OXY-PHENYL-GLYOXYLIC ACID $C_6H_4(OH).CO.CO_2H$. [44°]. Formed by adding acid to a solution of $NaNO_2$ and isatin in dilute NaOH, and heating the solution of the diazo-compound thus obtained to 60° (Baeyer a. Fritsch, *B.* 17, 973). Yields oα-di-oxy-phenyl-acetic acid on reduction with sodium-amalgam.

Di-oxy-phenyl-glyoxylic acid. *Methyl derivative* [4:3:1]$C_6H_3(OH)(OMe).CO.CO_2H$. [134°]. A product of the oxidation of acetyl-eugenol by $KMnO_4$ (Tiemann, *B.* 24, 2878). Prisms, v. sol. water and alcohol. *Di-methyl derivative* [4:3:1] $C_6H_3(OMe)_2.CO.CO_2H$. [139°]. Formed, together with veratric acid by oxidation of the methyl derivative of eugenol or iso-eugenol by $KMnO_4$ (Tiemann a. Matsmoto, *B.* 11, 141; Ciamician a. Silber, *B.* 23, 1165). Trimetric tables, melting at 100° when hydrated.

Methylene derivative $CH_2\Big<{O \atop O}\Big>C_6H_3.CO.CO_2H$. [149°]. Formed by oxidising iso-safrol with alkaline $KMnO_4$ (C. a. S.). Light-yellow needles, containing benzene of crystallisation (from benzene).—$C_9H_5AgO_5$.

o-OXY-PHENYL-HEXENOIC ACID $C_6H_4(OH).C_5H_8.CO_2H$. *Anhydride* $C_{12}H_{12}O_2$. [54°]. (301°). Formed by boiling sodium salicylic aldehyde with valeric anhydride (Perkin, *A.* 147, 235). Prisms (from alcohol), insol. cold Aq.

An isomeric lactone, prepared by heating phenyl-acetyl-butyric acid, is oily (Erdmann, *A.* 254, 182).

OXY-PHENYL-HEXOIC ACID $CHMe(OH).CH(CH_2Ph).CH_2.CO_2H$. [76°]. Small prisms (containing aq).—CaA'_2 6aq: minute prisms. *Anhydride* $C_{12}H_{14}O_2$. *Benzyl-valero-lactone.* [86°]. Formed by reducing benzyl-acetylpropionic acid with sodium-amalgam (Erdmann, *A.* 254, 182). Crystals (from CS_2).

o-OXY-PHENYL-HYDRAZINE. *Methyl derivative* $C_6H_4(OMe).NH.NH_2$. [43°]. (240°). By reducing $C_6H_4(OMe).N_2.SO_3Na$ with Zn and glacial acetic acid there is formed the salt $C_6H_4(OMe).N_2H_2SO_3Na$ aq; which is then warmed with HClAq (Reisenegger, *A.* 221, 314). Needles (from ligroïn). Yields B'HCl, $B'_2H_2C_2O_4$, and $B'C_6H_3N_3O_7$.

Acetyl derivative $C_9H_{12}N_2O_2$. [125°].

Di-o-oxy-di-phenyl-hydrazine. *Di-ethyl derivative* $\{C_6H_4(OEt)\}_2N_2H_2$. [89°]. Formed by reducing the azo- compound $N_2(C_6H_4OEt)_2$ by alcoholic ammonium sulphide (Schmitt a. Möhlau, *J. pr.* [2] 18, 202). Colourless needles, insol. water, sol. alcohol and ether. The *m*-isomeride forms colourless needles [85°] (Buchstab, *J. pr.* [2] 29, 300).

Tetra-oxy-diphenyl-hydrazine. *Tetra-methyl derivative* $C_6H_3(OMe)_2.NH.NH.C_6H_3(OMe)_2$. *Hydrazodi-methylhydroquinone.* Formed by reducing the di-methyl derivative of nitro-hydro-quinone in alkaline solution (Baessler, *B.* 17, 2126). Converted by acids into the tetra-methyl derivative of tetra-oxy-diamido-diphenyl.

p-OXY-PHENYL-IMIDO-DIACETIC ACID. *Di-ethyl derivative of the oxy-anilide*

$C_6H_4(OEt).N(CH_2.CO_2H).CH_2.CO.NH.C_6H_4.OEt$. [157°]. Got from $C_6H_4(OEt).NH.CH_2.CO_2H$ by heating at 260° (Bischoff a. Nastvogel, *B.* 22, 1790). Crystalline, insol. hot water.

DI-o-OXY-DI-PHENYL-IMIDO-ACETO-NITRILE. *Di-methyl derivative* $C_{18}H_{17}N_3O_2$ *i.e.* $NH(CHCy.C_6H_4.OMe)_2$. [123°]. Formed by heating $C_6H_4(OMe).CH(OH).CN$ with alcoholic NH_3 at 70° (Voswinckel, *B.* 15, 2025). Tables, insol. water, sol. alcohol.

***o*-OXY-PHENYL-αβ-IMIDO-PROPIONIC ANHYDRIDE.** *Di-benzoyl derivative* $\{C_6H_4(OH).C_2H_2(NBz).CO\}_2O$. Obtained by heating hippuric acid with salicylic aldehyde dissolved in acetic anhydride with addition of sodium acetate (Plöchl a. Wolfrum, *B.* 18, 1183). [160°]. Crystalline solid. By boiling its acetic acid solution with a few drops of aqueous HCl it is converted into the benzoyl derivative of imidocoumarin.

DI-o-OXY-DI-PHENYL-IMIDO-THIAZOLE. *Tetrahydride of the di-methyl derivative* $CH_2<\begin{smallmatrix}N(C_6H_4OMe)\\CH_2.S\end{smallmatrix}>C{:}N.C_6H_4OMe$. [128°]. Formed by boiling di-anisyl-thio-urea with $C_2H_4Br_2$ (Foerster, *B.* 21, 1864). Prisms. On heating with CS_2 at 200° it yields the compound $CH_2<\begin{smallmatrix}N(C_7H_7O)\\CH_2 - S\end{smallmatrix}>CS$ [136°].—$B'_2H_2PtCl_6$: unstable when moist.

***p*-OXY-PHENYL-INDAZOLE**
$C_6H_4<\begin{smallmatrix}N\\CH\end{smallmatrix}>N.C_6H_4.OH$. [195°]. Formed by boiling its ethyl derivative with HIAq and a little P (Paal, *B.* 24, 965). Groups of short prisms, v. sol. HClAq, sl. sol. ether.—B′HI. [200°]. Large yellow plates.

Ethyl derivative. [118°]. Formed by heating a conc. alcoholic solution of the ethyl derivative of *o*-nitro-benzyl-*p*-amido-phenol with tin and HCl. Pearly plates (from alcohol), prisms (from benzene-ligroïn), or needles (from dilute HOAc). The tin double salt crystallises in yellowish plates [138°].

OXY-PHENYL-INDOLE $C_{14}H_{11}NO$ *i.e.* $C_6H_4<\begin{smallmatrix}C(OH)\\NH\end{smallmatrix}>CPh$(?). [c. 163°]. Formed by heating the phenyl-hydrazide of ω-oxy-acetophenone with $ZnCl_2$ at 160° (Laubmann, *A.* 243, 246). Amorphous pp., v. sl. sol. ligroïn.

DI-OXY-DI-PHENYL KETONE *v.* DI-OXY-BENZOPHENONE.

Di-oxy-di-phenyl-diketone. *Di-methyl derivative v.* ANISIL. Anisil forms a monooxim [130°] and two di-oxims [195°] and [217°]. The (α)-dioxim [217°] forms a diacetyl derivative [139°], while the (β)-dioxim [195°] forms an isomeric di-acetyl derivative [130°] (Stierlin, *B.* 22, 377).

***o*-OXY-PHENYL MERCAPTAN**
$C_6H_4(SH)(OH)$. *Thiopyrocatechin.* [6°]. (217° cor.). S.G. $\frac{0}{0}$ 1·237; $\frac{100}{100}$ 1·189. Formed by reducing di-oxy-di-phenyl disulphide with sodium-amalgam (Haitinger, *M.* 4, 170). Formed also by the action of potassium xanthate on diazophenol chloride, the oxyphenyl ethyl xanthate being subsequently saponified by sodium sulphide (Leuckart, *J. pr.* [2] 41, 192). Oil, volatile with steam, sl. sol. water. Attacks the skin.

p-Oxy-phenyl mercaptan $C_6H_4(SH)(OH)$. [30°]. (168°). Formed in like manner from *p*-diazophenol (L.). Crystalline mass, forming a bluish-green solution in sulphuric acid.—$Pb(S.C_6H_4.OH)_2$: bulky yellow pp. Oxidised in alcoholic ammoniacal solution by air to di-*p*-oxy-di-phenyl disulphide [151°].

Acetyl derivative $C_6H_4(SH)(OAc)$. (280°).

Di-acetyl derivative [66°]. Plates.

Ethyl ethers $C_6H_4(SH)(OEt)$, [41°], (277°) and $C_6H_4(SEt)(OH)$, [41°], (287°). Crystalline.

OXY-PHENYL-METHACRYLIC ACID is described as OXY-PHENYL-CROTONIC ACID (*q. v.*).

OXY-DI-PHENYL-METHANE *v.* BENZYL-PHENOL.

o-**Oxy-tri-phenyl-methane** $CHPh_2.C_6H_4OH$. [118°]. Formed by passing air through a solution of diazoamido-tri-phenol-methane sulphate, and boiling the product in a current of CO_2 (O. Fischer, *A.* 241, 362). Sol. alcohol and ether.

Di-*p*-oxy-di-phenyl-methane $CH_2(C_6H_4.OH)_2$. [158°]. Formed by fusing di-phenyl-methane disulphonic acid with potash (Beck, *A.* 194, 318). Plates or needles (from hot water), not volatile with steam. Its sodium salts $C_{13}H_{11}NaO_2$ and $C_{13}H_{10}Na_2O_2$ form green solutions.—BaA″.

Di-acetyl derivative [70°]. Prisms.

Di-benzoyl derivative [156°]. Needles.

Di-methyl derivative $CH_2(C_6H_4.OMe)_2$. [52°] (M.); [49°] (B.). (335°). Formed from anisole, methylal, HOAc, and H_2SO_4 (Ter Meer, *B.* 7, 1200). Small plates (from alcohol).

Di-ethyl derivative $CH_2(C_6H_4.OEt)_2$. [39°]. Scales, v. sol. alcohol.

Isomeride *v.* OXY-DI-PHENYL-CARBINOL.

Di-*p*-oxy-tri-phenyl-methane
$CHPh(C_6H_4.OH)_2$. *Leucobenzaurin.* [161°]. Formed from di-oxy-tri-phenyl-carbinol, zinc-dust and HCl (Doebner, *B.* 12, 1462; *A.* 217, 230). Formed also from di-amido-tri-phenyl-methane by the diazo- reaction (O. Fischer, *A.* 206, 153), and from benzoic aldehyde, phenol, and H_2SO_4 (Russanoff, *B.* 22, 1943). Yellowish needles (from dilute alcohol), sl. sol. hot water. Absorbs atmospheric oxygen when heated above 160°, changing to di-oxy-tri-phenyl-carbinol. Potash-fusion gives di-oxy-benzophenone. Yields a di-nitro- compound [134°].

Di-acetyl derivative [111°]. Plates.

Di-benzoyl derivative [130°].

Tri-oxy-tri-phenyl methane $CH(C_6H_4.OH)_3$. *Leucaurin.* Formed by reducing tri-oxy-tri-phenyl-carbinol (aurin) with zinc-dust and NaOHAq (Dale a. Schorlemmer, *A.* 166, 286). Colourless prisms (from HOAc), sl. sol. water.

Tri-acetyl derivative [139°] (Zulkowsky, *A.* 202, 197). Small needles.

Tri-benzoyl derivative. Crystals.

Tetra-oxy-di-phenyl-methane ? $C_{13}H_{12}O_4$. Formed by fusing orcin with NaOH (Barth, *M.* 3, 646). Needles, turning brown at 260°.

Tetra-oxy-tri-phenyl-methane $C_{19}H_{16}O_4$ *i.e.* $CHPh(C_6H_4(OH)_2)_2$. [171°]. Formed by reducing the anhydride of the corresponding carbinol (' resorcinbenzeïn ') with zinc-dust and HCl (Doebner, *A.* 217, 236). Colourless needles (from dilute alcohol). Reoxidised by alkaline K_3FeCy_6 to the anhydride of the carbinol.

Octo-oxy-tri-phenyl-methane. *Methyl derivative* $C_6H_3(OMe)(OH).CH(C_6H_3(OH)_2)_2$. Formed from vanillin (1 pt.), pyrogallol (1·67 pts.), alcohol (20 pts.), and conc. HClAq (50 pts.) (Etti,

M. 3, 638). Colourless crystals, insol. water; turned violet by HCl. An isomeride is formed from vanillin and phloroglucin.

p-**OXY-DI-PHENYL-METHANE o-CARBOXYLIC ACID.** *Methyl derivative* $C_6H_4(OMe).CH_2.C_6H_4.CO_2H$. [111°]. Formed by reduction of $C_6H_4(OMe).CO.C_6H_4.CO_2H$ (Nourrisson, *B.* 19, 2105). White needles, insol. Aq.

Oxy-di-phenyl-methane carboxylic acid $C_6H_5.CH_2.C_6H_3(OH).CO_2H$. [140°]. Formed from sodium benzyl-phenol and CO_2 (Paterno a. Fileti, *J.* 1873, 440). Small needles (from water). —AgA′: small needles (from water).

Oxy-di-phenyl-methane di-carboxylic acid $CH(OH)(C_6H_4.CO_2H)_2$. Formed, as K salt, by heating 'diphthalylic acid' with KOHAq at 130° (Juillard, *C. C.* 1887, 1143). The free acid at once forms the lactone [205°] which yields a methyl ether [155°], an ethyl ether [99·5°], and an amide [160°].

Oxy-di-phenyl-methane tri-carboxylic acid $C(OH)(C_6H_4.CO_2H)_2.CO_2H$. Formed, as K salt, by heating 'diphthalylic' acid $C_2O_2(C_6H_4.CO_2H)_2$ with KOHAq at 110° (Juillard). The free acid changes to lactone.

Ethyl ether [108°].

Oxy-tri-phenyl-methane carboxylic acid $C_{20}H_{16}O_3$ *i.e.* $CHPh(C_6H_4OH).C_6H_4.CO_2H$. [210°]. Formed by reducing an alkaline solution of oxy-tri-phenyl-carbinol carboxylic anhydride with powdered zinc (Pechmann, *B.* 13, 1616). Needles.

Di-oxy-tri-phenyl-methane carboxylic acid $C_6H_3(OH)_2.CHPh.C_6H_4.CO_2H$. [184°]. Formed by reduction of di-oxy-tri-phenyl-carbinol carboxylic anhydride with zinc-dust and NH_3Aq (Pechmann, *B.* 14, 1859). Converted into anthranol by H_2SO_4.

Di-oxy-tri-phenyl-methane carboxylic acid $C_6H_4(CO_2H).CH(C_6H_4.OH)_2$. [225°]. Formed by boiling phenol-phthaleïn with zinc-dust and NaOHAq (Baeyer, *A.* 202, 80; 212, 350).

Di-acetyl derivative [146°]. Needles.

Anhydride $C_{20}H_{14}O_3$. [214°–217°]. Formed by reducing phenol-phthaleïn-anhydride with zinc-dust and alcoholic NaOH. Small needles (from alcohol). Warm H_2SO_4 forms a green solution turning red.

OXY-PHENYL-PENTAMETHENYL HYDRIDE *v.* PHENYL-METHYL-FURFURINE.

OXY-DI-PHENYL-DI-METHYL-DI-AMIDO-BUTYRIC ACID. *Lactone* $O<\begin{matrix}C(NMePh)_2.CH_2\\CO\text{———}CH_2\end{matrix}$. *Phenyl-methyl-succinimide.* [157°]. Got by heating succinic acid with phenyl-methyl-amine (Piutti, *G.* 16, 160). Needles or prisms, sl. sol. ether.

p-**OXY-DI-PHENYL-METHYL-AMINE.** *Methyl derivative* $MeN(C_6H_5)(C_6H_4.OMe)$. (313°). Formed by methylation of *p*-oxy-di-phenyl-amine (Philip a. Calm, *B.* 17, 2433). Oil, with an odour like geranium or violets.

OXY-DI-PHENYL-TETRAMETHYLENE-QUINONE (so-called) $C_{16}H_{10}O_3$. The following derivatives of this body are formed by the action of bases on the quinone $C_{16}H_{10}O_2$ got by oxidising di-phenyl-butinene (Zincke a. Breuer, *B.* 13, 631; *A.* 226, 38).

Imide $C_{16}H_9(OH)<\begin{matrix}O\\NH\end{matrix}$. [174°]. Red plates, yielding a diacetyl derivative [201°]. Aqueous SO_2 forms $C_{32}H_{22}O_5$ [187°].

Methylimide $C_{16}H_9(OH)<\begin{matrix}O\\NMe\end{matrix}$. [170°].

Ethylimide [130°]. Brown needles.

Phenylimide $C_{16}H_9(OH)O(NPh)$. [158°].

o-*Tolylimide* [108°]. Red needles.

p-Tolylimide [155°]. Violet needles.

(*a*)-*Naphthylimide* [148°].

Isomeride $C_{16}H_9(OH)O_2$. [144°]. Formed by warming the quinone $C_{16}H_{10}O_2$ with dilute NaOH (Z. a. B.). Needles or prisms (from alcohol). Yields phthalic acid on oxidation. Aqueous SO_2 yields an oxyquinhydrone [155°]. HI reduces it to an oxyhydroquinone [73°].—$Ca(C_{16}H_9O_3)_2$.—BaA'_2.—AgA′: brownish-red pp.

Acetyl derivative $C_{18}H_{12}O_4$. [111°].

Benzoyl derivative. Monoclinic crystals.

DI-OXY-DI-PHENYL-TRI-METHYLENE ψ-THIO-UREA. *Di-methyl derivative* $\begin{matrix}CH_2.CH_2.N.C_6H_4.OMe\\CH_2.S\text{——}C{:}N.C_6H_4OMe\end{matrix}$. [114°]. Formed from di-anisyl-thio-urea and trimethylene bromide (Foerster, *B.* 21, 1872). Prisms (from alcohol).

DI-OXY-DI-PHENYL-DI-METHYL-ETHYLENE-DIPYRAZOLE $C_{22}H_{22}N_4O_2$ *i.e.* $NPh<\begin{matrix}N\text{—}CMe\\CO.CH.CH_2.CH_2.CH.CO\end{matrix}\begin{matrix}CMe.N\\ \end{matrix}>NPh$. Formed by splitting off alcohol (2 mols.) from the phenyl-hydrazide of di-acetyl-adipic ether (Perkin a. Obrembsky, *B.* 19, 2049; *C. J.* 57, 206). Small crystals, solid at 250°. Sol. acids and alkalis.

OXY-PHENYL-METHYL-ETHYL-PYRAZOLE $C_{12}H_{14}N_2O$ *i.e.* $NPh<\begin{matrix}CO.CHEt\\N\ {:}CMe\end{matrix}$. [108°]. Formed by heating ethyl-acetoacetic ether with phenyl-hydrazine at 140° (Knorr a. Blank, *B.* 17, 2051). Crystals (containing aq). Oxidised by nitrous acid to $C_{24}H_{26}N_4O_2$ [160°].

OXY-PHENYL-METHYL-ETHYL-PYRIMIDINE $CPh<\begin{matrix}N{:}CMe\\N.C(OH)\end{matrix}>CEt$. [167°]. Formed from benzamidine hydrochloride, ethylaceto-acetic ether, and dilute (10 p.c.) NaOHAq (Pinner, *B.* 22, 1625). Prisms.

Di-oxy-phenyl-methyl-ethyl-pyrimidine. *Ethyl derivative* $C_6H_4(OEt).C<\begin{matrix}N{:}CMe\\N.C(OH)\end{matrix}>CEt$. [194°]. Formed from ethyl-acetoacetic ether and *p*-ethoxybenz-amidine (Pinner, *B.* 23, 2955). Needles (from alcohol), m. sol. hot alcohol.

OXY-PHENYL-DIMETHYL-TETRAHYDRO-PYRIDINE *v.* BENZYLIDENE-DIACETONE-ALCAMINE.

OXY-PHENYLMETHYL KETONE *v.* OXY-ACETOPHENONE and BENZYL-CARBINOL.

DI-OXY-DI-PHENYL-DI-METHYL-PYRAZINE DIHYDRIDE $NPh<\begin{matrix}CHMe.CO\\CO\text{—}CHMe\end{matrix}>NPh$. [183°]. Formed from phenyl-*a*-amido-propionic acid and Ac_2O in the cold (Nastvogel, *B.* 22, 1794; 23, 2012). Needles, insol. water.

An isomeride [146°] accompanies the preceding body. On heating with KOHAq both compounds yield $C_{18}H_{20}N_2O_3$ [80°].

OXY-PHENYL-METHYL-PYRAZOLE $NPh<\begin{matrix}CO.CH_2\\N{=}CMe\end{matrix}$. [127°]. (287° at 265 mm.).

Preparation.—1. By heating acetoacetic ether with phenyl hydrazine (Knorr, *B.* 17, 550, 2032; *A.* 238, 137).—2. By the action of NH_3Aq and H_2S on (*β*)-phenyl-azo-crotonic ether (Bender, *B.* 20, 2748).

Properties.—Crystals, sol. hot alcohol. Yields bromo-, dibromo-, and di-chloro- derivatives. Condenses with cinnamic aldehyde, acetone, and acetoacetic ether. Zinc-dust reduces it to phenyl-methyl-pyrazole. Excess of phenyl-hydrazine forms, on boiling, $C_{20}H_{18}N_4O_2$, whence $C_{20}H_{16}N_4O_2(SO_3H)_2$. Nitrous acid forms $C_{10}H_9N_3O_2$ [137°]. Diazobenzene chloride forms a compound $NPh\left<\begin{matrix}CO.C:N_2HPh\\N=CMe\end{matrix}\right.$ [155°], which is also got by heating azobenzene-acetoacetic amide with phenyl-hydrazine at 130° (Leuckart a. Holzapfel, *B.* 22, 1406; Buchka, *B.* 22, 2541). S_2Cl_2 forms a product which crystallises from alcohol as $C_{20}H_{18}N_4SO_2HClHOEt$ (Sprague, *C. J.* 59, 334). Alloxan forms a compound $C_{14}H_{12}N_4O_5$, whence dilute potash gives $C_{13}H_{11}N_3O_4$, converted by hot potash into $C_{11}H_{12}N_2O_2$, which on heating with alcohol gives rise to oxy-phenyl-methyl-methylene-pyrazole [178°] (Pellizzari, *A.* 255, 230).

Oxy-phenyl-di-methyl-pyrazole $C_{11}H_{12}N_2O$ *i.e.* $NPh\left<\begin{matrix}CO.CHMe\\N=CMe\end{matrix}\right.$. [117°–120°]. Formed by heating methyl-acetoacetic ether with phenyl-hydrazine at 140° (Knorr, *B.* 17, 2050; *A.* 238, 162). Formed also by heating oxy-phenyl-methyl-pyrazyl-acetic acid. Crystalline powder.

Oxy-phenyl-di-methyl-pyrazole $C_{11}H_{12}N_2O$ *i.e.* $NPh\left<\begin{matrix}CO-CH\\NMe.CMe\end{matrix}\right.$. *Antipyrine.* [113°]. Formed by methylation of oxy-phenyl-methyl-pyrazole (Knorr, *B.* 17, 2032) and by heating acetoacetic ether with *s*-phenyl-methyl-hydrazine (Knorr, *A.* 238, 203). Monoclinic crystals (from water); v. sol. water, alcohol, and ether. Febrifuge. $FeCl_3$ colours its solution deep-red. Nitrous acid gives a bluish-green colour. Sodium added to its alcoholic solution liberates methylamine. K_3FeCy_6 and HCl give a yellow colour. Chromic acid gives an orange pp. (Gay a. Fortuné, *Ph.* 18, 1066). Gives the usual reactions for alkaloids. ICl solution forms crystalline $C_{11}H_{11}IN_2O$ [160°] and $C_{11}H_{11}IN_2OICl$ [142°] (Dittmar, *B.* 18, 1617). Bromine forms $C_{11}H_{12}Br_2N_2O$ [c. 150°], whence water yields $C_{11}H_{11}BrN_2O$ [117°]. HNO_2 forms $C_{11}H_{11}N_3O_2$, which explodes at 200°. Alloxan yields $\begin{matrix}NPh.CO\\NMe.CMe\end{matrix}{>}C.C(OH)\left<\begin{matrix}CO.NH\\CO.NH\end{matrix}\right>CO$, decomposing at 261°, whence boiling conc. HClAq forms $C_{12}H_{12}N_2O_2$ [238°] (Pellizzari, *G.* 18, 340). Benzoic aldehyde in presence of HCl forms benzylidene-di-antipyrine $C_{29}H_{28}N_4O_2$ [201°]. Combines with chloral.

S a l t s. — $B'_2H_2PtCl_6$ 2aq. — $B'_2H_4FeCy_6$. — $B'C_6H_2(NO_2)_3OH$. [188°]. Long yellow needles.

Oxy-phenyl-tri-methyl-pyrazole $C_{12}H_{14}N_2O$ *i.e.* $NPh\left<\begin{matrix}CO-CMe\\NMe.CMe\end{matrix}\right.$. [83°]. (286° at 153 mm.). Formed by heating antipyrine with MeI and MeOH (Knorr). Crystals, v. sol. water and alcohol. Yields a picrate [94°].

Oxy-phenyl-tri-methyl-pyrazole $C_{12}H_{14}N_2O$ *i.e.* $NPh\left<\begin{matrix}CO.CMe_2\\N=CMe\end{matrix}\right.$. [56°]. (302° i. V.). Formed from oxy-phenyl-methyl-pyrazole NaOMe, and MeI (Knorr, *A.* 238, 165), and also by heating di-methyl-acetoacetic acid with phenyl-hydrazine. Insol. water, v. sol. alcohol.

Oxy-di-phenyl-methyl-pyrazole $C_{16}H_{14}N_2O$ *i.e.* $NPh\left<\begin{matrix}CO-CH\\NMe.CPh\end{matrix}\right.$. [150°]. Formed by methylation of oxy-di-phenyl-pyrazole (Knorr a. Klotz, *B.* 20, 2549). Needles (from ether), sl. sol. boiling water. Bromine in chloroform forms a di-bromide, whence water liberates $C_{16}H_{13}BrN_2O$ [110°–120°].

S a l t s.—B'HCl: needles. — $B'_2H_4FeCy_6$. — $B'C_6H_2(NO_2)_3OH$. [170°]. Yellow prisms.

Oxy-di-phenyl-methyl-pyrazole $NPh\left<\begin{matrix}CO.CH\\NPh.CMe\end{matrix}\right.$. [122°]. Formed by heating hydrazobenzene with acetoacetic ether at 120°; the yield being 60 p.c. of the theoretical (Müller, *B.* 19, 1771; Perger, *B.* 19, 2140; *M.* 7, 191). Crystals (containing $\frac{1}{2}$aq), v. sol. alcohol.

OXY-PHENYL-METHYL-PYRAZOLE CARBOXYLIC ACID $NPh\left<\begin{matrix}CO.CHMe\\N=C.CO_2H\end{matrix}\right.$. [221°]. Made from its ether, which is got by heating oxal-propionic ether with phenyl-hydrazine at 120° (Arnold, *A.* 246, 331). Plates (from alcohol).

Ethyl ether EtA'. [149°].

Oxy-phenyl-methyl-pyrazole carboxylic acid $NPh\left<\begin{matrix}CO.CH_2\\N=C.CH_2.CO_2H\end{matrix}\right.$. [134°]. Got from its ether [85°], which is formed by heating acetone dicarboxylic ether with phenyl-hydrazine (Pechmann, *A.* 261, 171). Prisms, sol. alcohol.

Oxy-phenyl-methyl-pyrazole dicarboxylic acid $NPh\left<\begin{matrix}CO.CH.CH_2.CO_2H\\N-C.CO_2H\end{matrix}\right.$. [229°]. Formed by saponifying its ether. Needles (containing aq), sl. sol. cold water. Gives a dark-violet colour with $FeCl_3$.

Ethyl ether Et_2A''. [130°]. Formed by heating oxalsuccinic ether with phenyl-hydrazine at 170° (Wislicenus, *B.* 22, 888). Needles.

Oxy-phenyl-di-methyl-pyrazole carboxylic acid $NPh\left<\begin{matrix}CO.CH.CH_2CO_2H\\N=CMe\end{matrix}\right.$. [178°]. Obtained from its ether [138°], which is got by heating acetyl-succinic ether with phenyl-hydrazine at 150° (Knorr). Needles (from water).

DI-OXY-DI-PHENYL-DI-METHYL-DI-PYRAZYL $C_{20}H_{18}N_4O_2$ *i.e.* $\begin{matrix}NPh.CO\\N\ \ :CMe\end{matrix}{>}CH.CH\left<\begin{matrix}CO\ .NPh\\CMe:N\end{matrix}\right.$. Formed by the action of phenyl-hydrazine (3 mols.) on acetoacetic ether (2 mols.). Formed also by the action of phenyl-hydrazine on di-acetyl-succinic ether, on isocarbopyrotritaric ether and on thioacetoacetic ether (Knorr, *B.* 17, 2044, 2058; 22, 160; Buchka a. Sprague, *B.* 22, 2554). Formed also from β-phenyl-azo-crotonic ether, alcoholic NH_3 and H_2S (Bender, *B.* 20, 2749). Yellowish powder. Decomposes on heating without melting. Insol. neutral solvents, sol. alkalis. Gives the pyrazole-blue reaction. Yields a bromo- derivative [217°].

Di-oxy-di-phenyl-tetra-methyl-dipyrazyl $\begin{matrix}NPh.CO\\N\ \ :CMe\end{matrix}{>}CMe.CMe\left<\begin{matrix}CO\ .NPh\\CMe:N\end{matrix}\right.$. [164°]. Formed by oxidation of oxy-phenyl-di-methyl-pyrazole with nitrous acid (Knorr a. Blank, *B.* 17, 2050). Long prisms (from HOAc), insol. water and alkalis, sol. conc. H_2SO_4.

Di-oxy-di-phenyl-tetra-methyl-dipyrazyl $\begin{matrix}NPh.CO\\NMe.CMe\end{matrix}{>}C.C\left<\begin{matrix}CO\ .NPh\\CMe.NMe\end{matrix}\right.$. *Bis-antipyrine.* [245°]. Formed by methylation of the preceding body (Knorr, *A.* 238, 210). Crystals (from MeOH),

nearly insol. water.—$B'H_2Cl_2$ 2aq.—$B'_3H_4PtCl_8$: orange-red prisms. Picrate [c. 161°].

Di-oxy-di-phenyl-di-methyl-dipyrazyl sulphide $\left(\begin{smallmatrix}NPh.CO\\N{=\!=}CMe\end{smallmatrix}{>}CH\right)_2S$. Formed by adding phenyl-hydrazine (2 mols.) dissolved in HOAc to thio-aceto-acetic ether (1 mol.) in the cold (Buchka a. Sprague, *B.* 23, 849). Formed also from oxy-phenyl-methyl-pyrazole and SCl_2 in chloroform. Small needles, decomposing at 183° without melting; sl. sol. alcohol, sol. alkalis.

OXY-PHENYL-METHYL-PYRIDAZINE

$NPh{<}\begin{smallmatrix}CO.CH\\N\ :CMe\end{smallmatrix}{>}CH$. [82°]. Formed, together with its chloro- derivative [137°], from the anhydride of the phenyl-hydrazide of levulic acid and PCl_5 at 160° (Ach, *A.* 253, 47). Translucent crystals, v. sol. alcohol. Na added to its alcoholic solutions forms a compound $C_{22}H_{24}N_4$? [200°], coloured violet by H_2SO_4 and CrO_3.—B'HCl.

Di-oxy-phenyl-methyl-pyridazine

$NPh{<}\begin{smallmatrix}CO.CO\\N\ :CMe\end{smallmatrix}{>}CH_2$. [196°]. Formed from the chloro- derivative, mentioned above, by treatment with alcoholic potash, the resulting $NPh{<}\begin{smallmatrix}CO.C(OEt)\\N{=}CMe\end{smallmatrix}{>}CH$ [146°] being heated with HClAq at 130°. White needles, sl. sol. hot water.

OXY-ν-PHENYL-DI-METHYL-PYRIDINE

$C_{13}H_{13}NO$ *i.e.* $NPh{<}\begin{smallmatrix}CMe:CH\\CMe:CH\end{smallmatrix}{>}CO$. *Phenyl-lutidone.* [197°]. (above 360°). Formed by the action of aniline on methyl dehydracetate (Perkin, *B.* 18, 682; *C. J.* 51, 498), and also by heating its carboxylic acids (Conrad a. Guthzeit, *B.* 20, 161; 22, 85). Needles or prisms (containing aq), v. sol. hot water and alcohol.—$B'_2H_2PtCl_6$: yellow needles (from water).—$B'C_6H_2(NO_2)_3OH$. [95°]. Transparent plates.

Oxy-phenyl-di-methyl-pyridine

$NMe{<}\begin{smallmatrix}CO\ .CH\\CMe:CH\end{smallmatrix}{>}CPh$. *Methyl-phenyl-ψ-picolostyril.* [112°]. Formed by heating 'methyl-carbo-phenyl-lutidylium dehydride' with conc. HClAq at 180° (Hantzsch, *B.* 17, 2915). Prisms. B'HCl 2aq.—$B'_2H_2PtCl_6$ 3aq: crystalline powder.

m-**Oxy-(*Py.* 3)-phenyl-(*Py.* 1:5)-di-methyl-pyridine** $C_{13}H_{13}NO$ *i.e.* $C_6H_4(OH).C_5NH_2(CH_3)_2$. *Oxy-phenyl-lutidine.* [191°]. From the corresponding amido- compound by the diazo-reaction. White crystalline solid (Lepetit, *B.* 20, 2399).—B'HCl 2aq.—$B'_2H_2PtCl_6$. [c. 200°].

OXY-ν-PHENYL-DI-METHYL-PYRIDINE CARBOXYLIC ACID $C_{14}H_{13}NO_3$ *i.e.* $NPh{<}\begin{smallmatrix}CMe:CH\text{———}\\CMe:C(CO_2H)\end{smallmatrix}{>}CO$. [257°]. Formed by heating the dicarboxylic acid at 227° (Conrad a. Guthzeit, *B.* 20, 161, 947; 22, 84). Formed also from β-phenyl-amido-crotonic ether and NaOEt at 90° (Knorr, *B.* 20, 1399). Satiny needles. Melts at 267° when quickly heated.—BaA'_2 4aq: needles, v. sol. water.

Methyl ether MeA'. [152°]. Formed from methyl dehydracetate and aniline (Perkin, jun., *B.* 18, 682; *C. J.* 51, 498). Needles.

Oxy-phenyl-di-methyl-pyridine dicarboxylic acid $NPh{<}\begin{smallmatrix}CMe:C(CO_2H)\\CMe:C(CO_2H)\end{smallmatrix}{>}CO$. Got by electrolysis of its ether. Prisms, v. sol. hot alcohol. —$Ba(HA'')_2$ aq.

Ethyl ether Et_2A''. [171°]. Formed by boiling an acetic acid solution of aniline and the product of the action of $COCl_2$ on cupric acetoacetic ether (Conrad a. Guthzeit, *B.* 19, 25; 20, 161). Crystalline solid, v. sol. alcohol.—$B'_2H_2PtCl_6$. [120°]. Orange-yellow pp.

m-**Oxy-(*Py.* 3)-phenyl-(*Py.* 1:5)-di-methyl-pyridine-(*Py.* 2:4)-di-carboxylic acid** $C_6H_4(OH).C_5N(CH_3)_2(CO_2H)_2$. *m-Oxy-phenyl-lutidine-di-carboxylic acid.*

Di-ethyl-ether $A''Et_2$. [174°]. From the corresponding amido- compound by the diazo-reaction (Lepetit, *B.* 20, 2398). White needles.

OXY-PHENYL-METHYL-PYRIMIDINE

$CPh{<}\begin{smallmatrix}N:CMe\\N.CO\end{smallmatrix}{>}CH_2$. [216°]. Formed by mixing a solution of benzamidine hydrochloride (1 mol.) with acetoacetic ether (1 mol.) and NaOH (1 mol.). Formed also by the action of benzimido-ether CPh(NH).OEt on acetoacetic ether at 100° and of benzamidine on acetyl-malonic ether (Pinner, *B.* 18, 759, 2851; 22, 1624, 2617; 23, 3820). Needles, v. sol. alcohol, sl. sol. water. —$B'_2H_2PtCl_6$ 2aq.—$B'C_6H_2(NO_2)_3OH$. [189°].—$B'_2H_2Cr_2O_7$ 5aq. [177°]. Orange-red prisms.

Acetyl derivative $C_{13}H_{12}N_2O_2$. [41°].

Ethyl derivative $C_{11}H_9(OEt)N_2$. [31°]. (300°). Formed from chloro-phenyl-methyl-pyrimidine and NaOEt. Thick prisms. — B'HCl 2aq. [86°].—B'HCl. [149°].—$B'_2H_2PtCl_6$. [197°].—B'HI ½aq. [144°]. Yellow prisms.

Oxy-phenyl-methyl-pyrimidine

$CMe{<}\begin{smallmatrix}N:CPh\\N.CO\end{smallmatrix}{>}CH_2$. [238°]. Formed from acetamidine hydrochloride, benzoyl-acetic ether, and dilute (10 p.c.) NaOHAq (Pinner, *B.* 22, 1618). Needles, m. sol. hot alcohol.

Oxy-phenyl-di-methyl-pyrimidine

$CPh{<}\begin{smallmatrix}N:CMe\\N.CO\end{smallmatrix}{>}CHMe$. [203°]. Formed from benzamidine hydrochloride, methyl-acetoacetic ether, and NaOHAq (Pinner, *B.* 22, 1624). Needles.

Oxy-di-phenyl-methyl-pyrimidine

$CPh{<}\begin{smallmatrix}N:CPh\\N.CO\end{smallmatrix}{>}CHMe$. [250°]. S. 1·95 at 20°. Formed from benzamidine and α-benzoyl-propionic ether (E. v. Meyer, *J. pr.* [2] 39, 197; 40, 303; Schwarze, *J. pr.* [2] 42, 12). Minute needles. Oxidised by $KMnO_4$ to oxy-di-phenyl-pyrimidine carboxylic acid [236°]. Yields a methyl derivative [122°].

Di-oxy-phenyl-methyl-pyrimidine. *Ethyl derivative* $C_6H_4(OEt).C{<}\begin{smallmatrix}N:CMe\\N.CO\end{smallmatrix}{>}CH_2$. [146°]. Formed by mixing *o*-ethoxy-benzamidine hydrochloride with NaOH and acetoacetic ether (Pinner, *B.* 23, 2953). Short columns, v. sol. alcohol.

An isomeride [204°] is formed from *p*-ethoxy-benzamidine and acetoacetic ether or acetyl-malonic ether.

Di-oxy-phenyl-di-methyl-pyrimidine. *Ethyl derivative* $C_6H_4(OEt).C{<}\begin{smallmatrix}N:CMe\\N.CO\end{smallmatrix}{>}CHMe$. [216°]. Formed from *p*-ethoxy-benzamidine and methyl-acetoacetic ether (P.). Small prisms.

Reference. — Bromo-oxy-phenyl-methyl-pyrimidine.

OXY-PHENYL-DI-METHYL-PYRIMIDINE CARBOXYLIC ACID

$CPh{<}\begin{smallmatrix}N:CMe\\N.CO\end{smallmatrix}{>}CH.CH_2.CO_2H$. [259°]. Got by saponifying its ether. Needles, sl. sol. water.

Ethyl ether EtA′. [178°]. Formed from acetyl-succinic ether and benzamidine (Pinner, *B.* 22, 2618). Crystals, sl. sol. water.

OXY-PHENYL-METHYL-PYRIMIDYLMETHYL METHYL KETONE

$CPh\langle{}^{N:CMe}_{N.CO}\rangle C.CH_2.CO.CH_3$. [225°]. Formed from di-acetyl-succinic ether and benzamidine (Pinner, *B.* 22, 2622). Needles, sl. sol. alcohol.

OXY-PHENYL-METHYL-PYRIMIDYL PROPIONIC ACID

$CPh\langle{}^{N:CMe}_{N.CO}\rangle CH.CH_2.CH_2.CO_2H$. [215°]. Formed by saponification of its ether [145°], which is got by the action of benzamidine on acetyl-glutaric ether (Pinner, *B.* 22, 2620). Powder, sl. sol. water.

OXY-TRI-PHENYL-METHYL-PYRROLE

$C_{23}H_{19}NO$ *i.e.* $NMe\langle{}^{CO\ .CPh_2}_{CPh:CH}$. *Tri-phenyl-methyl-pyrrholone.* [139°] and [143°]. Formed from $C_6H_5.CBz:CHBz$ and alcoholic methylamine (Japp a. Klingemann, *B.* 22, 2884; *C. J.* 57, 698). Colourless rhombohedra [139°]; $a:c = 1:2{\cdot}434$. Occurs also in triclinic forms [143°]; $a:b:c = {\cdot}906:1:{\cdot}870$; $\alpha = 79°\ 52'$; $\beta = 86°\ 3'$; $\gamma = 70°\ 26'$ (Tutton, *C. J.* 57, 724). Oxidised by chromic acid to $C_{23}H_{19}NO_3$ [167°]. Bromine in chloroform yields $C_{23}H_{18}BrNO$ [150°].

Dihydride $NMe\langle{}^{CO\ -\ CPh_2}_{CHPh.CH_2}$. *Tri-phenylmethylpyrrholidone.* [153·5°]. Mol. w. (by Raoult's method) 335 (calc. 327). Formed by reduction of the preceding body by sodium and boiling amyl alcohol. Monoclinic needles; $a:b:c = 1{\cdot}655:1:1{\cdot}043$; $\beta = 88°\ 29'$.

Oxy-tetra-phenyl-methyl-pyrrole $C_{29}H_{23}NO$ *i.e.* $NMe\langle{}^{CO\ .CPh_2}_{CPh:CPh}$. [161°]. Formed by heating $C_6H_5.CBz:CBz.C_6H_5$ with alcoholic methylamine at 200°, and also from benzoyl-tri-phenyl propiomethylamide and KOH (Klingemann a. Laycock, *C. J.* 59, 146; *B.* 24, 518). Small yellow monoclinic plates (from boiling alcohol), v. sol. CS_2.

OXY-PHENYL-METHYL-PYRROLE CARBOXYLIC ACID. *Ethyl ether*

$NH\langle{}^{CO\ .CHPh}_{CMe:C.CO_2Et}$. [128°]. Formed by the action of alcoholic ammonia on phenyl-acetyl-succinic ether (Emery, *A.* 260, 152). Needles.

Oxy-phenyl-methyl-pyrrole dihydride carboxylic acid $NPh\langle{}^{CO.CH_2}_{CMe(CO_2H)}\rangle CH_2$. [183°]. Obtained from its nitrile, which is made from levulic ether, HCy, and alcoholic aniline (Kühling, *B.* 22, 2364). Hard prisms, sl. sol. water.

Amide [127°]. Needles.

Nitrile. Oil. Converted by NH_3 and H_2S into $NPh\langle{}^{CO-CH_2}_{CMe(CS.NH_2)}\rangle CH_2$. [193°]. Hydroxylamine forms the amidoxim [120°].

OXY-PHENYL-METHYL-QUINAZOLINE

$C_6H_4\langle{}^{CO.NMe}_{N\ =\ CPh}$. [131°]. Formed by the action of KOH and MeI at 120° on *o*-benzoyl-amido-benzamide or on oxy-phenyl-quinazoline (Körner, *J. pr.* [2] 36, 162). Shining lamellæ, sol. alcohol.

Isomeride $C_6H_4\langle{}^{CO.NPh}_{N\ \ CMe}$. [147°]. Formed by heating the acetyl derivative of *o*-amido-benzoic anilide (K.). Four-sided prisms.

OXY-PHENYL-METHYL-QUINOLINE

$\begin{array}{l}CMe:CH.C.C(OH):CH\\ CH{=}CH.C.N{-\!-\!-}CPh\end{array}$. [291°]. Formed by heating its carboxylic acid at 250° (Just, *B.* 19, 1544). Plates (from alcohol).

Isomeride *v.* FLAVENOL.

OXY-PHENYL-METHYL-QUINOLINE CARBOXYLIC ACID $\begin{array}{l}CMe:CH.C.C(OH):C.CO_2H\\ CH\ :CH.C.N{=\!=\!=}CPh\end{array}$.

Formed by saponifying its ether [236°], which is got by heating to 160° the product of the action of $C_6H_4MeN:CClPh$ on sodium malonic ether (Just, *B.* 19, 1542). V. sl. sol. water and alcohol.

OXY-PHENYL-METHYL-(*Py.*)-QUINOPYRAZOL

$$C_6H_4\langle\begin{array}{l}\ \ \ N\ \text{—}\ NPh\\ \ \ \ \|\qquad\ \ |\\ C\ .\ C:CMe\\ \ \ \ \ \ \ \ \ \ |\\ N:C(OH)\end{array}$$

Inner-anhydride of o-*amido-di-phenyl-methyl-pyrazol-carboxylic acid.* [261°]. Formed by reduction of o-nitro-di-phenyl-methyl-pyrazol-carboxylic acid with $SnCl_2$ (Knorr a. Jödicke, *B.* 18, 2262). Fine needles. V. sol. alcohol, chloroform, and acetic acid; insol. water, alkalis, and dilute acids. It can be distilled undecomposed. It is a very stable body. By sodium and alcohol it is reduced to a hydro- compound which dissolves in strong H_2SO_4 with a deep-green colour.

OXY-PHENYL-METHYL-QUINOXALINE

$C_6H_3Me\langle{}^{N:C(OH)}_{N:CPh}$. [198°]. Formed from (1, 3, 4)-tolylene-diamine and phenyl-glyoxylic acid (Hinsberg, *A.* 237, 352). Pale-yellow needles.

γ-OXY-γ-PHENYL-s-DI-METHYL-SUCCINIC ACID $CHPh(OH).CH(CO_2H).CHMe.CO_2H$. *Phenyl-homo-itamalic acid.* The free acid is unstable, but the salts CaA″3aq, BaA″2aq, and Ag_2A'' are got by boiling its lactone with bases (Fittig a. Penfield, *B.* 216, 119; 20, 3179).

Lactone. [177°]. *Phenyl-homoparaconic acid.* Formed from benzoic aldehyde, sodium pyrotartrate, and Ac_2O by heating for 10 hours at 130°. Plates (from water). Yields AgA′. Forms phenyl-butylene (177°) on distillation. Conc. HBr at 0° forms $CHPhBr.CH(CO_2H).CHMe.CO_2H$ [149°] which on warming with water becomes $CHPh:CH.CHMe.CO_2H$. The lactone [177°] is accompanied by an isomeride [124·5°]. The lactone [177°] yields on distillation methyl-naphthol [89°], while the isomeride yields an isomeric methyl-naphthol [92°]. Both methyl-naphthols yield (β)-methyl-naphthalene on distillation with zinc-dust.

***o*-Oxy-phenyl-di-methyl-succinic acid** $C_6H_4(OH).CH_2.CH(CO_2H).CHMe(CO_2H)$. [145°–150°]. Formed by reducing coumaryl-propionic acid in alkaline solution with sodium-amalgam (Fittig a. Brown, *A.* 255, 288). Crystals, v. sol. water.—BaA″.—CaA″.—Ag_2A'': curdy pp.

Oxy-phenyl-methyl-succinic acid is described as OXY-BENZYL-SUCCINIC ACID.

OXY-DI-PHENYL-METHYL-ψ-THIO-UREA. *Methyl derivative*

$C_6H_4(OMe).NH.C(SMe):NPh$. [80°]. Formed by the action of MeI on phenyl-anisyl-thio-urea (Foerster, *B.* 21, 1870). Long white needles.

Di-oxy-di-phenyl-methyl-ψ-thio-urea. *Di-methyl derivative* $C_6H_4(OMe).NH.C(SMe):NC_6H_4OMe$. [87°]. Made by heating di-anisyl-thio-urea with MeI at 100° (Foerster, *B.* 21, 1860). Prisms, v. e. sol. hot alcohol. Yields on distillation MeSH and a substance [56°] which on boiling with dilute HCl gives di-anisyl-urea [184°].—$C_{16}H_{18}N_2SO_2HCl$: white plates.—$B'_2H_2PtCl_6$: prisms.

OXY-PHENYL-NAPHTHYL-ACETIC ACID $CPh(C_{10}H_7)(OH).CO_2H$. The salt NaA′2aq [145°] is formed from sodium phenyl (α)-naphthyl ketone, water, and CO_2 (Beckmann, *B.* 22, 915).

oα-DI-OXY-PHENYL-NAPHTHYL-KETONE $C_6H_4(OH).CO.C_{10}H_6(OH)$. [c. 106°]. Formed by heating (α)-phenonaphthoxanthone with alcoholic potash at 200° (Phomina, *A.* 257, 93). Yields a *methyl derivative* [66°], an *acetyl derivative* [137°] and an *acetoxim* [196°].

The oβ-isomeride [169°] yields K_2A'' and a *methyl derivative* [68°], an *ethyl derivative* [c. 141°], an *acetyl derivative* [108°], an *acetoxim* [188°], and a *phenyl-hydrazide* [198°].

DI-OXY-DI-PHENYL-OCTANE CPhPr(OH).CPhPr(OH). [64°]. Formed by the action of sodium-amalgam on a solution of phenyl *n*-propyl ketone in dilute alcohol (Schmidt a. Fieberg, *B.* 6, 499). Needles (from acetone).

Di-oxy-di-phenyl-octane $C_6H_{13}CMe(C_6H_4OH)_2$. [83·5°]. Formed from methyl hexyl ketone, phenol, and HCl (Dianin, *J. R.* 1888, 534). Needles. Yields a di-benzoyl derivative [114°].

OXY-PHENYL-OXANTHRANOL $C_{20}H_{14}O_3$ *i.e.* $C_6H_4\!<\!\begin{matrix}CO\text{———————}\\C(OH)(C_6H_4.OH)\end{matrix}\!>\!C_6H_4$. [194°]. Formed by oxidising oxy-phenol-anthranol with $KMnO_4$ (Pechmann, *B.* 13, 1617). Yellowish crystals. Yields anthraquinone on oxidation.

Acetyl derivative $C_{22}H_{16}O_4$. Needles.

Di-oxy-phenyl-oxanthranol *v.* PHENOL-PHTHALIDEÏN.

OXY-PHENYL-ISO-OXAZOLE $CPh\!<\!\begin{matrix}CH_2\\N.O\end{matrix}\!>\!CO$. [147°]. Formed from benzoyl-acetic ether and hydroxylamine in acid, neutral, or ammoniacal solution (Claisen a. Zedel, *B.* 24, 141; Hantzsch, *B.* 24, 502). Needles, sl. sol. cold alcohol. HClAq at 120° yields the oxim of acetophenone. Ammonia forms $CPh\!<\!\begin{matrix}CH\\N.O\end{matrix}\!>\!C.ONH_4$ [168°]. Yields a nitroso- derivative $CPh\!<\!\begin{matrix}C(NOH)\\N.O\text{——}\end{matrix}\!>\!CO$ [143°].

DI-OXY-DI-PHENYL OXIDE $C_{12}H_{10}O_3$ *i.e.* $O(C_6H_4OH)_2$? Formed from phenol and CrO_2Cl_2 (Etard, *Bl.* [2] 28, 276). Amorphous powder. Yields quinone on oxidation.

DI-OXY-DI-PHENYL-OXINDOLE $C_{20}H_{15}NO_3$ *i.e.* $NH\!<\!\begin{matrix}C_6H_4\\CO\end{matrix}\!>\!C(C_6H_4OH)_2$. *Phenolisatin.* [220°]. Formed by adding H_2SO_4 to a mixture of isatin and phenol (Baeyer a. Lazarus, *B.* 18, 2641). White needles, insol. water, sol. alkalis.

Acetyl derivative $C_{20}H_{14}O_3NAc$. [185°]. Colourless needles (from HOAc).

Di-methyl derivative $C_{20}H_{13}Me_2NO_3$. [65°]. Made from anisole, isatin, and H_2SO_4.

p-OXY-PHENYL PENTADECYL KETONE. *Methyl derivative* $C_{15}H_{31}.CO.C_6H_4.OMe$. [70·5°]. (280° at 15 mm.). Formed from anisole, palmityl chloride, and $AlCl_3$ (Krafft, *B.* 21, 2269).

Ethyl derivative [69°]. (289 at 15 mm.). Formed in like manner from phenetole. Plates.

Di-oxy-phenyl pentadecyl ketone. *Di-methyl derivative.* [63·5°]. (290° at 15 mm.). Formed in like manner from the di-methyl derivative of resorcin (K.). Plates.

DI-OXY-PHENYL-PENTANE CHPh(OH).CH(OH)Pr. [82°]. (287°). Formed by the action of alcoholic potash on a mixture of benzoic and isobutyric aldehydes (Swoboda, *M.* 11, 390). White crystals, v. sol. ether.

Di-acetyl derivative $C_{15}H_{20}O_4$. [55°]. (297°).

Di-oxy-phenyl-pentane $CHPh(OH).CH_2.CH_2.CH_2.CH_2.OH$. [54°]. Formed by reducing benzoyl-butyl alcohol with sodium-amalgam. The glycol is extracted with ether (Kipping a. Perkin, jun., *C. J.* 57, 312). Needles (from benzene), v. sol. ether.

Di-oxy-di-phenyl-pentane $CEt_2(C_6H_4OH)_2$. [200°]. Formed from di-ethyl ketone, phenol, and HCl (Dianin, *J. R.* 1888, 534). On fusion with NaOH it yields $C_5H_{11}.C_6H_4OH$ [76·5°] (253°).

OXY-PHENYL-PENTENOIC ACID *v.* OXY-PHENYL-ANGELIC ACID.

DI-OXY-DI-PHENYL-PENTINOIC ACID. *Di-methyl derivative* $C_6H_4(OMe).CH:CH.C(CO_2H):CH.C_6H_4OMe$. [160°]. Formed from *p*-methoxy-benzoic aldehyde, sodium succinate, and Ac_2O (Fittig a. Politis, *A.* 255, 299). Long yellow needles (from HOAc).—BaA'_2 2aq: silky plates.—CaA'_2 3aq.—AgA: light-yellow pp.

OXY - PHENYLPHENYLENE - ANTHRA - QUINONE DIHYDRIDE $C_{26}H_{16}O_3$ *i.e.* $CO\!<\!\begin{matrix}C_6H_2(OH)\\ \quad\!>\!CO\\C_6H_3\text{———}\end{matrix}\!>\!C_6H_5Ph$. [266°]. Formed by fusing truxone with potash (Liebermann a. Bergami, *B.* 23, 321). Yellow needles, sl. sol. alcohol. Yields an acetyl derivative $C_{26}H_{15}AcO_3$ [180°], v. sol. HOAc.

OXY-DI-PHENYL-PHOSPHINE. *Phenyl derivative* $P(C_6H_5)_2.OPh$. (265°–270° at 62 mm.). S.G. $\frac{24}{4}$ 1·14. V.D. 10·02 (obs.). Got by heating PPh_2Cl with phenol (Michaelis a. La Coste, *B.* 18, 2109). Oil. Readily absorbs oxygen from the air, becoming $(C_6H_5)_2PO.OPh$. Sulphur yields $(C_6H_5)_2PS.OPh$ [124°]. Selenium forms $Ph_2PSe(OPh)$ [115°]. Yields a crystalline *methylo-iodide* [c. 136°] and a benzylo-chloride $Ph_2P(OPh)C_7H_7Cl$ [232°-236°].

TETRA - OXY - DI - PHENYL - PHTHALIDE. *Anhydride v.* FLUORESCEIN.

OXY-PHENYL-PHTHALIMIDE *v.* AMIDO-PHENOL.

DI-OXY-DI-PHENYL-PROPANE $CMe_2(C_6H_4OH)_2$. [154° cor.]. Got from acetone, phenol, and BzCl (Dianin, *J. R.* 1888, 534). Flat needles. Yields, on soda-fusion, *p*-isopropyl-phenol [61°].

OXY-PHENYL-PROPIOLIC ACID *v.* COUMARILIC ACID.

α-OXY-β-PHENYL-PROPIONIC ACID $C_6H_5.CH_2.CH(OH).CO_2H$. [98°]. Formed from phenyl-acetic aldehyde, HCy, and HCl (Erlenmeyer, *B.* 13, 303; *A.* 219, 179). Got also by reducing phenyl-glycidic acid with sodium-amalgam (Plöchl *B.* 16, 2823). Prisms (from

water). Yields formic acid and phenyl-acetic acid on heating.—BaA'_2 aq : globular aggregates.

Nitrile [58°]. Needles (from benzene).

β-Oxy-β-phenyl-propionic acid $C_6H_5CH(OH).CH_2.CO_2H$. [93°]. Formed by the action of sodium-amalgam on the acid $C_6H_5.CH(OH).CHCl.CO_2H$ (Glaser, *A*. 147, 86) and by boiling β-bromo-β-phenyl-propionic acid with water (Fittig a. Binder, *A*. 195, 138). Got also by reducing benzoyl-acetic ether with sodium-amalgam (Perkin, *C. J.* 47, 254). Prisms, v. sol. cold water. Yields cinnamic acid on heating with baryta-water (Kast, *A*. 206, 26) or with dilute H_2SO_4 at 100° (Erlenmeyer).—KA'.—$BaA'_2 1\frac{1}{2}$aq.—$ZnA'_2 1\frac{1}{2}$aq.—AgA': needles.

Acetyl derivative [100·5°]. Crystals. Yields cinnamic acid when heated with Ac_2O at 120° (Slocum, *A*. 227, 59).

β-Oxy-α-phenyl-propionic acid $CH_2(OH).CHPh.CO_2H$. *Tropic acid.* Mol. w. 166. [118°]. S. 2 at 145°.

Formation.—1. By decomposing atropine or hyoscyamine with fuming HClAq or with baryta-water (Lossen, *A*. 138, 230; Kraut, *A*. 148, 238; Ladenburg, *B*. 13, 607).—2. From atropic acid by union with HOCl followed by reduction with zinc-dust, iron-filings, and conc. KOHAq (Ladenburg a. Rügheimer, *B*. 13, 379).—3. From atropic acid by heating it with fuming hydrogen chloride at 100° and digesting the resulting acid ($CH_2Cl.CHPh.CO_2H$) with aqueous Na_2CO_3 at 120° (Ladenburg, *A*. 217, 114).—4. From acetophenone cyanhydrin by treatment with HCl; the resulting chloro-phenyl-propionic acid being heated with sodium carbonate (Spiegel, *B*. 14, 237, 1352; Merling, *A*. 209, 5).

Properties.—Needles or tables, v. sol. water. Yields phenyl-acetic acid on fusion with potash. Chromic mixture oxidises it to benzoic acid.

Salts.—CaA'_2 4aq.—AgA': crystals.

Reference.—CHLORO-TROPIC ACID.

α-Oxy-α-phenyl-propionic acid $C_6H_5.CMe(OH).CO_2H$. *Atrolactic acid.* [94°].

Formation.—1. From atropic acid by successive treatment with HBr and aqueous Na_2CO_3 (Fittig a. Wurster, *A*. 195, 145; 206, 24).—2. By oxidation of α-phenyl-propionic acid with alkaline $KMnO_4$ (Ladenburg a. Rügheimer, *B*. 13, 373; *A*. 217, 107).—3. By reduction of the dibromo- derivative obtained by the action of H_2SO_4 on a mixture of dibromo-pyruvic acid and benzene (Böttinger, *B*. 14, 1238).—4. By dissolving the cyanhydrin of acetophenone in saturated HClAq (Spiegel, *B*. 14, 1353; Tiemann, *B*. 14, 1980).

Properties.—Trimetric needles or tables (containing $\frac{1}{2}$aq); $a:b:c = \cdot72:1:\cdot57$. Becomes anhydrous below 85°. Gives rise to atropic acid $CH_2:CPh.CO_2H$ on distillation with HCl.

Salts.—CaA'_2 8aq.—BaA'_2 2aq.—ZnA'_2 2aq: small crystals, v. sl. sol. cold water.

Ethyl derivative $CMePh(OEt).CO_2H$. '*Ethyl-tropic acid.*' [c. 62°]. Formed from acetophenone by treatment with PCl_5, acting upon the resulting $Ph.CCl_2.Me$ with KCy and dilute alcohol, and saponifying the product with baryta. Small prisms, sol. hot water.

Nitrile. Formed from acetophenone, KCy and HCl (S.). Oil.

p-Oxy-α-phenyl-propionic acid $C_6H_4(OH).CHMe.CO_2H$. *Phloretic acid.* [129°]. Formed from phloretin (7 g.) and KOH (55 c.c. of S.G. 1·2) by boiling for 3 hours (Hlasiwetz, *J.* 1855, 700; Schiff, *A*. 172, 357). Formed also from amido-phenyl-propionic acid by diazo- reaction (Trinius, *A*. 227, 268). Yellowish needles. V. sol. hot water, sol. alcohol and ether, insol. CS_2. Yields *p*-oxy-benzoic acid on fusion with potash. On heating with phloroglucin at 180° it yields the crystalline phloroglucide $C_{33}H_{32}O_{14}$. Heating with $POCl_3$ forms crystalline triphloretide $C_{27}H_{26}O_7$. Phloretic acid gives a green colour with $FeCl_3$, possibly due to phloroglucin.

Salts.—BaA'_2 2aq.—CuA'_2 (at 120°).

Ethyl ether EtA' (above 265°).

Isoamyl ether $C_5H_{11}A'$. (above 290°).

Methyl derivative $C_6H_4(OMe).CHMe.CO_2H$. [103°]. S. ·11 at 25°. Got by methylation (Körner a. Corbetta, *B*. 7, 1732). Yields BaA'_2 2aq and MeA' [38°] (278°).

Ethyl derivative [106·5°]. Scales.

Amide $C_9H_{11}NO_2$ [110°–115°]. Prisms.

Isophloretic acid, made by boiling isophloretin with KOHAq (Rochleder, *Z*. 1868, 711) is probably identical with phloretic acid.

o-Oxy-β-phenyl-propionic acid $C_6H_4(OH).CH_2.CH_2.CO_2H$. *Melilotic acid. Hydrocoumaric acid.* [83°]. S. 5 at 18°; 109 at 40°. Occurs, partly combined with coumarin, in yellow melilot (*Melilotus officinalis*) (Zwenger a. Bodenbender, *A*. 126, 257; *Suppl.* 5, 100). Formed by reducing coumarin with sodium-amalgam (Zwenger, *A. Suppl.* 8, 32; Dyson, *C. J.* 51, 70; Hochstetter, *A*. 226, 355; Tiemann, *B*. 10, 286). Trimetric crystals. Its ammoniacal solution turns blue in air. Yields salicylic acid when fused with potash. Conc. HBrAq converts it into the anhydride.

Salts.—KA'$x$aq.—$BaA'_2$3aq.—CaA'_2.—CaA'_2 2aq.—MgA'_2 4aq.—CuA'_2 aq.—PbA'_2.—ZnA'_2aq.—AgA': bulky pp.

Ethyl ether EtA'. [34°]. Prisms.

Methyl derivative $C_6H_4(OMe).CH_2.CH_2.CO_2H$. [92°]. Crystals (from alcohol) (Perkin, *C. J.* 39, 416).

Ethyl derivative $C_6H_4(OEt).CH_2.CH_2.CO_2H$. [80°]. Needles (from dilute alcohol). Yields the salts $Ba(C_{11}H_{13}O_3)_2$ and CaA'_2 2aq (Fittig a. Ebert, *A*. 216, 153).

Anhydride $C_9H_8O_2$. *Hydrocoumarin.* [25°]. (272°). Got by distilling the acid. Tables, sl. sol. hot water. Its oxim $C_6H_4{<}{\scriptstyle C_2H_4 \atop O}{>}C(NOH)$ is oily (Tiemann, *B*. 19, 1664).

Amide $C_9H_{11}NO_2$. [70°]. Needles.

m-Oxy-β-phenyl-propionic acid $C_6H_4(OH).CH_2.CH_2.CO_2H$. [111°]. Formed by reduction of *m*-coumaric acid (Tiemann a. Ludwig, *B*. 15, 2050). Long needles, insol. ligroïn.

Methyl derivative [c. 51°]. Needles.

p-Oxy-β-phenyl-propionic acid [4:1]$C_6H_4(OH).CH_2.CH_2.CO_2H$. *Hydroparacoumaric acid.* [129°]. Occurs in very slight quantity in human urine (Baumann, *H*. 4, 307). Formed by reducing paracoumaric acid with sodium-amalgam (Hlasiwetz a. Malin, *A*. 142, 358). Formed also from *p*-nitro-cinnamic ether by reduction followed by the diazo- reaction (Stöhr, *A*. 225, 57; *cf.* Buchanan a. Glaser, *Z*. [2] 5, 193). Occurs in putrid meat (Salkowski, *B* 13, 190). Formed also by putrefactive fermentation of tyrosine (Baumann, *B*. 12, 1450;

13, 279). Monoclinic prisms (from ether), sl. sol. cold water. Gives a bluish-grey colour with $FeCl_3$. Yields *p*-oxy-benzoic acid when fused with potash.—BaA'_2.—ZnA'_2 2aq. S. ·77 in the cold.—CuA'_2 2aq.—AgA′: minute needles.

Ethyl ether EtA′. Liquid smelling like rhubarb.

Methyl derivative $C_6H_4(OMe).CH_2.CH_2.CO_2H$. *Hydro-methyl-naringenic acid.* [102°]. Feathery crystals or long white needles.—A′Ag: small needles, sl. sol. hot water.—A'_2Ba 2aq.

Di-methyl ether of the methyl derivative $C_6H_4(OMe).CH_2.CH_2.CO_2Me$: [38°]; (265°–270°). Formed by methylation of *p*-hydro-coumaric acid (Eigl, *B.* 20, 2531).

Amide $C_6H_4(OH).CH_2.CH_2.CONH_2$. Needles.

α-Oxy-ββ-di-phenyl-propionic acid $CHPh_2.CH(OH).CO_2H$. [159°]. Formed by saponifying its ether with alcoholic potash. Thin needles, v. sol. alcohol. Forms a compound [c. 53°] when heated with dilute H_2SO_4 at 180°.

Ethyl ether EtA′. [66°]. Got from di-phenyl-acetic aldehyde-cyanhydrin by conversion by alcoholic hydrochloric acid into $CHPh_2.CH(OH).C(OEt)(NH_2Cl)$ [135°] and decomposition of this body by water (Weise, *A.* 248, 43). Small plates, insol. water.

Acetyl derivative [53°]. Prisms.

[4:3:1] **Di-oxy-phenyl-propionic acid** $C_6H_3(OH)_2.CH_2.CH_2.CO_2H$. *Hydrocaffeïc acid.* Formed by reducing caffeïc acid with water and sodium-amalgam (Hlasiwetz, *A.* 142, 353). Trimetric crystals, v. sol. water. Its salts are gummy.

Methyl derivative [4:3:1] $C_6H_3(OH)(OMe)CO_2H$. [90°]. Formed by reducing ferulic acid with sodium-amalgam (Tiemann a. Nagai, *B.* 11, 650; 14, 965). Minute tables, v. sol. alcohol.

Methyl derivative [4:3:1] $C_6H_3(OMe)(OH)CO_2H$. [147°]. Formed by reduction of isoferulic acid (T. a. N.). Needles.

Di-methyl derivative $C_6H_3(OMe)_2.CH_2.CH_2.CO_2H$. [97°]. Formed by reduction of $C_6H_3(OMe)_2.CH:CH.CO_2H$ (T. a. N.). Slender needles (containing aq).

Methylene derivative $CH_2{<}^{O}_{O}{>}C_6H_3.C_2H_4.CO_2H$. *Pipero-propionic acid.* [85°]. Formed by reduction of $CH_2O_2{:}C_6H_3.CH{:}CH.CO_2H$ (Lorenz, *B.* 13, 758) and by oxidising (β)-hydropiperic acid with Na_2CO_3 and $KMnO_4$ (Regel, *B.* 20, 421). Needles (from ligroïn), sl. sol. cold water.—CaA'_2 aq.—AgA′: feathery crystals.

(4,2,1)-**Di-oxy-phenyl-propionic acid** $C_6H_3(OH)_2.CH_2.CH_2.CO_2H$. Formed by reducing umbelliferone with sodium-amalgam (Hlasiwetz a. Grabowski, *A.* 139, 102). Crystalline, decomposing at 110°. Yields resorcin when fused with potash.

Di-methyl derivative $C_6H_3(OMe)_2.CH_2.CH_2.CO_2H$. [105°]. Formed by reduction of the di-methyl derivatives of (α)- and (β)-umbellic acid (Will, *B.* 16, 2116). White crystals (from alcohol).

oα-Di-oxy-phenyl-propionic acid $C_6H_4(OH).CH_2.CH(OH).CO_2H$. *Salicyllactic acid.* Formed by reduction of *o*-oxy-phenyl-glycidic acid with sodium-amalgam (Plöchl, *B.* 18, 1188). Syrup.—ZnA'_2.—CuA'_2 6aq: prisms, v. sol. Aq.

***p*α-Di-oxy-phenyl-propionic acid** $C_6H_4(OH).CH_2.CH(OH).CO_2H$. [144°]. Made from the corresponding di-amido- acid by the diazo- reaction (Erlenmeyer a. Lipp, *A.* 219, 226). Hemispherical groups of needles (containing aq) (from water at 0°), m. sol. alcohol. Melts at 140° after fusion. — CaA'_2 3aq. — CaA'_2 6aq: small crystals.

Di-oxy-phenyl-propionic acid [4:1] $C_6H_4(OH).CH(OH).CH_2.CO_2H$ (?). [164°]. Occurs in urine of dogs fed with much tyrosine (Blendermann, *H.* 6, 256). Needles (containing ½aq), m. sol. cold water.

αβ-Di-oxy-phenyl-propionic acid $CHPh(OH).CH(OH).CO_2H$. *β-Phenyl-glyceric acid.* [144°]. Formed by the action of alkalis on $C_6H_5.CH(OH).CHCl.CO_2H$ (Glaser, *A.* 147, 98; Lipp, *B.* 16, 1287), and by oxidising cumanic acid with dilute $KMnO_4$ (Fittig, *B.* 21, 920). Monoclinic plates (from ether). At 160° it yields phenyl-acetic aldehyde. Gaseous HCl yields $C_6H_5.CHCl.CH(OH).CO_2H$ (Erlenmeyer, jun., *B.* 20, 2466).—AgA′: amorphous pp.

Di-benzoyl derivative [187°].

Di-benzoyl derivative of the methyl ether [114°]. Formed by the action of AgOBz on $CHPhBr.CHBr.CO_2Me$ (Anschütz a. Kinnicutt, *B.* 12, 538). Small monoclinic crystals.

Di-benzoyl derivative of the ethyl ether $CHPh(OBz).CH(OBz).CO_2Et$. [109°].

Isomeride *v.* Atroglyceric acid.

Di-oxy-di-phenyl-propionic acid $C_{15}H_{14}O_4$ aq *i.e.* $CH_3.C(C_6H_4OH)_2.CO_2H$. Made from phenol, pyruvic acid, and H_2SO_4 at 0° (Böttinger, *B.* 16, 2071). Amorphous mass, carbonising above 268°, v. sol. acetone. Yields an amorphous di-acetyl derivative.

Tri-oxy-phenyl-propionic acid. *Tri-ethyl derivative* $C_6H_2(OEt)_3.C_2H_4.CO_2H$. [77°]. Formed by reduction of the tri-ethyl derivative of (α)- or (β)- æsculetic acid with sodium-amalgam (Will, *B.* 16, 2111).

An **isomeric acid** [85°] is got by reducing the di-ethyl derivative of daphnetic acid (Will a. Jung, *B.* 17, 1087).

Hexa-oxy-di-phenyl-propionic acid $C_{15}H_{14}O_8$ *i.e.* $CH_3.C(C_6H_2(OH)_3)_2.CO_2H$. [162°]. Formed, together with amorphous $C_{15}H_{12}O_7$, from pyrogallol, pyruvic acid, and H_2SO_4 at 0° (Böttinger, *B.* 16, 2404). Resinous mass. Yields, when heated with Ac_2O, the compounds $C_{15}H_{10}Ac_2O_7$ [110°] and $C_{15}H_8Ac_4O_7$ [c. 200°].

References.—Bromo-, Chloro-, Chloro-nitro-, and Iodo-, oxy-propionic acids.

***p*-OXY-DI-PHENYL-PROPYLAMINE.** *Methyl derivative* $C_{16}H_{19}NO$ *i.e.* $C_6H_4(OMe).CH_2.CHPh.CH_2NH_2$. Formed from the methyl derivative of α-phenyl-*p*-coumaric nitrile by reduction with alcohol and sodium (Freund a. Remse, *B.* 23, 2864). Yellow liquid, slightly volatile with steam.—$B'_2H_2PtCl_6$. [195°]. *Aurochloride* [87°]. Golden plates.

OXY-DI-PHENYL-PROPYLENE-DIAMINE $C_{15}H_{18}N_2O$ *i.e.* $CH(OH)(CH_2.NHPh)_2$. [54°]. Made by the action of aniline on epichlorhydrin (Faucounier, *C. R.* 107, 250). Needles (from alcohol). — $B'H_2C_2O_4$ 1⅓aq. [150°]. — $B'H_2PtCl_6$ 4aq: yellow plates.

Acetyl derivative $C_{15}H_{17}AcN_2O$ aq. [100°]. Prisms.

Nitrosamine $C_{15}H_{17}(NO)N_2O$. [109°].

DI-*p*-OXY-DI-PHENYL-PROPYLENE. *Di-methyl derivative* $CH_3.CH:C(C_6H_4OMe)_2$. [101°]. Formed from anisole, $AlCl_3$, and propionyl chloride (Gattermann, *B.* 22, 1130). Plates. Yields $CO(C_6H_4OMe)_2$ on oxidation. The homologous $CH_3.CH:C(C_6H_4OEt)_2$ crystallises in needles [77°].

OXY-PHENYL ISOPROPYL KETONE. *Ethyl derivative* $C_6H_4(OEt).CO.CHMe_2$. [41°]. Made from isobutyryl chloride, C_6H_5OEt, and $AlCl_3$ (Gattermann, *B.* 23, 1206). Tables (from ether). Yields an oxim [111°] crystallising in needles.

Oxy-phenyl propyl ketone $C_3H_7.CO.C_6H_4OH$. [91°]. (c. 280°). Formed from phenol and butyryl chloride (Perkin, *C. J.* 55, 546). Pearly plates.

DI-OXY-PHENYL-ISOPROPYL-PYRIMIDINE $CH\left\langle\begin{smallmatrix}CPh-N\\C(OH):N\end{smallmatrix}\right\rangle CMe_2(OH)$. [198°]. Formed from oxy-isobutyramidine hydrochloride, benzoyl-acetic ether, and NaOHAq (Pinner, *B.* 22, 2626). Prisms (from alcohol or benzene).

OXY-TRI-PHENYL-PROPYL-PYRROLE $C_{25}H_{23}NO$ *i.e.* $NPr\left\langle\begin{smallmatrix}CO\ .CPh_2\\CPh:CH\end{smallmatrix}\right.$. [105°]. Formed from $C_6H_5CBz:CHBz$ and alcoholic propylamine at 100° (Japp a. Klingemann, *C. J.* 57, 706). Monoclinic prisms [95°–98°] or trimetric prisms [105°]; $a:b:c = \cdot694:1:\cdot765$.

DI-*o*-OXY-DI-PHENYL-PROPYL-ψ-THIO-UREA. *Di-methyl derivative* $C(SPr)(NH.C_6H_4.OMe):N.C_6H_4.OMe$. [58°]. Made from di-anisyl-thio-urea and propyl chloride (Foerster, *B.* 21, 1864). Plates, insol. water.

OXY-DI-PHENYL-PYRAZINE. *Tetra-hydride* $NPh\left\langle\begin{smallmatrix}CH_2.CH_2\\CH_2.CO\end{smallmatrix}\right\rangle NPh$. [148°]. Formed from di-phenyl-ethylene-diamine, chloro-acetic acid, and NaOAc at 170° (Bischoff a. Nastvogel, *B.* 22, 1783; 23, 2026). Crystalline. Insol. Aq.

Di-oxy-di-phenyl-pyrazine. *Dihydride* $NPh\left\langle\begin{smallmatrix}CH_2.CH_2\\CO\ .CO\end{smallmatrix}\right\rangle NPh$. *Di-phenyl-aβ-diacipi-perazine.* [258°]. Got by oxidising the above with CrO_3 and HOAc, and also by heating di-phenyl-ethylene-diamine with oxalic acid at 200° (B. a. N.). Plates, v. sl. sol. alcohol and ether. Nitrous acid forms $C_{16}H_{10}N_6O_9$ [290°].

Di-oxy-di-phenyl-pyrazine. *Dihydride* $NPh\left\langle\begin{smallmatrix}CO\ .CH_2\\CH_2.CO\end{smallmatrix}\right\rangle NPh$. *Diphenyl-aγ-diacipi-perazine. Di-oxy-di-phenyl-piazine dihydride.* [263°]. Made from aniline and chloro-acetic acid (Hausdörfer, *B.* 22, 1797; *cf.* Meyer, *B.* 10, 1967; Abenius, *J. pr.* [2] 40, 431). Needles. Alcoholic potash forms phenyl-amido-acetic acid [127°] on boiling, and in the cold produces $NHPh.CH_2.CO.NPh.CH_2.CO_2H$ [130°].

Di-oxy-phenyl-pyrazine. *Dihydride* $NPh\left\langle\begin{smallmatrix}CH_2.CO\\CH_2.CO\end{smallmatrix}\right\rangle NH$. [158°]. Made from aniline and chloro-acetic amide (B.). Prisms.

Di-oxy-di-phenyl-pyrazine. *Dihydride* $NPh\left\langle\begin{smallmatrix}CH_2.CO\\CH_2.CO\end{smallmatrix}\right\rangle NPh$. *Diphenyl-aδ-diacipiper-azine.* [152°]. Formed by heating the mono-anilido of phenyl-imido-diacetic acid with Ac_2O at 160° (Bischoff, *B.* 23, 1990). Needles. Nitrous acid yields $C_{16}H_{12}N_2O_2$ [c. 95°] crystallising in golden plates.

Di-*p*-oxy-di-phenyl-pyrazine. *Di-methyl derivative of the hexahydride* $C_6H_4(OMe)N\left\langle\begin{smallmatrix}CH_2.CH_2\\CH_2.CH_2\end{smallmatrix}\right\rangle N.C_6H_4OMe$. [233°]. Formed from *p*-anisidine, ethylene-bromide, and NaOAc (Bischoff, *B.* 22, 1782). Tables.

Di-ethyl derivative of the hexa-hydride. [223°]. Gives a nitroso- derivative [c. 80°].

Tri-oxy-di-phenyl-pyrazine. *Di-ethyl derivative of the tetrahydride* $C_6H_4(OEt).N\left\langle\begin{smallmatrix}CH_2.CH_2\\CH_2.CO\end{smallmatrix}\right\rangle N.C_6H_4.OEt$. [162°]. Formed from $C_2H_4(NH.C_6H_4OEt)_2$ by heating with chloro-acetic acid and fused NaOAc at 150° (Bischoff, *B.* 23, 2030). Crystals, sl. sol. ether.

Tetra-oxy-di-phenyl-pyrazine. *Di-ethyl derivative of the dihydride* $C_6H_4(OEt).N\left\langle\begin{smallmatrix}CH_2.CO\\CO\ .CH_2\end{smallmatrix}\right\rangle N.C_6H_4OEt$. [265°]. Formed by heating *p*-ethoxy-phenyl-amido-acetic acid at 260° (B. a. N.). Needles.

OXY-PHENYL-PYRAZOLE $C_9H_7(OH)N_2$. [153°]. Got from bromo-oxy-phenyl-pyrazole by reduction with sodium-amalgam (Fischer a. Knoevenagel, *A.* 239, 201). Needles. Sol. conc. HClAq and alkalis. The Na salt forms needles.

Oxy-phenyl-pyrazole tetrahydride $C_9H_{12}N_2O$ *i.e.* $NPh\left\langle\begin{smallmatrix}NH\ .CH_2\\CH_2.CH(OH)\end{smallmatrix}\right.$? [104°]. Formed by the action of phenyl-hydrazine on epichlorhydrin in ethereal solution at 15° (Gerhard, *B.* 24, 352). Pearly prisms (from ether), v. sol. warm water. Yields aniline and phenyl-pyrazole on boiling with phenyl-hydrazine hydrochloride in benzene solution. Forms an acetyl derivative.—Salt: $B'_2H_2PtCl_6$ 2aq. [156°]. Yellowish-red prisms.

Oxy-di-phenyl-pyrazole $NPh\left\langle\begin{smallmatrix}NH\ .CO\\CPh:CH\end{smallmatrix}\right.$. *Di-phenylpyrazolone.* [251°]. Formed by heating cinnamoyl-phenyl-hydrazine (Knorr, *B.* 20, 1108). Needles (from alcohol), exhibiting green fluorescence.

Oxy-di-phenyl-pyrazole $NPh\left\langle\begin{smallmatrix}N\ :CPh\\CO.CH_2\end{smallmatrix}\right.$. [137°]. Formed from benzoyl-acetic ether and phenyl-hydrazine (Knorr a. Klotz, *B.* 20, 2546). Yields, with nitrous acid, the rod compound $NPh\left\langle\begin{smallmatrix}N\ :CPh\\CO.C:NOH\end{smallmatrix}\right.$ [200°]. Diazobenzene chloride forms $C_3HPh_2N_2O(N_2Ph)$ [171°]. Phenyl-hydrazine converts it into di-oxy-tetra-phenyl-dipyrazyl melting above 300°. — B′HCl. — $B'H_2SO_4$. Powder. Decomposes at 237°.

Oxy-di-phenyl-pyrazole $NPh\left\langle\begin{smallmatrix}N\ :CH\\CO.CHPh\end{smallmatrix}\right.$. [196°]. Formed from α-phenyl-glyoxylic acid and phenyl-hydrazine (Wislicenus, *B.* 20, 2932). Plates (from EtOH), sol. alkalis, sl. sol. ether.

Di-oxy-phenyl-metapyrazole $C_9H_8N_2O_2$ probably $\begin{matrix}C_6H_5.CH-N\diagdown\\ \mid\qquad\quad\ C(OH)\\ C(OH):N\diagup\end{matrix}$. [182°]. Obtained by boiling phenyl-uramido-aceto-nitrile $C_6H_5.CH(CN).NH.CO.NH_2$ (from benzaldehyde-cyanhydrin and urea) with dilute HCl. Colourless dimetric plates. Dissolves readily in alkalis (Pinner a. Lifschütz, *B.* 20, 2355).

OXY-PHENYL-PYRAZOLE CARBOXYLIC ACID $C_{10}H_8N_2O_3$ *i.e.* $NPh<\begin{smallmatrix}N\ :C(CO_2H)\\ CO.CH_2\end{smallmatrix}$. [263°]. Formed by the action of HCl or NaOH on the phenyl-hydrazide of oxalacetic ether (Buchner, *B.* 22, 2931). Colourless needles, v. sl. sol. cold water. $FeCl_3$ colours its solution dark blue.

Ethyl ether [182°]. Formed by heating the above phenyl-hydrazide by itself (Wislicenus, *A.* 246, 306).

OXYPHENYL PYRIDINE $C_{11}H_9NO$. Formed by heating aniline chelidonate (Lerch, *M.* 5, 407). Crystallises from water in needles (containing aq).

Oxy-di-phenyl-pyridine $C_{17}H_{13}NO$ *i.e.* $NH<\begin{smallmatrix}CPh:CH\\ CPh:CH\end{smallmatrix}>CO$. [267°]. Formed by heating dehydro-benzoyl-acetic acid with alcoholic NH_3 at 160° (Feist, *B.* 23, 3736). Plates.

DI-OXY-PHENYL-PYRIDINE CARBOXYLIC ACID $C_5H(OH)_2NPh.CO_2H$. Made by boiling a solution of comenic acid with aniline (Mennel, *J. pr.* [2] 32, 177). Tetrahedra (containing aq), m. sol. water. Coloured violet by $FeCl_3$.

OXY-PHENYL-PYRIMIDINE $C_{10}H_8N_2O$ *i.e.* $CPh<\begin{smallmatrix}N - CH\\ N:C(OH)\end{smallmatrix}>CH$. [199°]. Made by heating its carboxylic acid (Pinner, *B.* 22, 2616). Small prisms, sl. sol. hot Aq, v. sol. alkalis and acids.

Oxy-di-phenyl-pyrimidine $C_{16}H_{12}N_2O$ *i.e.* $CPh<\begin{smallmatrix}N - CPh\\ N:C(OH)\end{smallmatrix}>CH$. [284°]. Formed from benzamidine hydrochloride, benzoyl-acetic ether, alcohol, and dilute (10 p.c.) NaOH (Pinner, *B.* 22, 1626). Formed also by heating amido-di-phenyl-pyrimidine with HClAq at 180° (Schwarze, *J. pr.* [2] 42, 15). Needles, v. sl. sol. hot alcohol.

Oxy-tri-phenyl-pyrimidine $C_{22}H_{16}N_2O$. [340°]. Formed by heating the corresponding amido-compound with HClAq at 170° (Wache, *J. pr.* [2] 39, 255). Needles.

Di-oxy-di-phenyl-pyrimidine. *Ethyl derivative* $C_6H_4(OEt).C<\begin{smallmatrix}N.CPh\\ N:C(OH)\end{smallmatrix}>CH$. [274°]. Formed from *p*-ethoxy-benzamidine and benzoyl-acetic ether (Pinner, *B.* 23, 2955).

OXY-PHENYL-PYRIMIDINE CARBOXYLIC ACID $CPh<\begin{smallmatrix}N.C(CO_2H)\\ N:C(OH)\end{smallmatrix}>CH$. [247°]. Formed from benzamidine hydrochloride, oxalacetic ether, and dilute (10 p.c.) NaOH (Pinner, *B.* 22, 1628, 2616). Granules, sl. sol. water.—BaA″.—CaA′$_2$. Prisms.—*Amide*: prisms, sl. sol. water. —*Benzamidide* $C_{18}H_{14}N_4O_2$ [263°].

Oxy-di-phenyl-pyrimidine carboxylic acid $CPh<\begin{smallmatrix}N.CPh\\ N:C(OH)\end{smallmatrix}>C.CO_2H$. [236°]. Made by oxidising oxy-di-phenyl-methyl-pyrimidine with $KMnO_4$ (E. von Meyer, *J. pr.* [2] 40, 303). Yellowish prisms (from alcohol). Yields oxy-di-phenyl-pyrimidine [284°] on heating.

Di-oxy-phenyl-pyrimidine carboxylic acid. *Ethyl derivative* $C_7H_4(OEt).C<\begin{smallmatrix}N\ .\ C(CO_2H)\\ N=C(OH)\end{smallmatrix}>CH$. [246°]. Made from *p*-ethoxy-benzamidine and oxalacetic ether (Pinner, *B.* 23, 2956). Needles, sl. sol. hot alcohol.—*Salt* $C_6H_4(OEt)CN_2H_4A'$. [280°].

OXY-TRI-PHENYL-PYRROLE $C_{22}H_{17}NO$ *i.e.* $NH<\begin{smallmatrix}CO\ .CPh_2\\ CPh:CH\end{smallmatrix}$. Mol. w. 311. [221°]. Formed by boiling C_6H_5.CBz:CHBz for a long time with alcoholic ammonia (Japp a. Klingemann, *B.* 22, 2884; *C. J.* 57, 682). Triclinic crystals; $a:b:c = \cdot779:1:\cdot512$; $\alpha = 78°\,56'$; $\beta = 73°\,23'$; $\gamma = 87°\,32'$ (Tutton, *C. J.* 57, 720). Sl. sol. hot alcohol.

Dihydride $NH<\begin{smallmatrix}CO - CPh_2\\ CHPh.CH_2\end{smallmatrix}$. [201°]. Formed by reduction with sodium and amyl alcohol. Ac_2O at 180° yields an acetyl derivative $NAc<\begin{smallmatrix}CO - CPh_2\\ CHPh.CH_2\end{smallmatrix}$ [105°].

***o*-Oxy-tri-phenyl-pyrrole** $C_6H_4(OH).N<\begin{smallmatrix}CPh:CH\\ CPh:CH\end{smallmatrix}$ [176°]. Made by heating its carboxylic acid with lime (Paal a. Braikoff, *B.* 22, 3094). Yellowish needles, v. sol. alkalis.

Oxy-tetra-phenyl-pyrrole $C_{28}H_{21}NO$ *i.e.* $NH<\begin{smallmatrix}CO\ .CPh_2\\ CPh:CPh\end{smallmatrix}$. [207°]. Formed by heating CPhBz:CPhBz with alcoholic NH_3 at 200° (Klingemann a. Laycock, *C. J.* 59, 144; *B.* 24, 513). Pale-yellow plates.

Dihydride $NH<\begin{smallmatrix}CO - CPh_2\\ CHPh.CHPh\end{smallmatrix}$. [237°].

Oxy-tetra-phenyl-pyrrole $C_{28}H_{21}NO$. [182°]. Formed from CPhBz:CHBz and alcoholic NH_3 at 200°. Yellow prisms. Changed into the isomeride [207°] by heating to 310°.

***o*-OXY-TRI-PHENYL-PYRROLE CARBOXYLIC ACID** $C_6H_4(OH).N<\begin{smallmatrix}CPh:C.CO_2H\\ CPh:CH\end{smallmatrix}$. [245°]. Made from its ethyl ether [159°] which is got by the action of *o*-amido-phenol on phenacyl-benzoyl-acetic ether (Paal a. Braikoff, *B.* 22, 3093). Nodular groups of needles, v. sol. ether.

OXY-PHENYL-QUINAZOLINE.

Dihydride $C_6H_4<\begin{smallmatrix}CH_2.NPh\\ NH.CO\end{smallmatrix}$. [143°]. Formed from phenyl-ω-oxy-tolyl-urea and HCl (Söderbaum a. Widman, *B.* 22, 1670). Needles.

Oxy-phenyl-quinazoline $C_6H_4<\begin{smallmatrix}C(OH):N\\ N=CPh\end{smallmatrix}$. [234°]. S. (alcohol) 2. Formed by heating benzoyl-*o*-amido-benzamide (Körner, *J. pr.* [2] 36, 157). Needles, insol. water. —$B'_2H_2PtCl_6$: brick-red needles.

Oxy-phenyl-quinazoline $C_6H_4<\begin{smallmatrix}CO.NPh\\ N=CH\end{smallmatrix}$. [139°]. Formed by oxidation of phenyl-quinazoline dihydride with $KMnO_4$ (Paal a. Busch, *B.* 22, 2691). Plates, v. sol. benzene. With hydrazine N_2H_4 it forms $C_6H_4<\begin{smallmatrix}C(N_2H_2).NPh\\ N=CH\end{smallmatrix}$ [204°].—B′HCl. [214°].—*Platinochloride* [above 300°]. Yellow needles.

Di-oxy-phenyl-quinazoline. *Dihydride* $\begin{smallmatrix}CH_2.CH_2.C.N=CPh\\ CO\ .CH_2.C.C(OH):N\end{smallmatrix}$. [272°]. Formed from di-oxy-terephthalic ether, dihydride, and benzamidine (Pinner, *B.* 22, 2623). Slender needles, sol. alkalis, sl. sol. alcohol.

OXY-PHENYL-QUINAZOLINE CARBOXYLIC ACID $C_6H_4<\begin{smallmatrix}N=CH\\ CO.N.C_6H_4.CO_2H\end{smallmatrix}$. [320°]. Made by oxidising oxy-*p*-tolyl-quinazoline (Paal a. Busch, *B.* 22, 2683). White crystals.

(α) - OXY - (*Py.* 1) - PHENYL - QUINOLINE $C_{15}H_{11}NO$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{C(C_6H_4OH):CH}{N{=\!=\!=\!=\!=}CH}$. *Phenol-quinoline.* [243°]. Formed by diazotising (α)-amido-(*Py.* 1)-phenyl-quinoline [150°], and boiling the dilute H_2SO_4 solution (Kœnigs a. Nef, *B.* 20, 629). Colourless flat needles or plates. Volatilises undecomposed. V. sol. alcohol and chloroform, sl. sol. benzene, nearly insol. ether. By CrO_3 and H_2SO_4 it is oxidised to cinchonic acid. The hydrochloride forms glistening plates, the sulphate yellow tables; both are v. sol. hot water, sl. sol. cold. The platinochloride forms hair-fine yellow needles, v. sol. conc. HCl. The K and Na salts are colourless glistening plates, which dissolve in water with a yellow colour.

(β)-Oxy-(*Py.* 1)-phenyl-quinoline $C_{15}H_{11}NO$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{C(C_6H_4OH):CH}{N{=\!=\!=\!=\!=}CH}$. *Phenol-quinoline.* [235°]. Formed by diazotising the corresponding amido- compound [198°] and boiling the dilute H_2SO_4 solution (Kœnigs a. Nef, *B.* 20, 630). Colourless granular crystal. Sl. sol. alcohol, nearly insol. ether. Volatilises undecomposed. Dissolves with a yellow colour in alkalis and acids. By CrO_3 and H_2SO_4 it is oxidised to cinchonic acid. KOH fusion yields di-oxy-phenyl-quinoline [305°]. The sulphate crystallises in glistening yellow needles, the hydrochloride in yellow tables; both are m. sol. cold water.

o-Oxy-(*Py.* 3)-phenyl-quinoline $C_6H_4<\genfrac{}{}{0pt}{}{CH:CH}{N{=}C.C_6H_4.OH}$. [115°]. Got by heating its (*Py.* 1)-carboxylic acid [238°] (Doebner, *A.* 249, 101). Light-yellow needles (from alcohol), sol. alkalis and acids.—$B'_2H_2PtCl_6$.—$B'C_6H_3N_3O_7$. [184°]. Yellow needles.

***m*-Oxy-(*Py.* 3)-phenyl-quinoline** $C_6H_4<\genfrac{}{}{0pt}{}{CH:CH}{N\ :C.C_6H_4OH}$. [156°]. Formed by the action of nitrous acid upon *m*-amido-phenyl-quinoline (Miller a. Kinkelin, *B.* 18, 1908). Long needles, v. sol. alcohol and ether.

***p*-Oxy-(*Py.* 3)-phenyl-quinoline** $C_6H_4<\genfrac{}{}{0pt}{}{CH:CH}{N\ :C.C_6H_4OH}$. [238°]. Formed from the amido- compounds (Weidel, *M.* 8, 127). Monoclinic needles, insol. water, v. sol. hot benzene. Yields quinoline carboxylic acid [157°] on oxidation. Yields a crystalline tetrahydride on reduction.—$B'HCl\,2aq$.—$B'_2H_2PtCl_6$.

Acetyl derivative [123°]. Plates.

(*Py.* 1, 4)-Oxy-phenyl-quinoline $C_6H_4<\genfrac{}{}{0pt}{}{C(OH):CH}{N{=\!=\!=}CPh}$. [254°]. Formed, by heating to 250°, from the phenyl-β-amido-cinnamic ether $NPhH.CPh:CH.CO_2Et$, got by the action of aniline on benzoyl-acetic ether (Conrad a. Limpach, *B.* 21, 521; Knorr, *A.* 245, 377). Got also by heating its carboxylic acid (Just, *B.* 19, 1462). Plates, v. sl. sol. water, insol. ether.—B'HCl. [230°]. Needles (from alcohol).—$B'HCl\,\frac{1}{2}aq$ (J.).

(*B.* 2)-Oxy-(*Py.* 3)-phenyl-quinoline. *Methyl derivative* $\genfrac{}{}{0pt}{}{C(OMe):CH.C.CH:CH}{CH:CH{-\!-\!-}C.\ N\ :CPh}$. [133°]. Got by heating its carboxylic acid [237°] (Doebner, *A.* 249, 106). Plates (from dilute alcohol).—B'HCl: needles, sol. hot water.—$B'_2H_2PtCl_6$.—Picrate [205°].

(*B.* 4)-Oxy-(*Py.* 3)-phenyl-quinoline. *Methyl derivative* $\genfrac{}{}{0pt}{}{CH:CH{-\!-\!-}C.CH:CH}{CH:C(OMe).C.\ N\ :CPh}$. Formed by heating its carboxylic acid [216°] (D.). Oil.—$B'_2H_2PtCl_6\,2aq$: orange needles.

Di-oxy-phenyl-quinoline $C_{15}H_{11}NO_2$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{C(C_6H_4OH):CH}{N{=\!=\!=\!=\!=}C.OH}$ (?). [305°]. Formed by potash-fusion from (β)-oxy-(*Py.* 1)-phenyl quinoline [235°]; the yield being 75 p.c. (Koenigs a. Nef, *B.* 20, 632). Needles, v. sol. alcohol. Has no basic properties. An isomeride, solid at 315°, appears to be formed from (α)-oxy-(*Py.* 1)-phenyl-quinoline by potash-fusion.

Di-oxy-phenyl-quinoline. [114°]. Formed in small quantity when *p*-amido-(*Py.* 3)-phenyl-quinoline is acted upon by nitrous acid (Weidel, *M.* 8, 127). Prisms, insol. water. Reduced by zinc-dust to (*Py.* 3)-phenyl-quinoline.

Di-oxy-phenyl-quinoline $\genfrac{}{}{0pt}{}{C(OH):CH.C\ .\ CH:CH}{CH = CH.C{-}\ N\ :C(C_6H_4OH)}$. [247°]. Formed from (*B.* 2)-oxy-*p*-amido-(*Py.* 3)-phenyl-quinoline by the diazo- reaction (Weidel a. Georgievitch, *M.* 9, 138). Pale-yellow mass of hair-like needles, sl. sol. hot water. Yields (*Py.* 3)-phenyl-quinoline when distilled with zinc-dust.

Di-oxy-(*Py.* 1)-phenyl-quinoline. *Methyl derivative* $\genfrac{}{}{0pt}{}{C(OH):CH.C.C(C_6H_4.OH):CH}{CH:CH{-\!-}C.N{=\!=\!=\!=\!=}CH}$. [188°]. Got by boiling the diazo- compound of *m*-amido-(*Py.* 1)-phenyl-(*B.* 2)-methoxy-quinoline with dilute H_2SO_4 (Miller a. Kinkelin, *B.* 20, 1922). Plates. Its solution in dilute H_2SO_4 gives with chlorine-water, a little NaOH, and ammonia, a dark-green colour.

Tetrahydride [111°]. Tablets. Gives a deep-green with $FeCl_3$ and HCl.—B'HCl: plates.

(*Py.* 4)-OXY-(*Py.* 2)-PHENYL-ISOQUINOLINE $C_{15}H_{11}ON$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{CH:CPh}{CO.NH}$ or $C_6H_4<\genfrac{}{}{0pt}{}{CH\ \ :CPh}{C(OH):N}$. *Isobenzylidene-phthalimidine.* [197°]. Formed by the action of ammonia on deoxybenzoïn o-carboxylic acid $CH_2Bz.C_6H_4.CO_2H$. Prepared by heating crude isobenzylidene-phthalide (15 g.) with alcoholic NH_3 (30 c.c.) at 100° for 8–10 hours (Gabriel, *B.* 18, 2449, 3470; 19, 830). Triclinic crystals, $a:b:c$ = ·8608 : 1 : ?, $\alpha = 88°\ 28'$, $\beta = 111°\ 24'$, $\gamma = 74°\ 47'$. Sl. sol. cold alcohol. By heating with $POCl_3$ or PCl_3 it is converted into (*Py.* 4)-chloro-(*Py.* 2)-phenyl-isoquinoline; PCl_5 yields (*Py.* 1,4)-di-chloro-(*Py.* 2)-phenyl-quinoline. Nitrous acid converts it into (*Py.* 1)-nitro-(*Py.* 4)-oxy-(*Py.* 2)-phenyl-isoquinoline.

Ethyl ether $C_{15}H_{10}N(OEt)$. [46°]. Formed by heating chloro-phenyl-isoquinoline with alcoholic sodium ethylate (Gabriel, *B.* 19, 835). Flat colourless needles; v. sol. ordinary solvents; weak base.—$B'_2H_2Cl_2PtCl_4$: reddish pp.

Di-oxy-phenyl-iso-quinoline $C_6H_4<\genfrac{}{}{0pt}{}{C(OH):CPh}{CO{-\!-\!-}NH}$. [257°]. Formed from nitro-benzylidene-phthalide, P, and HI (Gabriel, *B.* 18, 3471; 20, 2866). Crystals, sl. sol. boiling Aq.

Methyl ethers. Two isomeric methyl ethers [237°] and [121°] may be prepared. Both are crystalline.

Reference. — CHLORO-OXY-PHENYL-ISOQUINOLINE.

(*Py.* 1, 3, 2)-**OXY-PHENYL-QUINOLINE CARBOXYLIC ACID** $C_6H_4<\begin{smallmatrix}C(OH):C.CO_2H\\N \!=\!=\! CPh\end{smallmatrix}$. [232°]. Made from its ethyl ether [262°] which is formed by heating $NPh:CPh.CH(CO_2Et)_2$ to 150°, alcohol being split off (Just, *B.* 18, 2632; 19, 1462). Crystals (containing aq), v. sl. sol. hot water.—AgA′: sl. sol. water.

o-Oxy-(*Py.* 3, 1)-phenyl-quinoline carboxylic acid $C_6H_4<\begin{smallmatrix}C(CO_2H):CH\\N \!=\!=\!=\! C.C_6H_4.OH\end{smallmatrix}$. [238°]. Made from salicylic aldehyde, aniline, and pyruvic acid (Doebner, *A.* 249, 98). Needles, v. sol. alcohol. —AgA′.—$H_2A'_2H_2PtCl_6$: golden-yellow needles.

(*B.* 2; *Py.* 3, 1)-**Oxy-phenyl-quinoline carboxylic acid.** *Methyl derivative* $\begin{smallmatrix}C(OMe):CH.C.C(CO_2H):CH\\CH:CH \!-\!-\! C \!-\!-\!-\! N:CPh\end{smallmatrix}$ *Phenyl-quinic acid.* [237°]. Formed by heating together equimolecular quantities of *p*-amido-anisole, benzoic aldehyde, and pyruvic acid in an alcoholic solution (Doebner, *A.* 249, 105). Needles, insol. water.—AgA′.—$H_2A'_2H_2PtCl_6$: orange-red crystals.

(*B.* 4; *Py.* 3, 1)-**Oxy-phenyl-quinoline carboxylic acid.** *Methyl derivative* $\begin{smallmatrix}CH:CH \!-\!-\! C.C(CO_2H):CH\\CH:C(OMe).C \!-\!-\!-\! N:CPh\end{smallmatrix}$ [216°]. Formed in like manner from $[2:1]C_6H_4(NH_2).OMe$, benzoic aldehyde, and pyruvic acid (D.). Yellow needles.—PbA'_2aq.—AgA′.—$H_2A'_2H_2PtCl_6$.

DI-OXY-DI-PHENYL-QUINOXALINE. *Di-ethyl derivative* $\begin{smallmatrix}CH:C(OEt).C.N.CPh\\CH:C(OEt).C.N.CPh\end{smallmatrix}$ [163°]. Formed by the action of benzil and NaOAc on an alcoholic solution of the di-ethyl ether of (α)-di-amido-hydroquinone (Nietzki a. Rechberg, *B.* 23, 1212). Yellow needles.

Di-oxy-di-phenyl-quinoxaline. Dihydride. *Di-methyl derivative* $C_6H_4<\begin{smallmatrix}N.CH.C_6H_4OMe\\N.CH.C_6H_4OMe\end{smallmatrix}$ *Phenylanisaldehydine.* [129°]. Formed from anisic aldehyde and phenylene-o-diamine (Rügheimer a. Ladenburg, *B.* 11, 1660). Needles (from alcohol).

α-OXY-PHENYL-SUCCINIC ACID $C_6H_5.C(OH).CO_2H.CH_2.CO_2H$. *Phenyl-malic acid.* [188°]. S. 1·59 at 15°. Formed by heating α-bromo-phenyl-succinic acid with hot water (Alexander, *A.* 258, 76). Needles (from chloroform). Yields, on heating, phenyl-maleïc anhydride [119°], phenyl-fumaric acid [161°], and a sublimate [106°] probably atropic acid.

β-Oxy-phenyl-succinic acid $C_6H_5.CH(CO_2H).CH(OH).CO_2H$. [150°–160°]. S. 37·35 at 15°. Got from $C_6H_5CH(CHO).CO_2Et$, potassium cyanide, and HCl (A.). Crystalline powder, v. sol. water. Yields phenyl-maleïc anhydride when heated to 160°.

Di-oxy-di-phenyl succinic acid $CO_2H.CPh(OH).CPh(OH).CO_2H$. The *nitrile* of this acid CPh(OH)Cy.CPh(OH)Cy [132°] is formed by union of benzil with HCy (Zinin, *A.* 34, 189; Jacoby, *B.* 19, 1519). It is converted in the cold by HOAc saturated with HBr into the *amide* $C_{16}H_{16}N_2O_4$ [150°–230°] (Burton, *B.* 16, 2232).

DI-OXY-DI-PHENYL SULPHIDE $S(C_6H_4.OH)_2$. [151·5°]. Formed from 'thio-aniline' by the diazo- reaction (Krafft, *B.* 7, 1165; 22, 821), and also by the action of SCl_2 on phenol in presence of CS_2 (Tassinari, *G.* 17, 83). Silvery plates, sl. sol. cold water.

Di-acetyl derivative [93°].

An isomeride [129°] may be obtained from $S(C_6H_3Br.OH)_2$ [176°] by reduction with zinc-dust (T.).

Reference.—DI-BROMO-DI-OXY-DI-PHENYL SULPHIDE.

Di-*p*-oxy-di-phenyl disulphide $S_2(C_6H_4.OH)_2$. [151°]. Formed by oxidising *p*-oxy-phenyl mercaptan (thio-hydroquinone) with dilute $FeCl_3$ (Leuckart, *J. pr.* [2] 41, 196). Yellow needles, v. e. sol. alcohol.

Di-acetyl derivative [89°]. Plates.

Di-*o*-oxy-di-phenyl disulphide $S_2(C_6H_4OH)_2$. Formed by heating sodium phenate (2 mols.) with sulphur (1 at.) at 190° (Haitinger, *M.* 4, 165). Thick oil. Yields o-oxy-phenyl mercaptan on reduction. — NaHA″ 6aq. — KHA″ 5aq.—PbA″: yellow pp.

Di-methyl derivative Me_2A''. [119° cor.]. Yields anisole *o*-sulphonic acid on oxidation.

DI-OXY-DI-PHENYL SULPHONE $SO_2(C_6H_4.OH)_2$. [239°]. S.G. $\frac{15}{}$ 1·366. Formed by heating phenol (2 pts.) with fuming H_2SO_4 (1 pt.) at 190° (Glutz, *A.* 147, 52; Annaheim, *J. pr.* [2] 1, 14; 2, 385; *B.* 8, 1059; 11, 1668; *A.* 172, 28). Trimetric crystals; $a:b:c = 1·283:1:0·534$. V. sol. hot water and alcohol.—K_2A''. Sol. alcohol (Guareschi, *G.* 8, 246).—NH_4HA''.—NaHA″aq.—AgHA″.—Ag_2A''.

Di-acetyl derivative. Needles (Glutz).

Di-methyl ether Me_2A''. [130°].

Di-ethyl ether. [159°]. Laminæ.

Di-isoamyl ether. [98°]. Plates.

Di-oxy-di-phenyl sulphone $SO_2(C_6H_4OH)_2$. [187°]. Got from its acetyl derivative which is made by oxidation of $C_6H_4(OAc)(SH)$ [1:2 or 3] (Tassinari, *C. C.* 1888, 1354). Crystalline, sl. sol. water.

References.—DI-BROMO-, DI-BROMO-DI-NITRO-, DI-CHLORO-, TETRA-IODO-, DI-IODO-DI-NITRO-, and DI-NITRO-, DI-OXY-DI-PHENYL-SULPHONE.

OXY-PHENYL SULPHONIC ACID *v.* PHENOL SULPHONIC ACID.

Oxy-diphenyl sulphonic acid $C_{12}H_8(OH).SO_3H$. Made, together with the di-sulphonic acid, by heating oxydiphenyl (1 pt.) with H_2SO_4 (3 pts.) (Latschinoff, *J. R.* 5, 54).—KA′ aq: plates, sl. sol. water.—BaA'_2aq.—$CaA'_2$3aq.—$K_2CuA'_4$ 6aq: green laminæ.

Oxy-diphenyl disulphonic acid $C_{12}H_7(OH)(SO_3H)_2$. Made as above.—K_2A'' 1½aq.

Di-oxy-diphenyl disulphonic acid $[4:2:1]C_6H_3(OH)(SO_3H).C_6H_3(SO_3H)(OH)[1:2:4]$. Made from benzidine disulphonic acid by the diazo-reaction (Limpricht, *A.* 261, 334). Crystalline mass. The K salt forms laminæ, v. e. sol. water.—BaA″ 2aq.—PbA″ 4aq: rhombohedra.

Di-*p*-oxy-diphenyl disulphonic acid $C_{12}H_6(OH)_2(SO_3H)_2$. Got by warming di-oxy-diphenyl with fuming H_2SO_4 (Doebner, *B.* 9, 130). Probably identical with the preceding acid.—K_2A'': prisms, sl. sol. cold water.

Di-*p*-oxy-diphenyl trisulphonic acid $C_{12}H_5(OH)_2(SO_3H)_3$. Formed, together with the tetra-sulphonic acid, from benzidine by diazotising and warming with conc. H_2SO_4 (Griess, *J.* 1866, 462). — $Pb_3C_{12}H_6S_3O_{12}$2aq.—$Pb_3C_{12}H_6S_3O_{12}$2PbO.

Di-*p*-oxy-diphenyl tetrasulphonic acid $C_{12}H_4(OH)_2(SO_3H)_4$. Made as above.—Ba_2A^{iv} 5aq: prisms.—$Pb_6C_{12}H_6S_4O_{12}$: amorphous pp.

α-OXY-PHENYL-SULPHONO-ISOBUTYRIC ACID $C_6H_5.SO_2.CH_2.CMe(OH).CO_2H$. [121°]. Made by oxidising $CH_2(SPh).CMe(OH).CO_2H$ with $KMnO_4$ in the cold (Delisle, *A.* 260, 259). Prisms (from ether).—KA′ 2aq: needles.—BaA'_2.—CaA'_2 aq: groups of needles.

OXY-PHENYL SULPHURIC ACID $C_6H_4(OH).O.SO_2.OH$. The K salts of the o-, *m*-, and *p*- compounds are formed by the action of $K_2S_2O_7$ on potassium-pyrocatechin, resorcin, and hydroquinone respectively (Baumann, *B.* 11, 1913). They are crystalline, sol. water, and unstable. Potassium-pyrogallol yields, in like manner, $C_6H_3(OH)_2SO_4K$ crystallising in needles.

OXY-PHENYL-THIAZOLE $\begin{matrix}S & .C(OH)\\ CH{:}CPh & \end{matrix}\!\!>\!N$. [204°]. Formed from bromo-acetophenone by the action of xanthamide (Hubacher, *A.* 259, 249), or by successive treatment with barium sulphocyanide and dilute HCl (Arapides, *A.* 249, 14; *cf.* Dyckerhoff, *C. J.* 32, 327). Needles, insol. water, sol. cold NaOHAq. Converted by PCl_5 into chloro-oxy-phenyl-thiazole [206°] and another body [98°] (Schatzmann, *A.* 261, 18). Sodium and EtI yield $\begin{matrix}S & .CO\\ CH{:}CPh & \end{matrix}\!\!>\!NEt$ [71°], which on heating with HCl at 220° gives $NEtH_2$.

Di-*exo*-*o*-oxy-phenyl-thiazole dihydride. *Methyl derivative* $\begin{matrix}S—CO\\ CH_2.CH_2\end{matrix}\!\!>\!N.C_6H_4OMe$. [116°]. Formed by the action of boiling alcoholic chloro-acetic acid on the product of the action of CS_2 on the substance formed from ethylene bromide and di-anisyl-thio-urea (Foerster, *B.* 21, 1867. Plates, v. e. sol. alcohol.

***p*-OXY-PHENYL-THIOCARBIMIDE.** *Acetyl derivative* $C_6H_4(OAc).NCS$. [36°]. Made by heating di-*p*-oxy-di-phenyl-urea with Ac_2O (Kalckhoff, *B.* 16, 1831). Plates, sol. alcohol.

Methyl derivative $C_6H_4(OMe).NCS$. (265°). Formed from anisidine and CS_2 (Hofmann, *B.* 20, 1796; *cf.* Salkowski, *B.* 7, 1012).

Isomeride: OXY-METHENYL-AMIDO-PHENYL-MERCAPTAN.

Di-oxy-phenyl-thiocarbimide. *Di-methyl derivative* $C_6H_3(OMe)_2.NCS$. Formed by heating $CS(NH.C_6H_3(OMe)_2)_2$ with conc. HClAq (Bechhold, *B.* 22, 2381). Occurs in three crystalline forms [57°], [120°], and [155°]. Sol. aniline and H_2SO_4.

DI-o-OXY-DI-PHENYL-THIOHYDANTOÏN. *Di-methyl derivative* $C_{17}H_{18}N_2SO_3$ *i.e.* $\begin{matrix}C_6H_4(OMe).N{:}C.N(C_6H_4OMe)\\ S.CH_2.CO\end{matrix}\!\!>$. [190°]. Made from di-anisyl-thio-urea and fused chloro-acetic acid (Foerster, *B.* 21, 1867). Needles.

ν-OXY-PHENYL-THIO-UREA $C_7H_8N_2SO$ *i.e.* $C_6H_5NH.CS.NH(OH)$. [108°]. Formed from phenyl-thiocarbimide and aqueous hydroxylamine (Schiff; E. Fischer, *B.* 22, 1935; Tiemann, *B.* 22, 1939; Von der Kall, *A.* 263, 260; Voltmer, *B.* 24, 378). White plates, insol. water, sl. sol. ether, v. sol. alcohol. Fehling's solution ppts. Cu_2S. Dilute acids and alkalis decompose it, yielding phenyl cyanamide.

Methyl derivative NHPh.CS.NH.OMe. [116°]. Formed from phenyl-thiocarbimide and methyl-hydroxylamine.

Ethyl derivative. [103°]. Prisms. Decomposed, by boiling its alcoholic solution, into phenyl cyanamide, alcohol, and S.

Benzyl derivative. [115°]. Prisms.

o-Oxy-phenyl-thio-urea $C_6H_4(OH).NH.CS.NH_2$. [161°]. Made from o-amido-phenol hydrochloride and potassium sulphocyanide (Bendix, *B.* 11, 2263). Needles, sol. hot water.—$B'_2H_2PtCl_6$.

Methyl derivative $C_6H_4(OMe).NH.CS.NH_2$. [152°]. Needles (from alcohol) (Mühlhäuser, *B.* 13, 923).

Ethyl derivative. [110°]. Tablets, sol. alkalis (Berlinerblau, *J. pr.* [2] 30, 106).

***p*-Oxy-phenyl-thio-urea** [4:1] $C_6H_4(OH).NH.CS.NH_2$. [214°]. Got by evaporating to dryness, on the water-bath, a solution of potassium sulphocyanide and *p*-amido-phenol hydrochloride (Kalckhoff, *B.* 16, 375). Tables, sl. sol. cold water.

Ethyl derivative. Crystalline (B.).

o-Oxy-diphenyl-thio-urea $NHPh.CS.NH.C_6H_4OH$. [146°]. Formed by the action of phenyl-thiocarbimide on *o*-amido-phenol (Kalckhoff, *B.* 16, 1829). White pearly plates. Heated by itself or with HgO it loses H_2S, yielding anilido-carbamido-phenol.

Methyl derivative $NHPh.CS.NHC_6H_4OMe$. [127°]. Formed from anisyl-thiocarbimide and aniline, and also from phenyl-thiocarbimide and anisidine (Foerster, *B.* 21, 1868). Prisms. With ethylene bromide it forms crystals [143°] whence platinic chloride yields $(C_{16}H_{16}N_2OS)_2H_2PtCl_6$.

***p*-Oxy-di-phenyl-thio-urea** $NHPh.CS.NH.C_6H_4OH$. *p-Oxy-thiocarbanilide.* [162°]. Formed by the action of phenyl-thiocarbimide on *p*-amido-phenol (K.). V. sol. alcohol and alkalis, nearly insol. water.

Acetyl derivative. [137°]. Insol. alkalis.

Di-o-oxy-di-phenyl-thio-urea. *Di-methyl derivative* $CS(NH.C_6H_4OMe)_2$. [135°]. Formed from o-anisidine, CS_2, and alcoholic potash (Mühlhäuser). Formed also from anisidine and thio-urea in alcoholic solution (F.). Needles, sl. sol. water. With methyl iodide it forms $C_6H_4(OMe)N{:}C(SMe).NH.C_6H_4OMe$. [87°]. EtI forms $C_{17}H_{20}N_2SO_2$ [82·5°], while propyl iodide gives $C_{18}H_{22}N_2SO_2$ [58°]. Ethylene bromide gives $CH_2\!\!<\!\!\begin{matrix}CH_2.N.C_6H_4OMe\\ S\ \ .CS\end{matrix}$ crystallising in trimetric prisms [136°] and yielding $C_{10}H_{11}NS_2OMeI$ [c. 141°] and, on boiling with alcohol and chloro-acetic acid, $S\!\!<\!\!\begin{matrix}CO\\ C_2H_4\end{matrix}\!\!>\!NC_6H_4OMe$ [116°].

Di-*p*-oxy-di-phenyl-thio-urea. [222°]. Got from *p*-amido-phenol and CS_2 (K.). Pearly plates, v. sol. alkalis.

Di-methyl derivative. [185°]. Plates (Salkowski, *B.* 7, 1012). Sl. sol. alcohol.

Di-oxy-di-phenyl-thio-urea. *Di-methyl derivative* $NHPh.CS.NH.C_6H_3(OMe)_2$. [137°]. Formed by the combination of phenyl-thiocarbimide with amido-di-methyl-hydroquinone (Baessler, *B.* 17, 2123). Minute needles; v. sol. hot benzene and hot alcohol.

Tetra-oxy-di-phenyl-thio-urea. *Tetra-methyl derivative* $CS(NH.C_6H_3(OMe)_2)_2$. [160°]. Formed from the di-methyl derivative of amido-resorcin and CS_2 (Bechhold, *B.* 22, 2380). White mass (from alcohol-ether), insol. alkalis.

An isomeride [109°] is formed from the di-methyl derivative of amido-hydroquinone (Baessler).

Reference.—DI-CHLORO-DI-OXY-DI-PHENYL-THIO-UREA.

OXY-PHENYL-TOLYLAMINE *v.* TOLYL-AMIDO-PHENOL.

TRI-OXY-DI-PHENYL-TOLYL-CARBINOL. *Anhydride* $C_{20}H_{16}O_3$ *i.e.* $\begin{matrix}C_6H_4(OH)—\\C_6H_3Me(OH)\end{matrix}\!\!>C<\!\!\begin{matrix}C_6H_4\\O—\end{matrix}\!\!>$. *Rosolic acid. Corallin.* Formed by the action of nitrous acid on rosaniline (Caro a. Wanklyn, *J. pr.* 100, 49; *A.* 179, 192). Got also by heating a mixture of phenol and cresol with H_2SO_4 and arsenic acid (Zulkowsky, *B.* 10, 1201). Red plates with green lustre, nearly insol. water, sol. chloroform, alcohol, and acids. Alkalis form a red solution. Reduced by sodium-amalgam to tri-oxy-di-phenyl-tolyl-methane. Water at 240° yields phenol and $C_6H_4(OH).CO.C_6H_3Me(OH)$. KCy followed by HCl forms crystalline $C_{21}H_{17}NO_3$, whence Ac_2O yields $C_{21}H_{14}Ac_3NO_3$ [142°].

p-OXY-PHENYL-p-TOLYL-HYDRAZINE. *Ethyl derivative* $C_6H_4(OEt).NH.NH.C_6H_4Me$. Formed by reducing $C_6H_4(OEt).N_2.C_6H_4Me$ with alcoholic ammonium sulphide (Noelting a. Werner, *B.* 23, 3258; *Bl.* [3] 4, 794). Needles, v. sol. hot alcohol. The isomerides $C_6H_5NH.NHC_6H_3Me(OEt)$[1:3:4] [76°] and $C_6H_5NH.NHC_6H_3Me(OEt)$ [1:5:2] [105°] are formed in like manner.

DI-OXY-PHENYL-TOLYL-KETONE $C_6H_4(OH).CO.C_6H_3Me(OH)$. [200°]. Formed by heating rosolic acid with water at 220°–250° (Graebe a. Caro, *A.* 179, 196). Crystals, sol. hot water.

Di-acetyl derivative [150°]. Needles.

Di-oxy-phenyl-tolyl-ketone. *Anhydride* $C_6H_4<\!\!\begin{matrix}O\\CO\end{matrix}\!\!>C_6H_3Me$. [105°]. Made by boiling *p*-tolyl salicylate for a long time (Graebe a. Feer, *B.* 19, 2612). V. e. sol. hot alcohol.

Tri-oxy-phenyl-tolyl-ketone $C_6H_4(OH).CO.C_6H_2Me(OH)_2$. *Anhydride* $C_{14}H_{10}O_3$. [140°]. Made by fusing salicylic acid with orcin and $ZnCl_2$ (Michael, *Am.* 5, 95). Yellow needles (from alcohol).—NaA′ 1½aq.

Acetyl derivative $C_{14}H_9AcO_3$ [152°].

DI-OXY-PHENYL-DI-TOLYL-METHANE $CHPh(C_6H_3Me.OH)_2$. [171°]. Formed from o-cresol-benzoïn and boiling SO_2Aq (Schroeter, *A.* 257, 70). Yellow needles. Yields a di-bromo-derivative [130°] and a di-nitro-derivative [127°].

Di-acetyl derivative $C_{21}H_{18}Ac_2O_2$. [94°].

Di-benzoyl derivative [91·5°]. Plates.

Tri-oxy-di-phenyl-tolyl-methane $C_6H_3Me(OH).CH(C_6H_4.OH)_2$. *Phenolphthalol.* [190°]. Obtained by boiling phenol-phthalin $CO_2H.C_6H_4.CH(C_6H_4OH)_2$ with HOAc and sodium-amalgam (Baeyer, *A.* 202, 87). Prisms (from dilute HOAc), v. sol. alcohol.

Tri-acetyl derivative $C_{26}H_{24}O_6$. [40°].

Tri-oxy-di-phenyl-tolyl-methane $C_{20}H_{18}O_3$ *i.e.* $C_6H_3Me(OH).CH(C_6H_4OH)_2$. *Leucorosolic acid.* Got by reducing rosolic acid with potash and zinc-dust (Graebe a. Caro, *A.* 179, 198). Needles (from alcohol), v. sl. sol. water.

Tri-acetyl derivative. [149°]. Needles.

DI-OXY-PHENYL-o-TOLYL-PYRAZINE. *Dihydride* $NPh<\!\!\begin{matrix}C(OH):CH\\CH:C(OH)\end{matrix}\!\!>N.C_6H_4Me$. [166°]. Formed by heating aniline with chloro-acetyl-*o*-tolyl-amido-acetic acid at 160° (Abenius, *J. pr.* [2] 40, 443). Formed also by the action of o-toluidine on chloro-acetyl-phenyl-amido-acetic acid in presence of NaOAc (Bischoff, *B.* 23, 1996). White needles, v. e. sol. hot alcohol. The isomeric compound from *p*-toluidine also crystallises in needles [221°].

OXY-PHENYL-p-TOLYL-PYRIMIDINE $C_6H_4Me.C<\!\!\begin{matrix}N.CPh\\N:C(OH)\end{matrix}\!\!>CH$. [above 290°]. Made from tolenyl-amidine and benzoyl-acetic ether (Pinner, *B.* 23, 3826). Slender needles, sl. sol. hot alcohol.

ω-OXY-PHENYL-o-TOLYL-THIO-UREA $CH_2(OH).C_6H_4.NH.CS.NHPh$. [c. 136°]. Made from phenyl thiocarbimide and o-amido-benzyl alcohol (Söderbaum a. Widman, *B.* 22, 1671). Prisms. Alcohol and HgO convert it into $C_6H_4<\!\!\begin{matrix}CH_2.NPh\\NH.CO\end{matrix}$ [146°].

ω-OXY-PHENYL-TOLYL-UREA $CH_2OH.C_6H_4.NH.CO.NHPh$ [191°]. Made from o-amido-benzyl alcohol and PhNCO (Söderbaum a. Widman, *B.* 22, 1670). Needles.

ν-OXY-PHENYL-UREA $C_6H_5NH.CO.NH.OH$. [140°]. Made from phenyl cyanate and aqueous hydroxylamine (E. Fischer, *B.* 22, 1935; von der Kall, *A.* 263, 264). Crystals, v. sl. sol. water, sol. alkalis. Reduces hot Fehling's solution. On boiling with alkalis it yields aniline, CO_2, and hydroxylamine.

Benzyl derivative $NHPh.CO.NH.OCH_2Ph$. [106°]. Needles (Tiemann, *B.* 22, 1940; Voltmer, *B.* 24, 384).

o-Oxy-phenyl-urea $C_6H_4(OH).NH.CO.NH_2$. [154°]. Made from o-amido-phenol hydrochloride and potassium cyanate (Kalckhoff, *B.* 16, 374). Prisms, v. sol. water.

Methyl derivative $C_6H_4(OMe)NH.CO.NH_2$. [147°]. Crystals (Mühlhäuser, *B.* 13, 922; *A.* 207, 244).

p-Oxy-phenyl-urea $C_7H_8N_2O_2$. [168°] (K.). Needles or tables; sol. acids and alkalis.

Ethyl derivative. [160°]. Made from $C_6H_4(NH_2).OEt$ and KCyO (Berlinerblau, *J. pr.* [2] 30, 103). Nitrous acid passed into its alcoholic solution forms brick-red crystals of $C_9H_{11}N_3O_4$.

Di-o-oxy-di-phenyl-urea. *Di-methyl derivative* $CO(NH.C_6H_4.OMe)_2$. [182°]. Made from $COCl_2$ and *o*-anisidine (M.; Conrad, *B.* 21, 1649). Crystals, v. sol. alcohol.

Di-*p*-oxy-di-phenyl-urea. *Di-methyl derivative* $C_{15}H_{16}N_2O_2$. [234°]. Prisms or needles (Lossen, *A.* 175, 295; Pieschel, *A.* 175, 312). V. sl. sol. hot alcohol.

β-OXY-PHENYL-VALERIC ACID $C_{11}H_{14}O_3$ *i.e.* $CHPh(OH).CMe_2.CO_2H$. *Phenyl-oxypivalic acid.* [134°]. Formed from benzoic aldehyde, sodium isobutyrate, and isobutyric anhydride by Perkins's reaction (Fittig a. Jayne, *A.* 216, 119; Ott, *A.* 227, 61). Needles, sl. sol. cold water. Split up at 150° into CO_2 and phenyl-butylene.—BaA'_2 4aq.—CaA'_2 4aq: plates, m. sol. water.

Acetyl derivative. [137°]. Monoclinic crystals (from CS_2). Yields $Ba(C_{13}H_{15}O_4)_2$ 2aq and CaA'_2 2aq.

Anhydride $C_{26}H_{30}O_7$. [155°]. Prisms.

Iso-butyryl derivative. [65°]. Needles, v. sl. sol. water. Yields $Ba(C_{15}H_{19}O_4)_2$ 2aq, CaA'_2 2aq, and AgA'.

β-Oxy-phenyl-n-valeric acid $C_6H_5CH_2.CH_2.CH(OH).CH_2.CO_2H$. [131°]. Got by boiling β-styryl-propionic acid with NaOHAq (Fittig, *B.* 24, 84). Prisms.

β-Oxy-phenyl-valeric acid $CH_3.CH(OH).CH(CH_2Ph).CO_2H$. [153°]. Got by reducing benzyl-aceto-acetic ether (Ehrlich, *B.* 8, 1036; *A.* 187, 26). Needles (from benzene). —BaA'_2 2aq.—Zn(OH)A'.—Cu(OH)A'.

γ-Oxy-α-phenyl-valeric acid $CH_3.CH(OH).CH_2.CHPh.CO_2H$. Formed from α-phenyl-β-acetyl-propionic acid by reduction with sodium-amalgam (Weltner, *B.* 17, 73). The free acid at once forms the oily anhydride $C_{11}H_{12}O_2$.—$Ca(C_{11}H_{13}O_3)_2$ aq: crystalline.

γ-Oxy-γ-phenyl-isovaleric acid. The oily lactone $C_6H_5.CH\langle{}^{CHMe}_{O.CO}\rangle CH_2$ is made by warming γ-bromo-γ-phenyl-isovaleric acid with aqueous Na_2CO_3 (Fittig a. Liebmann, *A.* 255, 271). It yields $Ba(C_{11}H_{13}O_3)_2$.

Oxy-phenyl-valeric acid. *Methyl derivative* $C_6H_4(OMe).CH_2.CH_2.CH_2.CH_2.CO_2H$. Got by reducing $C_6H_4(OMe).C_4H_6.CO_2H$ with sodium-amalgam (Perkin, *C. J.* 39, 438).—Oil.—BaA'_2.

Di-oxy-phenyl-valeric acid. *Methylene derivative* $C_{12}H_{14}O_4$ *i.e.* $CH_2O_2{:}C_6H_3.CH_2.CH_2.CH_2.CH_2.CO_2H$. *Piperhydronic acid.* [96°]. Made by reducing (β)-hydropiperic acid with sodium-amalgam (Fittig a. Buri, *A.* 216, 178). Thin tables (from alcohol).—CaA'_2 aq: v. sl. sol. cold water.

Di-oxy-phenyl-valeric acid $C_6H_5.CH(OH).CH_2.CH(CO_2H).CH(OH).CH_3$. The oily anhydride of this acid is got by reducing phenacyl-acetoacetic ether (Wellner, *B.* 17, 69).

Tri-oxy-phenyl-valeric acid. *Methylene derivative* $CH_2O_2{:}C_6H_3.CH_2.CH(OH).CH_2.CH_2.CO_2H$. [95°]. Made by reducing with sodium-amalgam the acid $CH_2O_2{:}C_6H_3.CH_2.CO.CH_2.CH_2.CO_2H$ (Weinstein, *A.* 227, 38). Crystals, m. sol. hot water. Yields an oily lactone.—BaA'_2.—AgA': flocculent pp.

Tri-ppγ-oxy-di-phenyl-valeric acid. *Dimethyl derivative* $C_6H_4(OMe).CH(OH).CH_2.CH(CO_2H).CH_2.C_6H_4OMe$. The lactone [83°] is got by the action of sodium-amalgam on its bromo- derivative [136°], which is formed by dissolving di-bromo-di-p-methoxy-di-phenyl-valeric acid in HOAc (Fittig a. Politis, *A.* 255, 305). It yields a gummy Ba salt.

Tetra-oxy-phenyl-valeric acid. *Methylene derivative* $CH_2O_2{:}C_6H_3.CH_2.CH(OH).CH(OH).CH_2.CO_2H$. [123°]. Made by oxidising (α)-hydropiperic acid with $KMnO_4$ at 0° (Regel, *B.* 20, 415). Slender crystals.—BaA'_2.—AgA': needles.

Anhydride $C_{11}H_{12}O_5$. [104·5°]. Crystals.

An isomeric acid $CH_2O_2{:}C_6H_3.CH_2.CH_2.CH(OH).CH(OH).CO_2H$ [165°], formed by oxidising (β)-hydropiperic acid, yields the salts CaA'_2 aq and AgA'.

Reference.—TETRA-BROMO-OXY-PHENYL-VALERIC ACID.

c-OXY-PHTHALIC ACID $C_6H_3(OH)(CO_2H)_2$ [1:2:3]. [c. 200°]. S. 20 at 17°. Obtained by potash-fusion from its methyl derivative (Jacobsen, *B.* 16, 1965), and from c-sulpho-phthalic acid (Stokes, *Am.* 6, 282). Got also from c-amido-phthalic acid (Bernthsen, *B.* 20, 937). Prisms (from water), v. sol. alcohol and ether. Coloured red by $FeCl_3$. Forms a fluoresceïn when heated with resorcin.—KHA": needles.—Ag_2A'': pp., sl. sol. hot water.

Anhydride $C_6H_3(OH)\langle{}^{CO}_{CO}\rangle O$. [c. 148°]. Formed by heating the acid.

Methyl derivative $C_6H_3(OMe)(CO_2H)_2$. [160°]. Formed by oxidation of c-methoxy-toluic acid with $KMnO_4$. Minute prisms.

Anhydride of the methyl derivative $C_6H_3(OMe)C_2O_3$. [87°]. Needles (by sublimation).

i-Oxy-phthalic acid $C_6H_3(OH)(CO_2H)_2$ [1:3:4]. [185°] (Rée); [205°] (Claus). S. 3 at 10°.

Formation.—1. From i-amido-phthalic acid by the diazo- reaction (Baeyer, *B.* 10, 124, 1079). 2. By oxidising i-methoxy-o-toluic acid with potassium permanganate, and heating the resulting $C_6H_3(OMe)(CO_2H)_2$ with hydrochloric acid (Schall, *B.* 12, 816).—3. By potash-fusion from $C_6H_3(SO_2NH_2)(CO_2H)_2$, which is got by oxidising [3:4:1] and [5:2:1] $C_6H_3Me(SO_2NH_2)(CO_2H)$ (Jacobsen, *B.* 14, 42).—4. By fusing i-sulpho-phthalic acid with NaOH (Graebe a. Rée, *C. J.* 49, 524; *B.* 18, 1130, 1630).—5. By fusing di-chloro-(α)-naphthoquinone sulphonic acid with potash (Claus, *J. pr.* [2] 37, 194).—6. By fusing di-nitro-naphthol sulphonic acid with potash (Rée, *A.* 233, 230).

Properties.—Needles, sl. sol. cold water, sol. alcohol and ether. Gives a yellowish-red colour with $FeCl_3$. Dilute HCl at 180° forms m-oxy-benzoic acid. Gives the fluoresceïn reaction with resorcin at 200°.—Ag_2A'': tufts of needles.

Methyl ether Me_2A''. [102°]. Plates.

Anhydride $C_8H_4O_4$. [165°]. Made by heating the acid.

Methyl derivative $C_6H_3(OMe)(CO_2H)_2$. [138°–144°]. Needles. Forms on heating an anhydride [93°].—$Ag_2C_9H_6O_5$: curdy pp.

s-Oxy-isophthalic acid $C_6H_3(OH)(CO_2H)_2$ [1:3:5]. [288° cor.]. S. ·0305 at 5°; 19 at 99°. Made by fusing s-sulpho-isophthalic acid with potash (Heine, *B.* 13, 491; Lönnies, *B.* 13, 705). Got also from rufigallic acid by potash-fusion (Schreder, *M.* 1, 437), and by the action of nitrous acid on s-amido-isophthalic acid (Beyer, *J. pr.* [2] 25, 515). Needles (containing 2aq), v. sol. hot water, alcohol, and ether.—BaA" 3aq.—$Cu_3(C_8H_3O_5)_2$ 4aq.—Ag_2A''.—AgHA": needles.

Di-methyl ether Me_2A''. [160°]. Needles.

Di-ethyl ether Et_2A''. [103°]. Prisms.

c-Oxy-isophthalic acid $C_6H_3(OH)(CO_2H)_2$ [1:2:6]. [239°]. S. 3 at 100°; ·14 at 24°.

Formation.—1. Obtained by potash-fusion from (2,1,6)-aldehydo-oxy-benzoic acid (Tiemann a. Reimer, *B.* 10, 1562), and also from the acid [1:2:6] $C_6H_3(SO_2NH_2)(CO_2H)_2$ (Jacobsen, *B.* 11, 902).—2. From (1,2,6)-methoxy-toluic acid by oxidising with $KMnO_4$, and heating the resulting $C_6H_3(OMe)(CO_2H)_2$ with HCl at 160° (Schall, *B.* 12, 826).—3. In small quantity, in the preparation of the following isomeride, by the action of CCl_4 and KOH on salicylic acid (Hasse, *B.* 10, 2185).—4. By oxidising α-naphthol with CrO_3 and HOAc (Miller, *A.* 208, 247).—5. From c-amido-isophthalic ether (M.).

Properties.—Needles (containing aq), v. sol.

alcohol and ether. Melts at 244° after drying at 100° (T. a. R.). Coloured cherry-red by $FeCl_3$. Forms salicylic acid when strongly heated. Its solutions exhibit bluish-violet fluorescence.—Ag_2A'': minute plates.—Et_2A'': oil.

Mono-methyl ether $C_6H_3(OH)(CO_2H)(CO_2Me)$. [135°]. Made from [1:2]$C_6H_4(ONa).CO_2CH_3$ by heating with CO_2 at 150° under pressure (Hähle, *J. pr.* [2] 44, 6). Grouped needles, which melt under water. Coloured red by $FeCl_3$. Gives NaA′ as colourless needles.

Methyl derivative $C_6H_3(OMe)(CO_2H)_2$. [218°]. Prisms, sol. hot water.

i-**Oxy-isophthalic acid** $C_6H_3(OH)(CO_2H)_2$ [1:2:4]. [306°]. S. ·02 at 10°; ·625 at 100°.

Formation.—1. By potash-fusion from (2,1,4)- and (4,1,2)-aldehydo-oxy-benzoic acid (Tiemann a. Reimer, *B.* 10, 1562), from *m*-xylenol (Jacobsen, *B.* 11, 377), from *m*-xylene sulphonic acid (Remsen, *B.* 11, 580), from $C_6H_3(SO_2NH_2)(CO_2H)_2$ (Remsen, *Am.* 1, 131), and from benzoic acid (Barth, *M.* 3, 803).—2. By the action of KOH, dilute alcohol, and CCl_4 on salicylic acid (Hasse). 3. By heating $C_6H_4(ONa).CO_2Na$ [1:2] or [1:4] in a current of CO_2 (Ost, *J. pr.* [2] 14, 93; 15, 301; Kupferberg, *J. pr.* [2] 16, 428).

Preparation.—A mixture of C_6H_5ONa (3 mols.) and C_6H_5OK (1 mol.) is heated in a current of CO_2 at 300°. The yield is 30 p.c. of the phenol used (Ost).

Properties.—Needles, sl. sol. water, insol. chloroform. Not volatile with steam. Its aqueous solution is coloured cherry-red by $FeCl_3$. Yields salicylic acid and phenol when distilled. Br yields tri-bromo-phenol on heating.—Na_2A''aq.—$Ca_3(C_8H_3O_5)_2$ 5aq. — CdA″$5\frac{1}{2}$aq. — Ag_2A''. — AgHA″: needles.

Methyl ether Me_2A''. [96°].

Mono-ethyl ether $C_6H_3(OH)(CO_2H)(CO_2Et)$ [4:3:1]. [195°]. Made from [4:1] $C_6H_4(ONa).CO_2Et$ and CO_2 at 170° under pressure (Hähle, *J. pr.* [2] 44, 12). Monoclinic leaflets.

Di-ethyl ether Et_2A''. [52°].

Phenyl ethyl ether $C_6H_3(OH)(CO_2Ph)(CO_2Et)$ [4:3:1]. [65°]. Got from HEtA″, phenol, and $POCl_3$ (H.).

Amide $C_6H_3(OH)(CONH_2)_2$. [250°].

Methyl derivative $C_9H_8O_5$. [261°].

Oxy-isophthalic acid. *Hexahydride* $\begin{matrix}CH_2.CH_2.C(OH)(CO_2H)\\CH_2.CH(CO_2H).CH_2-\end{matrix}\!\!>$. Formed by saponification of its semi-nitrile [130°–140°] which is the product of the union of prussic acid with $\begin{matrix}CH_2.CH_2.CO\\CH_2.CH(CO_2H)\end{matrix}\!\!>CH_2$ (Baeyer a. Tutein, *B.* 22, 2186). Nodules (from alcohol).—Ag_2A''.

Di-oxy-phthalic acid. *Methyl derivative* $C_6H_2(OMe)(OH)(CO_2H)_2$. *Normethylhemipic acid.* [225°] (Wegscheider, *M.* 3, 378). Made by warming hemipic acid with conc. HIAq (Liechti, *A. Suppt.* 7, 151; Beckett a. Wright, *C. J.* 29, 281). Nodules (containing 2aq). Melts at 150°–155° when hydrated. V. sol. water and alcohol. Coloured blue by $FeCl_3$. Yields protocatechuic acid when fused with potash. The anhydride $C_9H_6O_5$ 2aq forms crystals [148°].—KHA″aq.

Di-methyl derivative v. Hemipic acid.

Methylene derivative $CH_2O_2:C_6H_2(CO_2H)_2$. [175°]. *Hydrastic acid.* Got by the action of boiling potash on the methylimide [233°] which is obtained by oxidising hydrastinic acid (Freund a. Lachmann, *B.* 22, 2325). Needles (from Aq).—$NMeH_3A'$. [224°].

Di-oxy-phthalic acid. *Hexahydride* $C_8H_{12}O_6$. [180°]. Got by the action of baryta on 'bromo-malophthalic' acid (Baeyer, *A.* 166, 355). Prisms (containing 2aq), v. sol. water.—PbA″aq: needles.

Reference.—Oxyterephthalic acid.

(α)-OXY-ISOPHTHALIC ALDEHYDE $C_6H_3(OH)(CHO)_2$ [4:3:1]. [108°]. Formed by boiling *p*-oxy-benzoic aldehyde with chloroform and NaOHAq, and also, together with the (β)-isomeride, from salicylic aldehyde in like manner (Voswinckel, *B.* 15, 2021). Needles, sol. ether, sl. sol. water, almost insol. ligroïn.

(β)-Oxy-isophthalic aldehyde $C_6H_3(OH)(CHO)_2$ [2:3:1]. [88°]. Made as above. Needles (from water), v. sol. ligroïn. Yields *e*-oxy-isophthalic acid on fusion with potash.

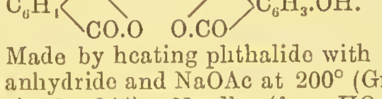
Di-oxy-isophthalic aldehyde $C_6H_2(OH)_2(CHO)_2$. *Resorcylic dialdehyde.* [127°]. Made by the action of chloroform and NaOHAq on resorcin (Tiemann a. Lewy, *B.* 10, 2212). Needles (from hot water). With alcoholic aniline it yields yellow crystals [199°]. Phenyl-hydrazine acetate forms $C_6H_2(OH)_2(CHO)_2$ [c. 230°] (Rudolph, *A.* 248, 105). Yields a dioxim [209°] (Marcus, *B.* 24, 3652).

Methyl derivatives $C_6H_2(OMe)(OH)(CHO)_2$. Two isomerides, [179°] and [89°], are formed from [1:3] $C_6H_4(OMe)(OH)$, chloroform, and NaOHAq.

OXY-PHTHALIDE $C_8H_6O_3$ *i.e.* $C_6H_3(OH)\!<\!\begin{matrix}CH_2\\CO\end{matrix}\!>\!O$. [222°]. Got by reducing oxyphthalimide with tin and HCl, treating with nitrous acid, and heating the resulting nitroso-oxy-phthalidine with NaOHAq (Graebe a. Rée, *C. J.* 49, 526). Prisms or needles, sl. sol. ether.

OXY-PHTHALIMIDE $C_6H_3(OH)\!<\!\begin{matrix}CO\\CO\end{matrix}\!>\!NH$ or $C_6H_3(OH)\!<\!\begin{matrix}C(NH)\\CO\end{matrix}\!>\!O$. [290°]. Formed by saturating *i*-oxy-phthalic acid with NH_3 (Rée, *A.* 233, 232; *C. J.* 49, 525). Yellow crystals, sl. sol. ether. When reduced by tin and HCl it yields a product from which a nitroso-compound [170°] may be prepared.

OXY-DIPHTHALYL $C_{16}H_8O_5$ *i.e.*

 [above 374°].

Made by heating phthalide with *i*-oxy-phthalic anhydride and NaOAc at 200° (Graebe a. Guye, *A.* 233, 244). Needles (from HOAc).

A di-oxy-diphthalyl [250°] appears to be formed by dissolving di-chloro-diphthalyl in alcoholic potash (Ador, *A.* 164, 245).

DI-OXY-PROPANE *v.* Propylene glycol.

DI-OXY-PROPANE TRI-CARBOXYLIC ACID $C_3H_3(OH)_2(CO_2H)_3$. Formed by oxidation of isosaccharin with HNO_3 (Kiliani, *B.* 18, 638). Colourless syrup. By HI it is reduced to glutaric acid $C_3H_6(CO_2H)_2$.—A'''_2H_4Ca: small prisms.

An isomeric acid, formed by boiling chloro-citric acid with lime, forms the salts $Ca_3A'''_2$ 9aq, $Ba_3A'''_2$ 5aq, and $Cd_2C_6H_4O_8$ 3aq (Pavolleck, *A.* 178, 157). The same acid, yielding $Ca_3A'''_2$ 10aq,

occurs in beet-root juice (Lippmann, *B.* 16, 1078).

Tri-oxy-propane tri-carboxylic acid $C_6H_8O_9$ *i.e.* $CO_2H.CH(OH).CH(OH).C(OH)(CO_2H)_2$. Got by oxidising mannite with alkaline $KMnO_4$ (Pabst, *J.* 1880, 611). Yields a soluble NH_4 salt.

OXY-PROPANE PHOSPHONIC ACID $C_3H_9PO_4$ *i.e.* $CHEt(OH).PO(OH)_2$. [162°]. Formed from propionic aldehyde and PCl_3, followed by water (Fossek, *M.* 7, 29). Plates, v. sol. water.—CaA″.

OXY-PROPANE SULPHONIC ACID $C_3H_6(OH)(SO_3H)$. Formed from *n*-propyl alcohol and SO_3, and also by boiling allyl alcohol with aqueous $KHSO_3$ (Max Müller, *B.* 6, 1441). The same, or an isomeric acid, is got from propylene oxide and $NaHSO_3$ (Erlenmeyer, *A.* 158, 260). The K salt crystallises in small needles.

Oxy-propane disulphonic acid $CH(OH)(CH_2SO_3H)_2$. Formed by boiling glycerin dichlorhydrin with aqueous K_2SO_3 (Schäuffelen, *A.* 148, 111) and, in like manner, from epichlorhydrin (Pazschke, *J. pr.* [2] 1, 86; *Z.* [2] 5, 613). Syrup.—K_2A'' 2aq: trimetric octahedra: $a:b:c$ = ·41: ·48:1.—BaA″ 2aq: m. sol. water.—PbA″ 2aq. —Ag_2A'': crystals, v. sol. alcohol.

Reference.—Chloro-oxy-propane sulphonic acid.

TRI-OXY-PROPENYL-BENZENE. *Tri-methyl derivative* [1:2:4:5]$C_6H_2(OMe)_3.CH:CHMe$. This is the constitution of asarone (*q.v.*) (Eykmann, *B.* 22, 3172).

OXY-PROPENYL-BENZOIC ACID $C_6H_3(C_3H_5)(OH)CO_2H$ [4:2:1]. *Propenyl-salicylic acid.* [146°]. Formed from oxyisopropyl-salicylic acid $C_6H_3(CMe_2OH)(OH)CO_2H$, by elimination of H_2O by warming with dilute HCl. White slender needles. V. sol. alcohol, ether, and CS_2, sl. sol. water. Sublimable. Volatile with steam. Gives a deep reddish-violet colouration with Fe_2Cl_6. By sodium amalgam it is reduced to oxy-cuminic acid $C_6H_3Pr(OH)CO_2H$ [4:2:1].

Salts.—A′Ag: sparingly soluble white crystalline pp.—A'_2Cu 2aq: small green crystals, nearly insol. water.

Polymeride $(C_{10}H_{10}O)_x$. [230°]. Formed by boiling oxy-propenyl-benzoic acid with strong HCl. Small white crystals. M. sol. hot acetic acid, alcohol, and ether, insol. water and CS_2. Gives a deep bluish-violet colouration with Fe_2Cl_6. Not volatile with steam.—$(CuA''\ 1\frac{1}{4}aq)_x$. —$(AgA')_x$: white pp. (Heymann a. Königs, *B.* 19, 3313; 20, 2390).

OXY-PROPIONAMIDINE $CH_3.CH(OH).C(NH).NH_2$. The hydrochloride B′HCl is formed from $(CH_3.CH(OH).C(NH).OC_5H_{11})$ HCl, and alcoholic NH_3 (Pinner, *B.* 23, 2947). Needles; converted by $AgNO_3$ into $B'HNO_3$ [84°], v. sol. water.

OXY-PROPIONIC ACID *v.* Lactic acid and Hydracrylic acid. *V.* also Bromo-, Chloro-, and Iodo-, Oxy-propionic acids.

Di-oxy-propionic acid *v.* Glyceric, Glyoxylic, Pyruvic, and Glycidic acids.

a-OXY-PROPIONIC ORTHALDEHYDE. *Tri-methyl derivative* $C_6H_{14}O_3$ *i.e.* $CH_3.CH(OMe).CH(OMe)_2$. (148°). S.G. $\frac{0}{}$ ·948. Formed by heating acroleïn (2 vols.) with methyl alcohol (6 vols.) and HOAc (1 vol.) at 100° (Alsberg, *J.* 1864, 495). Liquid, with pleasant smell, sl. sol. water.

Tri-ethyl derivative (186°). S.G. $\frac{15}{}$ ·90.

OXY-PROPIONIC IMIDO-ISOAMYL ETHER $CH_3.CH(OH).C(NH).OC_5H_{11}$. The hydrochloride B′HCl [69°], formed by the action of HCl gas on a solution of aldehyde-cyanhydrin in isoamyl alcohol, crystallises in thin needles. The homologous $CH_3.CH(OH).C(NH_2Cl).OC_3H_7$ also melts at 69° and gradually decomposes forming lactamide and ammonium chloride (Pinner, *B.* 23, 2947).

OXYPROPYL-AMIDO-BENZOIC ACID $C_6H_3(CMe_2OH)(NH_2)CO_2H$ [4:2:1]. [158°]. Made by reduction of nitro-oxypropyl-benzoic acid with $FeSO_4$ and ammonia (Widman, *B.* 19, 271). Prisms. Exhibits blue fluorescence in ethereal solution.

Acetyl derivative $C_6H_3(C_3H_6.OH)(NHAc)CO_2H$. [174°]. Trimetric tables, v. sol. hot alcohol.

Oxypropyl-amido-benzoic acid $C_6H_3(CMe_2OH)(NH_2)(CO_2H)$ [4:3:1]. Made by reducing the corresponding nitro-acid (Widman, *B.* 16, 2570; 17, 1305). Prisms, v. sol. alcohol, v. sl. sol. ether. With $ClCO_2Et$ it forms $C_6H_3(CMe_2OH)(NH.CO_2Et).CO_2H$ [167°] and $C_{21}H_{28}N_2O_9$ [above 300°] which is converted by H_2SO_4 into $CO(NH.C_6H_3(CMe_2OH)(CO_2H))_2$.

Acetyl derivative. Crystalline.

a-OXY-PROPYLAMINE $CH_3.CH(OH).CH_2NH_2$. *Amido-iso-propyl-alcohol.* [30°]. (176°). Formed from allylamine and H_2SO_4, followed by water (Liebermann a. Paal, *B.* 16, 531). Needles.

Benzoyl derivative $CH_3.CH(OBz).CH_2NH_2$. Got by boiling bromo-propyl benzamide with HBrAq. Oil, v. sol. water. Converted into $CH_3.CH(OBz).CH_2OH$ by nitrous acid. Boiling NaOHAq converts it into the isomeric $CH_3.CH(OH).CH_2NHBz$ [93°] (Hirsch, *B.* 23, 970).—$C_{10}H_{13}NO_2HBr$. [133°]. Needles. — $B'C_6H_3N_3O_7$. [189°]. Needles. — $B'_2H_2PtCl_6$: yellow needles (from water).

β-Oxy-propylamine $CH_2(OH).CH_2.CH_2NH_2$. Formed by heating bromo-propyl-phthalimide with dilute (1:2) H_2SO_4 for 5 hours at 200° (Gabriel, *B.* 21, 2672).—$B'_2H_2PtCl_6$: yellow plates.—$B'HAuCl_4$: plates.

Sulphuric acid derivative $CH_2(O.SO_3H).CH_2.CH_2NH_2$. [221°]. Formed from β-bromo-propylamine hydrobromide and aqueous Ag_2SO_4 at 100° (Gabriel a. Lauer, *B.* 23, 91). Prisms (from warm water). Indifferent body.

Benzoyl derivative $NH_2.C_3H_6.OBz$. Liquid, v. sol. water. Formed from phenyl-pentoxazoline and HBr (Gabriel a. Elfeldt, *B.* 24, 3216). Yields B′HBr [135°], $B'_2H_2PtCl_6$ [205°] and $B'C_6H_3N_3O_7$ [178°].

Phenyl derivative $PhO.C_3H_6.NH_2$. (242°). Got from phenoxy-propyl-phthalamic acid and HCl (Lohmann, *B.* 24, 2634). Yields B′HCl [168°] crystallising in shining plates, and $PhO.C_3H_6.NHBz$ [118°]. Cyanic acid forms $PhO.C_3H_6.NH.CO.NH_2$ [114°].

Oxy-di-propyl-amine $(C_3H_6OH)(C_3H_7)NH$ (175°). [30°]. S.G. $\frac{18}{18}$ ·9018. Prepared by heating propyl-allyl-amine with H_2SO_4 and pouring the product into water (Liebermann a. Paal, *B.* 16, 531). Needles. $B'_2H_2PtCl_6$ 2aq: efflorescent.

Oxy-tri-propyl-amine $(C_3H_6OH)N(C_3H_7)_2$. Got by heating di-propyl-allyl-amine with

H_2SO_4 and pouring the product into water (L. a. P.).—$B'_2H_2PtCl_6$.

OXY-PROPYL-AMYL-AMINE $C_8H_{19}NO$ *i.e.* $(C_3H_6OH)(C_5H_{11})NH$ (c. 200°). [c. 2°]. Formed by heating allyl-amyl-amine with H_2SO_4 and pouring the product into water (Liebermann a. Paal, *B.* 16, 531). Solidifies to long fine needles.

Oxy-propyl-di-isoamyl-amine $(C_5H_{11})_2N(C_3H_6OH)$. (243°). Formed from propylene chlorhydrin and di-isoamylamine (Louïse, *A. Ch.* [6] 13, 433). Oil, sl. sol. water. Inactive to light.—$B'_2H_2PtCl_6$: orange crystals. The acetyl and benzoyl derivatives form crystalline oxalates, the latter being $C_{20}H_{33}NO_2H_2C_2O_4$.

OXY-PROPYL-BENZENE *v.* PROPYL-PHENOL and PHENYL-PROPYL ALCOHOL.

Di-oxy-propyl-benzene $CH_3.CH(OH).CH(OH).C_6H_5$. [53°]. Made from phenyl-propylene bromide by successive treatment with KOAc and alcoholic potash (Zincke, *B.* 17, 709). Tables (from ether ligroïn), v. e. sol. water. A more sparingly soluble isomeride [93°], made from phenyl propylene bromide by boiling with aqueous K_2CO_3, crystallises from ether in monoclinic tables.

Tri-oxy-propyl-benzene *v.* PROPYL-PYROGALLOL.

Tetra-oxy-propyl-benzene. *Methylene derivative* $CH_2(OH).CH(OH).CH_2.C_6H_3O_2CH_2$. [83°]. Formed from safrol and dilute $KMnO_4$ at 75° (Tiemann, *B.* 24, 2881). White needles, v. sol. boiling water and ether. Yields piperonal, piperonylic acid, and $CH_2O_2{:}C_6H_3.CH_2.CO_2H$ on further oxidation. Phenyl cyanate forms $CH_2O_2{:}C_6H_3.CH_2.C_2H_3(O.CO.NHPh)_2$ [127°].

Acetyl derivative $CH_2O_2{:}C_6H_3.CH_2.C_2H_3(OAc)_2$. (240° at 18 mm.).

OXY-PROPYL-BENZENE SULPHONIC ACID $Me_2C(OH).C_6H_4.SO_3H$. Got from cumene *p*-sulphonic acid, KOH and $KMnO_4$ (R. Meyer, *A.* 219, 302).

Salts.—KA'.—BaA'$_2$. Splits off H_2O at 140°. —PbA'$_2$. Splits off $2H_2O$ at 110°, probably forming lead propenyl-benzene sulphonate.

Reaction.—PCl_5 followed by ammonia forms the amide of propenyl-benzene sulphonic acid [152°].

OXY-*o*-ISOPROPYL-BENZOIC ACID $CMe_2(OH).C_6H_4.CO_2H$. The salt KA' [197°] is formed by the action of conc. KOHAq on di-methyl-phthalide (Wislicenus, *A.* 248, 59). The free acid is unstable, at once forming di-methyl-phthalide [68°].

Oxy-*p*-isopropyl-benzoic acid $CMe_2(OH).C_6H_4.CO_2H$. [156°]. Formed by oxidising cuminic acid, or cymene, with alkaline $KMnO_4$ (R. Meyer, *B.* 11, 1283, 1790; *A.* 219, 248; Remsen a. Emerson, *A. C. J.* 1, 267; Widman, *B.* 19, 583). Thin triclinic prisms (from water), v. sol. alcohol and ether. Gives no colour with $FeCl_3$. Yields terephthalic and acetyl-benzoic acids on oxidation by CrO_3. Boiling HClAq forms two isomeric propenyl-benzoic acids.—BaA'$_2$ aq.—CaA'$_2$ 2½aq.—CuA'$_2$ 3aq.—AgA' ¼aq: crystalline pp.

An isomeric or identical acid is got by boiling bromo-propyl-benzoic acid with alcoholic potash (Czumpelik, *B.* 3, 478).

Isomerides *v.* OXY-CUMINIC ACIDS.

Di-oxy-isopropyl-benzoic acid $C_6H_3(CMe_2OH)(OH).CO_2H$ [1:2:4]. [173°]. Formed by the action of nitrous acid on oxy-amido-isopropyl-benzoic acid (Widman, *B.* 17, 722). Crystals (from water), v. sol. alcohol and ether. Coloured dark brown by $FeCl_3$.

Di-oxy-isopropyl-benzoic acid $C_6H_3(CMe_2OH)(OH).CO_2H$ [1:3:4]. [130°–135°]. Formed by oxidising carvacryl-sulphuric acid with alkaline $KMnO_4$ (Heymann a. Königs, *B.* 19, 3310). Flat needles (from water), v. e. sol. alcohol.—CuA'$_2$ aq.—AgA': needles.

DI-OXY-DI-ISOPROPYL-DI-CARBOXY-DI-PHENYL-ALLOPHANIC ETHER $C_{24}H_{28}N_2O_9$ *i.e.* $N(CO_2Et)C_6H_3(CMe_2OH).CO_2H$ / $CO.NH.C_6H_3(CMe_2OH).CO_2H$. [above 300°]. Formed, with $CO(NH.C_6H_3(CMe_2OH).CO_2H)_2$ and $CO_2Et.NH.C_6H_3(CMe_2OH).CO_2H$ [167°], by the action of $ClCO_2Et$ on oxy-amido-isopropyl-benzoic acid (Widman, *B.* 17, 1306). Tables (from HOAc), almost insol. water.

OXY-PROPYLENE-DIAMINE $C_3H_{10}N_2O$ *i.e.* $CH(OH)(CH_2NH_2)_2$. Formed from glycerin di-chlorhydrin and alcoholic NH_3 (Claus, *A.* 168, 36).—$B''H_2PtCl_6$.

OXY-PROPYLENE-TETRA-METHYL-DI-AMINE $C_3H_5(OH)(NMe_2)_2$. (170°–185°). Formed by heating *s*-dichlorhydrin with NMe_2H (Berend, *B.* 17, 510). Liquid, v. sol. water.

Benzoyl derivative. Crystalline.

OXY-PROPYL-ETHYL-AMINE *v.* ETHYL-OXY-PROPYL-AMINE.

OXY-PROPYL-MALONIC ACID $CO_2H.CH(CH_2.CHMeOH).CO_2H$. The free acid at once splits off water, leaving the lactonic acid. The salts $BaC_6H_8O_5$, CaA'', and Ag_2A'' may, however, be prepared.

Lactonic acid $C_6H_8O_4$. Got by combining allyl-malonic acid with HBr, and boiling the product with water (Hjelt, *B.* 15, 621; *A.* 216, 53). Syrup, v. sol. water, sl. sol. ether. Yields $Ba(C_6H_7O_4)_2$ crystallising in soluble plates.

Di-oxy-propyl-malonic acid $(CO_2H)_2.CH.CH_2.CH(OH).CH_2OH$. The free acid in aqueous solution remains unchanged at 15°, but at 100° it splits off water, forming a lactonic acid whose barium salt is $(C_6H_7O_5)_2Ba$.

Salts.—BaA''. Got by boiling di-bromo-propyl-malonic acid with baryta (Hjelt, *A.* 216, 58).—Ag_2A'': flocculent pp.

Di-oxy-di-propyl-malonic acid $(CH_3.CH(OH).CH_2)_2C(CO_2H)_2$.

Dilactone $C_9H_{12}O_4$. [106°]. Obtained from di-allyl-malonic acid by evaporating with conc. HBrAq (Hjelt). Thin plates (from alcohol), long needles (from water), or trimetric crystals (from conc. HBrAq) $a{:}b{:}c = \cdot61{:}1{:}\cdot94$. Warm baryta-water forms $(C_3H_7O)_2C(CO_2)_2Ba$, which on heating splits up into $BaCO_3$ and the neutral lactone $C_3H_7O.CH{<}^{CH_2.CHMe}_{CO\ .\ \ O}{>}$.

Reference.—DI-BROMO-DI-OXY-DI-PROPYL-MALONIC ACID.

DI-OXY-ISOPROPYL-TRIMETHYLENE so-called $CHPr{<}^{CH.OH}_{CH.OH}$? (126°). S. 10. Formed from isobutyric aldehyde and ethylene glycol by heating in a sealed tube (Lochert, *Bl.* [2] 48, 716). Liquid, lighter than water, v. sol. alcohol and ether. Decomposed by water at 100° into its constituents. Bromine yields a heavy oil $C_3H_4Br.CH(CH.OH)_2$ (c. 187°).

α-OXY-*p*-PROPYL-PHENYL-ACETIC ACID $C_{11}H_{14}O_3$ *i.e.* $C_6H_4(C_3H_7).CH(OH).CO_2H$. [158°]. S. ·19 at 21°. Formed from cuminic aldehyde, HCy, and HCl (Raab, *B.* 8, 1148; Plöchl, *B.* 14, 1316). Small needles (from water).—BaA'_2 4aq.—PbA'_2.—AgA′: stellate needles.

OXY-ISOPROPYL-DIPHENYLENE-KETONE CARBOXYLIC ACID $C_{17}H_{14}O_4$ *i.e.*

$$CO{<}{\begin{matrix}C_6H_4\\C_6H_2(CMe_2OH).CO_2H\end{matrix}}\begin{bmatrix}1&6\\5&2\end{bmatrix}.\ [190°].$$

Formed by oxidising retene-quinone with alkaline $KMnO_4$ (Bamberger a. Hooker, *B.* 18, 1030, 1750; *A.* 229, 150). Yellow plates, sl. sol. cold water and ether, m. sol. alcohol.—BaA'_2 aq.—CuA'_2.—AgA′: yellow flocculent pp.

Oxim. Not melted at 270°.

TRI-OXY-TRI-PROPYL-PHOSPHINE. *Hydrate* $PH(OH)(CH(OH).C_2H_5)_3$. Formed by the action of conc. KOHAq upon $(C_3H_7O)_3PHI$, which is got, together with the crystalline oxy-propylo-iodide $(C_3H_7O)_4PI$ by dissolving PH_4I in propionic aldehyde at 0° (De Girard, *A. Ch.* [6] 2, 24). Syrup, sl. sol. water.

OXY-PROPYL-PHTHALIMIDE $C_{11}H_{11}NO_3$ *i.e.* $C_6H_4:C_2O_2:N.CH_2.CH_2.CH_2OH$. Formed from bromo-propyl-phthalimide and hot conc. KOHAq (Gabriel a. Lauer, *B.* 23, 87). Needles (from Aq).

Phenyl derivative $C_6H_4:C_2O_2:N.C_3H_6OPh$. [88°]. Formed from the bromo-propyl- derivative of phenol and potassium phthalimide at 220° (Lohmann, *B.* 24, 2633). Needles, converted by KOH into $PhO.C_3H_6.NH.CO.C_6H_4.CO_2Et$ [134°] a white crystalline powder.

OXY-PROPYL-PIPERIDINE $C_5H_{10}N.C_3H_6.OH$. So-called '*piperpropylalkine.*' (194°). S.G. $\frac{0}{}$ ·947; $\frac{10}{}$ ·936. V.D. 4·79 (obs.). Made from piperidine and propylene chlorhydrin (Ladenburg, *B.* 14, 1880, 2407; 15, 1144; Laun, *B.* 17, 680). Liquid, sol. water.—$B'HAuCl_4$.—$B'_2H_2PtCl_6$.—Mandelate: dilute HCl forms $C_{16}H_{23}NO_3$, which gives $B'HAuCl_4$.

Acetyl derivative $C_8H_{16}NO$.—$B'HAuCl_4$.

Benzoyl derivative $C_5H_{10}N.C_3H_6.OBz$.—$B'HAuCl_4$.—$B'C_6H_3N_3O_7$: yellow powder.

Oxy-propyl-piperidine $C_5H_9(CH_2.CH(OH).CH_3)NH$. So-called '(α)-*pipecolyl methylalkine.*' [47°]. (225°). Got by reducing the corresponding oxypropyl-pyridine with sodium and alcohol (Ladenburg, *B.* 22, 2588). Crystalline, v. sol. water, alcohol, and ether. Yields an oily nitrosamine.—$B'_2H_2PtCl_6$. [149°]. Small crystals (from alcohol).

Oxy-propyl-piperidine $C_5H_9(CH(OH)Et)NH$. [100°]. Got by reducing (α)-pyridyl ethyl ketone in amyl alcohol with sodium (Engler a. Bauer, *B.* 24, 2533). Needles. Probably identical with the ψ-conhydrin in *Conium maculatum.*

Dioxypropyl-piperidine $C_8H_{17}NO_2$. Made by heating piperidine with glycerin chlorhydrin (Roth, *B.* 15, 1150). Silky plates.—B′HBr.—$B'HAuCl_4$: yellow needles.

OXY-PROPYL-PYRIDINE $C_8H_{11}NO$ *i.e.* $C_5H_4(CH_2.CH_2.CH_2OH)N$. So-called '(α)-*lutidylalkine.*' (c. 130° at 17 mm.). Formed from (α)-ethyl-pyridine and formic aldehyde (Ladenburg a. Adam, *B.* 24, 1673). V. sol. water.—$B'HAuCl_4$. [71°].—$B'_2H_2PtCl_6$. [142°].

Hexahydride $C_8H_{17}NO$.—B′HBr.

Oxypropyl-pyridine $C_5H_4(CH_2.CH(OH).CH_3)N$. '(α)-*picolylmethylalkine.*' (176°–181° at 18 mm.). Made from (α)-methyl-pyridine and acetic aldehyde (L.). Liquid, sl. sol. water. — $B'_2H_2PtCl_6$. [189°]. Small tables, sl. sol. water.

Oxy-propyl-pyridine $C_5H_4(CH(OH)Et)N$. (215°). Got, together with coniine and another body [69°], by reducing (α)-pyridyl ethyl ketone with sodium-amalgam at 30°–40° (Engler a. Bauer, *B.* 24, 2532).—$B'_2H_2PtCl_6$.

Oxy-propyl-pyridine. *Tetrahydride*

$$CH_2{<}{\begin{matrix}CH(C_3H_7).CO\\CH_2\text{———}CH_2\end{matrix}}{>}NH.\quad [57°].\quad (274°).$$

Made by heating δ-amido-α-propyl-valeric acid to 200° (Aschan, *B.* 23, 3701). Flat snowy needles.

OXY-PROPYL-PYRIDINE DIHYDRIDE CARBOXYLIC ACID *v.* Morrhuic acid.

(*Py.* 3)-OXY-(*B.* 3)-ISOPROPYL-QUINOLINE

$$\begin{matrix}CH:CH.C.CH:CH\\CPr:CH.C.N\ \ :C.OH\end{matrix}\ .$$

Cumostyril. [169°]. Made by boiling the hydrochloride of phenyl-o-amido-cumyl-acrylic acid with water and a few drops of HCl for 5 hours (Widman, *B.* 19, 264). Needles, v. sol. hot alcohol, sl. sol. hot water.

Oxy-*n*-propyl-quinoline. *Dihydride*

$$\begin{matrix}CH:CH.C.CH_2.CH_2\\CPr:CH.C.NH.CO\end{matrix}\ .$$

[134°]. Formed, by intra-molecular change, by reducing the preceding body, and also from nitro-*n*-cumyl-propionic acid (Widman, *B.* 19, 2778). Prisms (from benzene-ligroïn), insol. water.

OXY-PROPYL-SUCCINIC ACID. *Lactonic acid*

$$CH_3.CH{<}{\begin{matrix}CH_2.CH.CH_2.CO_2H\\O\ —\ CO\end{matrix}}.\quad [69°].$$

(c. 260°). Formed from allyl-succinic acid and conc. HBrAq (Hjelt, *B.* 16, 334). Crystals (from alcohol).

OXY-ISOPROPYL-SULPHOBENZOIC ACID $CMe_2(OH).C_6H_3(SO_3H).CO_2H$. [1:3:4]. Made by oxidising cymene sulphonic acid, an intramolecular change taking place. Got also from iso-cymene sulphonic acid and $KMnO_4$ (R. Meyer a. Boner, *A.* 220, 8, 30; *B.* 13, 1495; 14, 2391; Remsen, *Am.* 8, 262).—K_2A'' 5aq. Triclinic crystals; $a:b:c = ·675:1:·542$; $\alpha = 131°\ 14'$; $\beta = 104°\ 26'$; $\gamma = 66°\ 27'$.—K_2A'' 2aq.—BaA″ aq. An isomeric acid, got from *m*-isocymene sulphonic acid, yields BaA″ and PbA″.

OXYPROPYL-*p*-TOLUIDINE $C_{10}H_{15}NO$ *i.e.* $C_6H_4Me.NH.C_3H_6OH$. [74°]. (293° cor.). Formed from propylene oxide and *p*-toluidine (Morley, *C. J.* 41, 387; *B.* 15, 179). Needles (from light petroleum), insol. water, v. sol. benzene and ether.—$B'H_2C_2O_4$. [151°]. Pearly plates.

(α)-OXY-PYRIDINE C_5H_5NO *i.e.*

$$N{<}{\begin{matrix}C(OH).CH\\CH{=\!=}CH\end{matrix}}{>}CH.\quad [107°].\ \ V.D.\ 2·8\ (obs.).$$

Formed by distilling its carboxylic acids (Königs, *B.* 16, 2160; 17, 590, 2391; 19, 2433; Pechmann, *B.* 17, 2384; Weidel a. Strache, *M.* 7, 297). Dimetric needles, v. e. sol. water and alcohol. Coloured red by $FeCl_3$. Yields a di-bromo-oxy-pyridine [207°].

Tetrahydride C_5H_9NO *i.e.*

$$NH{<}{\begin{matrix}CO\ .CH_2\\CH_2.CH_2\end{matrix}}{>}CH_2.\quad [40°].\ (255°).$$

Made by distilling δ-amido-valeric acid (Schotten, *B.* 21, 2235; Gabriel, *B.* 23, 1770). Crystalline mass. Yields an acetyl derivative (238°).

(β)-Oxy-pyridine C_5H_5NO *i.e.*

$$N{<}{\begin{matrix}CH.C(OH)\\CH{=\!=}CH\end{matrix}}{>}CH.\quad [124·5°].$$

Formed by

potash-fusion from pyridine sulphonic acid (Fischer a. Renouf, *B.* 17, 763, 1896). Needles, v. sol. water and alcohol. Coloured red by $FeCl_3$. —Oxalate. [175°]. White needles.

Acetyl derivative. (210° uncor.). Oil.

Ethyl derivative. Made by ethylation, and also from bromo-pyridine and alcoholic potash (Weidel a. Blau, *M.* 6, 664). Oil.—$B'_2H_2PtCl_6$. [192°]. Prisms.

Methylo-iodide B'MeI. Needles.

Methylo-chloride B'MeCl. Needles.—$B'_2Me_2PtCl_6$: Orange prisms, sl. sol. alcohol.

(γ)-**Oxy-pyridine** $NH<\genfrac{}{}{0pt}{}{CH:CH}{CH:CH}>CO$. *Pyridone.* [148°]. (above 350°). S. 100 at 15°. Formed by heating chelidamic acid under reduced pressure at 230° or with water at 196° (Lerch, *M.* 5, 402; Haitinger a. Lieben, *M.* 6, 300). Formed also by distilling its carboxylic acid (Ost, *J. pr.* [2] 29, 65). Small efflorescent grains (from alcohol), prisms (containing aq), or trimetric tables; $a:b:c = \cdot55:1:1\cdot5$. V. sol. water and alcohol. Melts below 100° when hydrated. Converted by treatment with MeI and KOH into $NMe<\genfrac{}{}{0pt}{}{CH:CH}{CH:CH}>CO$, a deliquescent mass [89°] which gives $(C_6H_7NO)_2H_2PtCl_6$ aq [176°], B'MeI, and $B'_2Me_2PtCl_6$. Does not yield an acetyl derivative.

Salts. — $B'_2H_2PtCl_6$ aq. — $B'_2H_2PtCl_6$ 2aq. Efflorescent monoclinic needles [200°], converted by boiling water into $B'_3H_2Pt_2Cl_{10}$ aq.—$B'HNO_3AgNO_3$: tables.—$B'HgCl_2$.—$B'HHg_2Cl_5$.

Methyl derivative $N<\genfrac{}{}{0pt}{}{CH.CH}{CH:CH}>C.OMe$. (191° cor.) at 738 mm. Formed from (γ)-chloro-pyridine and NaOMe (H. a. L.). Liquid, sol. water. Alkaline in reaction. Changes at 220° into the crystalline isomeride (*v. supra*). Gives a deep-blue liquid with aqueous $CuSO_4$. Conc. HIAq converts it into (γ)-oxy-pyridine. — $B'_2H_2PtCl_6$: crystals, sl. sol. water.

Di-oxy-pyridine $C_5H_3(OH)_2N$. [c. 255°] (K. a. G.); [239°] (W. a. B.). Formed by potash-fusion from its ethyl derivatives and also from pyridine disulphonic acid (Königs a. Geigy, *B.* 17, 1835; Weidel a. Blau, *M.* 6,651). Needles (containing ½aq), v. sol. water, sl. sol. alcohol. Coloured red by $FeCl_3$.—B'HCl: needles.

Mono-ethyl derivative C_7H_9NO. [128°]. Formed, together with the di-ethyl derivative, by heating dibromopyridine [111°] with alcoholic potash. Tables, sl. sol. cold water.—$B'HNO_3$.—$B'_2H_2PtCl_6$: red triclinic needles.

Di-ethyl derivative $C_5H_3(OEt)_2N$. (c. 244°). Made as above. Liquid, nearly insol. water.—$B'_2H_2PtCl_6$: yellow needles.—$B'HHgCl_3$. [106°]. Crystals (from HClAq).

Di-oxy-pyridine. *Di-oxim of the dihydride* $NH<\genfrac{}{}{0pt}{}{C(NOH).CH_2}{C(NOH).CH_2}>CH_2$. [193°]. A product of the action of hydroxylamine on tri-methylene cyanide (Biedermann, *B.* 22, 2967). Yields a di-acetyl derivative [127°] and a dibenzoyl derivative [180°].

Picrate. [175°]. Needles.

Tri-oxy-pyridine $C_5H_5NO_3$ *i.e.* $N<\genfrac{}{}{0pt}{}{C(OH).CH}{C(OH):CH}>C.OH$ [220°–230°]. Formed by boiling di-oxy-amido-pyridine (glutazine) with conc. HClAq (Stokes a. Von Pechmann, *Am.* 8, 384; *B.* 19, 2701). Yellowish sandy powder, v. sol. hot water. On evaporation of its solution it is partly converted into its anhydride. $FeCl_3$ gives a red colour. Forms with bromine $CBr_3.CO.CBr_2.CONH_2$. NH_4OAc at 140° converts it into glutazine.—BaA'_2.—AgA'.—B'HCl.

Oxim $NH<\genfrac{}{}{0pt}{}{CO.CH_2}{CO.CH_2}>C:NOH$. [196°]. Made by boiling tri-oxy-pyridine or glutazine with hydroxylamine hydrochloride. Minute hexagonal plates (containing aq), m. sol. hot water.—B'HCl: plates.

Phenyl-hydrazide $NH<\genfrac{}{}{0pt}{}{CO.CH_2}{CO.CH_2}>C:N_2HPh$. [230°]. Tables.

Anhydride $C_{10}H_8N_2O_5$. Made by boiling glutazine with dilute H_2SO_4. Minute flesh-coloured prisms, sl. sol. water.—$BaA'_2$4aq: yellow prisms.—AgHA''.—$B'H_2SO_4$.—B'HCl.

References.—Di-bromo-, Di-chloro-, and Di-iodo-, oxy-pyridine.

OXY-PYRIDINE CARBOXYLIC ACID $C_5H_3N(OH).CO_2H$. (α)-*Oxypicolinic acid.* [267°]. Made by heating di-chloro-oxy-pyridine carboxylic acid [282°] with HI in HOAc at 210° (Ost, *J. pr.* [2] 27, 289). Long needles (containing aq) or short anhydrous needles; v. sol. hot water and alcohol, insol. ether. Coloured reddish-brown by $FeCl_2$. $AgNO_3$ is not reduced, but gives a white pp.—BaA'_2 aq.—CaA'_2.—$C_5H_3N(OK).CO_2K$ aq: groups of needles.

Oxy-pyridine carboxylic acid $C_5H_3N(OH).CO_2H$. (β)-*Picolinic acid.* [250°]. Made by the action of HI in HOAc on chloro-oxy-pyridine carboxylic acid [257°] at 200° (Ost). Formed also without by-products by boiling comanic acid $C_5H_3O_2(CO_2H)$ with NH_3Aq (Ost, *J. pr.* [2] 29, 64). Glittering plates. Yields oxypyridine [148°] on heating strongly.—Salt: BaA'_2 2aq: small needles, m. sol. water.

Oxy-pyridine carboxylic acid $C_5H_3N(OH).CO_2H$. (γ)-*Oxy-picolinic acid.* [258°]. Formed by the action of tin and HClAq on chloro-oxy-pyridine carboxylic acid [224°] (Bellmann, *J. pr.* [2] 29, 7). Small trimetric pyramids (containing aq), sl. sol. water, sol. conc. HClAq. Coloured brown by $FeCl_3$.—BaA'_2: prisms.—$CaA'_2$4aq: needles.

Oxy-pyridine carboxylic acid $C_5H_3N(OH).CO_2H$ *i.e.* $C(OH)<\genfrac{}{}{0pt}{}{N\ .CH}{CH:CH}>C.CO_2H$. *Oxy-nicotinic acid.* [302°]. Formed by heating oxy-pyridine di-carboxylic (oxyquinolinic) acid with water at 195° (Königs a. Geigy, *B.* 17, 589). Formed also by the action of NH_3Aq on the methyl ether of coumalic acid (*v.* vol. ii. p. 264), the product being saponified (Pechmann a. Welsh, *B.* 17, 2384; *C. J.* 47, 145). Needles, sl. sol. hot water. May be sublimed. PCl_5 yields chloro-pyridine carboxylic acid, whence tin and HCl form nicotinic acid. $FeCl_3$ gives a light-yellow colour.—PbA'_2 2½aq: needles, sol. hot water.

Methyl derivative $C_5H_3N(OMe).CO_2H$. [238°]. Formed by methylating the acid, and also from methyl coumalate and methylamine, the product being saponified. Needles (containing aq), nearly insol. cold water.

Phenyl derivative $C_5H_3N(OPh).CO_2H$.

[280°]. Formed by the action of boiling NaOHAq on methyl coumal-anilidate (*loc. cit.*). Needles.

Oxy-pyridine carboxylic acid
$CH{<}\substack{N:C(OH)\\ CH.CH}{>}C.CO_2H$. (α)-*Oxy-nicotinic acid.* [256°]. Formed by heating (α)-oxy-isocinchomeronic acid with HOAc and a little Ac_2O at 210° (Weidel a. Strache, *M.* 7, 295). Slender needles (from water). Yields (α)-oxy-pyridine when heated.—AgA′: silky needles.

Oxy-pyridine dicarboxylic acid $C_7H_5NO_5$ *i.e.* $N{<}\substack{C(CO_2H):CH\\ C(OH).C(CO_2H)}{>}CH$. (α)-*Oxyisocinchomeronic acid.* Formed by oxidising (α)-diquinolyl with $KMnO_4$ (Weidel a. Strache, *M.* 7, 293). Vitreous crystals. Gives no colour with $FeCl_3$.—BaA″.—Ag_2A'': needles, nearly insol. water.

Oxy-pyridine dicarboxylic acid
$C_5H_2N(OH)(CO_2H)_2$ *i.e.*
$N{<}\substack{C(CO_2H):C(CO_2H)\\ C(OH)\text{———}CH}{>}CH$. *Oxyquinolinic acid.* Formed from quinolinic acid by potash-fusion (Königs a. Körner, *B.* 16, 2158). Small crystals (from dilute H_2SO_4), blackening at 254°. $FeCl_3$ colours its aqueous solution red. Its Ag salt yields (α)-oxy-pyridine on heating.—BaA'_2 4aq: needles (from hot water).

Methyl derivative $C_5H_2N(OMe)(CO_2H)_2$. [140°]. Got by adding $KMnO_4$ to an aqueous solution of the methyl derivative of (γ)-amido-carbostyril (Feer a. Königs, *B.* 18, 2398). Needles, v. e. sol. water.—$AgH_3A''_2$. Needles (from water).

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Di-oxy-pyridine carboxylic acid $C_6H_5NO_4$ *i.e.* $N{<}\substack{C(OH).CH\\ C(OH):CH}{>}C.CO_2H$? *Citrazic acid.* Formed by heating the mono-, di-, or tri- amide of citric acid with HCl or H_2SO_4 (Behrmann a. Hofmann, *B.* 17, 2687). Crystalline powder, nearly insol. water, sl. sol. hot HClAq. Carbonises at 300°. PCl_5 converts it into di-chloro-pyridine carboxylic acid [210°]. Gives a deep-blue colour with $NaNO_2$. Tin and HCl reduce it to tricarballylic acid.—BaA'_2 2aq.

Di-acetyl derivative. Crystalline.

Methyl ether MeA′. Plates, decomposing above 220°.

Ethyl ether EtA′. Plates.

Amide $C_5H_2N(OH)_2.CONH_2$. Formed by the action of conc. NH_3Aq on ethyl acetyl-citrate and on aconitic ether (Ruhemann, *C. J.* 51, 405; *B.* 20, 3366). Small grey crystals (from water).

Di-oxy-pyridine carboxylic acid
$C_5H_2N(OH)_2CO_2H$. *Comenamic acid. Di-oxy-picolinic acid.* Formed by heating hydrogen ammonium comenate at 190°, or by boiling comenic acid with NH_3Aq. The yield is about 45 p.c. of the comenic acid used (How, *T. E.* 20 [2] 255; *A.* 80, 65; 83, 350; Ost, *J. pr.* [2] 27, 269). Tables (containing 2aq), m. sol. hot water and alcohol. Not decomposed by boiling NaOHAq. Gives a purple colour with $FeCl_3$.

Reactions.—1. Yields pyridine on distillation with zinc-dust (Lieben a Haitinger, *B.* 16, 1263). 2. Conc. HIAq at 200° does not attack it, but when heated with it for two days at 270° pyro-comenamic acid (probably a di-oxy-pyridine) $C_5H_5NO_2$ is formed. This body crystallises in needles (containing aq), gives a violet colour with $FeCl_3$, and forms B′HBr.—3. PCl_5 (3 mols.) acting on the acid (1 mol.) at 100° forms a product which on treatment with tin and HClAq yields a di-oxy-methyl-pyridine $C_6H_7NO_2$, crystallising in trimetric prisms (containing aq), and forming the salts B′HCl and $B'H_3PO_4$. PCl_5 and $POCl_3$ at 200° convert this di-oxy-methyl-pyridine at 200° into hexa-chloro-methyl-pyridine and $C_5H_2Cl_2N(CCl_3)$, which is converted by boiling water into chloro-(γ)-oxy-pyridine (α)-carboxylic acid (Bellmann, *J. pr.* [2] 29, 19). Excess of PCl_5 (5 mols.) at 220° acting on comenamic acid in presence of $POCl_3$ forms penta- and hexa-chloro-methyl-pyridine, and other bodies, whence water produces chloro-(γ)-oxy-pyridine (α)-carboxylic acid and chloro-cyamic acid $C_8H_8ClNO_4$, which crystallises in needles [186°], and gives a blue colour with $FeCl_3$. Chlorocyamic acid yields the salts AgA′ and BaA'_2 aq.—4. Ammonium comenamate forms, among other products, on distillation, a very poisonous base called ‘Oxycomazine’ $C_{10}H_7N_3O$ (Krippendorff, *J. pr.* [2] 32, 153). The base crystallises from alcohol in four-sided prisms, S. ·0035 at 20°. Its solutions in dilute acids show green fluorescence, and in strong acids a blue fluorescence. Tin and HCl reduce it to oxy-amido-pyridine. Oxycomazine forms the following salts: $B'H_2Cl_2$, [c. 265°], $B'H_2PtCl_6$, $B'H_2SO_4$ 3aq, [c. 295°], and $C_{10}H_6AgN_3O$.—5. $KMnO_4$ oxidises comenamic acid to tri-oxy-pyridine carboxylic acid.

Salts. — NH_4A': very small grains. — $BaC_6H_3NO_4$ aq: pp.—BaA'_2 2aq: crystalline.

Ethyl ether EtA′. [205°]. Needles (containing aq), sol. hot water (Reibstein, *J. pr.* [2] 24, 284). Yields $Ba(C_8H_8NO_4)_2$ 2aq and EtA′HCl aq, both crystalline. When heated with AcCl it yields an anhydride $C_8H_7NO_3$ [261°] and two derivatives, $C_5H_2N(OH)(OAc).CO_2Et$ [152°] and $C_5H_2N(OAc)_2CO_2Et$ [38°]. BzCl forms $C_5H_2N(OBz)_2CO_2Et$ [102°].

Di-oxy-pyridine carboxylic acid $C_6H_5NO_4$. *Oximido-comanic acid.* Made from comanic acid and hydroxylamine (Ost, *J. pr.* [2] 29, 378). Small needles, decomposing at 200°. Reduced by tin and HCl to (β)-oxy-picolinic acid.

Di-oxy-pyridine dicarboxylic acid. *Ethyl derivative* $N{<}\substack{C(OEt):C(CO_2H)\\ C(OH)\ .C(CO_2H)}{>}CH$. [182°]. Formed by the action of NaOHAq on the mono-ethyl ether EtHA″ [160°], which is made by treating ethoxy-(α)-pyrone dicarboxylic ether with NH_3Aq (Guthzeit a. Dressel, *B.* 22, 1427; *A.* 262, 104). Needles (containing aq). Conc. HClAq at 140° forms glutaconic acid [134°]. PCl_5 in $POCl_3$ at 250° gives di-chloro-pyridine dicarboxylic acid [230°] whence Et_2A'' [76°] and, by treatment with HI, pyridine dicarboxylic acid [322°] may be prepared.—Ag_2A''.

Mono-ethyl ether
$CH{<}\substack{C(OEt):C(CO_2Et)\\ C(OH)\ .C(CO_2H)}{>}N$. [160°]. Needles. Yields AgA′ and an acetyl derivative $C_{13}H_{15}NO_7$ [100°].

Di-ethyl ether Et_2A''. [81°].

Tri-oxy-pyridine carboxylic acid $C_6H_5NO_5$. *Tri-oxy-picolinic acid. Oxy-comenamic acid.* Formed, in small quantity, by oxidising comenamic acid with potassium permanganate and H_2SO_4 in the cold. Prepared by heating oxy-comenic acid $C_5HO_2(OH)_2.CO_2H$ with conc. NH_3Aq at 160° (Reibstein, *J. pr.* [2] 24, 290; Ost, *J. pr.* [2] 27, 265). Small needles (contain-

ing aq) (from water). Does not form a hydrochloride. Gives an azure pp. with $BaCl_2$ and NH_3. Alcoholic potash gives, in alcoholic solutions, a blue flocculent pp., forming a colourless solution in water. $FeCl_3$ gives an indigo-blue colour. $AgNO_3$ gives a white pp., soon turning black. Br forms bromo-tri-oxy-pyridine carboxylic acid, crystallising with 2aq. Nitric acid added to the ethereal solution forms oxypyridoquinone carboxylic acid $C_5HNO_2(OH).CO_2H$, crystallising in orange tables (containing 2aq).

References.—BROMO-, CHLORO-, and BROMO-NITRO-, OXY-PYRIDINE CARBOXYLIC ACID.

a-OXY-PYRIDYL-ETHYL-FURFURANE $CH\lessdot^{CH.CH}_{CH:N}\gtrdot C.CH_2.CH(OH).C\lessdot^{CH.CH}_{O\ \ .CH}$ [43°]. (164° at 20 mm.). Formed from (a)-methyl-pyridine, furfuraldehyde, and some water at 150° (Klein, *B.* 23, 2693). Greenish mass, v. sol. alcohol.—$B'_2H_2PtCl_6$. [162°].—$B'HHgCl_3$. [c. 150°].—$B'HCdI_3$.—$B'C_6H_3N_3O_7$. [c. 160°].

Acetyl derivative. Oil.—$(C_{11}H_{10}AcNO_2)_2H_2PtCl_6$. [165°].—$B'HHgCl_3$. [c. 155°]. Small needles.

Benzoyl derivative $C_{11}H_{10}BzNO_2$. [49°].—$B'_2H_2PtCl_6$. [140°-145°].—$B'HHgCl_3$.

OXY-PYRIDYL-MALONIC ACID $C_5H_4N.C(OH)(CO_2H)_2$. Formed by oxidising pilocarpine with $KMnO_4$ (Hardy a. Calmels, *Bl.* [2] 48, 228). Syrup. Yields pyridine (β)-carboxylic acid on further oxidation.—BaA″.—BaA″ 3aq.—$Cu_2A''(OH)_2$ aq.—Ag_2A'' : pp.

OXY-PHENYL-PYRIDYL-PROPIONIC ACID. *Hexahydride* $C_5H_{10}N.CHPh.CH(OH).CO_2H$. [244°]. Formed from piperidine and sodium phenyl-glycidate (Erlenmeyer, *B.* 22, 1482).

a-OXY-(β)-PYRIDYL-PROPIONIC ACID $C_5H_4N.CH_2.CH(OH).CO_2H$. Formed by boiling pilocarpine with water for 12 hours (Hardy a. Calmels, *Bl.* [2] 48, 227). Gummy mass.—B'HCl.—B'_2PtCl_4.—$B'AuCl_3$. [154°]. Prismatic needles.

a-Oxy-(a)-pyridyl-propionic acid $C_5H_4N.CH_2.CH(OH).CO_2H$. [125°]. Formed by the action of hot dilute caustic soda on $C_5H_4N.CH_2.CH(OH).CCl_3$, the product of the union of chloral with (a)-picoline (Einhorn, *B.* 23, 219; *A.* 265, 211). Prisms.—$Cu_2A'_2O$: needles.—$(HA')_2H_2PtCl_6$. [204°].—$HA'HAuCl_4$. [174°]. Orange prisms.—AgA' : white needles.—HA'HCl. [86°].—HA'HBr.

Benzoyl derivative. [145°]. Needles.—$B'_2H_2PtCl_6$. [179°]. Yellow prisms.

Methyl ether MeA'.—$MeA'HAuCl_4$. [119°].—Benzoyl derivative of the ether $C_5H_4N.CH_2.CH(OBz).CO_2Me$. [c. 41°]. Yields $B'_2H_2PtCl_6$, [193°], crystallising in yellow needles.

β-Oxy-(a)-pyridyl-propionic acid $C_5H_4N.CH(OH).CH_2.CO_2H$. [86°]. Formed by warming β-bromo-pyridyl-propionic acid with NaOHAq (Einhorn, *B.* 23, 221). White needles, v. e. sol. water.—$Cu_2A'_2O$: blue crystals.—B'HCl. [147°]. Prisms.—$B'_2H_2PtCl_6$. [191°].

Benzoyl derivative. [135·5°]. Prisms.

Methyl ethyl MeA'. Yields $(MeA')_2H_2PtCl_6$ [178·5°] and a benzoyl derivative [79°] crystallising in prisms.

Ethyl ether EtA'. Yields $(EtA')_2H_2PtCl_6$.

Di-oxy-pyridyl-propionic acid $C_5H_4N.CH(OH).CH(OH).CO_2H$. [190°]. Formed by oxidising pyridyl-acrylic acid with alkaline $KMnO_4$ (Einhorn, *B.* 23, 223). White crystals.

Ethyl ether EtA'. [96°]. Tables. Yields a benzoyl derivative [122°] crystallising in needles.

DI-OXY-PYRIMIDINE *v.* HYDROQUINONE TETRACARBOXYLIC ACID.

OXY-PYRONE DICARBOXYLIC ACID. *Ethyl derivative of the ethyl ether* $CH\lessdot^{C(CO_2Et):C(OEt)}_{C(CO_2Et)-CO}\gtrdot O$. *Anhydride of tri-ethyl propylene-tetracarboxylate.* [94°]. Formed by distilling di-carboxy-glutaconic ether at 210° under 15 mm. pressure (Guthzeit a. Dressel, *B.* 22, 1415). Needles, insol. water and alcohol. Converted by HClAq into glutaconic acid.

OXY-PYROTARTARIC ACID $C_5H_8O_5$ *i.e.* $CH_3.C(OH)(CO_2H).CH_2.CO_2H$. Mol. w. 148. [108°]. Formed by the action of boiling dilute HCl upon $CH_3.C(OH)(CN).CH_2.CO_2Et$, which is got by heating acetoacetic ether for three days with dry HCy at 100° (Morris, *C. J.* 37, 7; *cf.* Demarçay, *Bl.* [2] 27, 120). Made also by oxidation of isovaleric acid by long boiling with dilute HNO_3 (Bredt, *B.* 14, 1782; 15, 2318). Deliquescent, star-like groups of needles, sol. water, alcohol, and ether. On dry distillation it splits up into water and citraconic anhydride.—BaA″ 2aq. Not decomposed by boiling with water.—CaA″ 1½aq.—Ag_2A'' ½aq : needles.

Oxy-pyrotartaric acid $CH_3.CH(CO_2H).CH(OH).CO_2H$. *Citramalic acid.* [119°]. Formed by the action of zinc on a dilute solution of chloro-citramalic acid (which melts at 139° according to Melikoff, *A.* 253, 88); HCl is added towards the end of the reaction (Carius, *A.* 129, 160; Morawski, *Sitz. W.* 76 [2] 670; *J. pr.* [2] 10, 69). Large hygroscopic crystals, yielding citraconic anhydride and water on distillation.—Salts: K_2A'' *x*aq.—$BaH_2A''_2$ 2aq.—MgA.″—CaA″ 2aq.—CaA″ 1½aq.—$CaH_2A''_2$ 5aq. ZnA″ 2aq.—$Pb_2A''O$ 2aq.—PbA″ 3½aq.—Ag_2A''.

Oxy-pyrotartaric acid $CH_2(OH).CH(CO_2H).CH_2.CO_2H$. *Itamalic acid.* Formed from itaconic acid by successive treatment with HBr and hot water. Formed also by boiling *ita*-chloro-pyrotartaric acid with aqueous Na_2CO_3 (Swarts, *Bull. Acad. Belg.* [2] 24, 25; *Bl.* [2] 9, 317; Fittig, *A.* 188, 76; Morris, *C. J.* 37, 14). The free acid, liberated from its Ca salt by oxalic acid, or from its Ag salt by H_2S, changes on evaporation, even at 15°, into its lactone [58°].—Na_2A''.—$(NH_4)HA''$.—CaA″aq.—CaA″ 3aq.—PbA″.—CuA″.—$Cu_3A''_2O$.—AgA'.—EtA' : oil.

Lactone $CH(CO_2H)\lessdot^{CH_2.CO}_{CH_2.O}$. *Paraconic acid.* [58°]. Formed as above, and also by boiling *ita*-bromo-pyrotartaric acid (1 pt.) with water (10 pts.) (Beer, *A.* 216, 90). Crystalline. Yields citraconic anhydride on distillation. With bases it yields salts of itamalic acid.—$NaC_5H_5O_4$.—CaA'_2 3aq. Small needles. Yields calcium itamalate on boiling with $CaCO_3$.—AgA'.

Chloro-itamalic acid $C_5H_7ClO_5$. [150°]. Made by passing chlorine into a solution of sodium itaconate. Crystals, v. e. sol. water.

Oxypyrotartaric acid [c. 135°] described by Maxwell Simpson (*Pr.* 13, 44) as got from glycerin dichlorhydrin by successive treatment with KCy and KOH, is probably β-oxy-glutaric acid. It yields Ag_2A'' and Et_2A'' (298°). An isomeric or identical acid, made by fusing

sulpho-pyrotartaric acid with potash, yields Ag_2A''aq (Wieland, *A.* 157, 41). A liquid isomeride, got by potash fusion from bromo-cyano-butyric acid, yields Ag_2A''.

Di-oxy-pyrotartaric acid $C_5H_8O_6$. *Citratartaric acid.* Formed by the action of boiling baryta-water on chloro-citramalic acid prepared from barium citraconate and HOCl (Carius, *A.* 129, 159) and by heating oxycitraconates with water at 120° (Morawski, *J. pr.* [2] 11, 432). Amorphous, deliquescent mass.—Pb_2A'' aq.

Isomeride *v.* ITATARTARIC ACID.

DI-OXY-DI-PYRRYL-BUTANE $C_{12}H_6N_2O_2$ *i.e.* $C_5H_4N.CMe(OH).CMe(OH).C_5H_4N$. [120°]. Formed from pyrryl-methyl-ketone, water, and sodium-amalgam (Dennstedt a. Zimmermann, *B.* 19, 2204). Monoclinic prisms (containing 2aq). Melts at 98° when hydrated. V. e. sol. alcohol.

OXY-PYRUVIC ACID $C_3H_4O_4$ *i.e.* $CH_2(OH).CO.CO_2H$. Formed by dissolving 'nitro-cellulose' (collodion) in dilute NaOHAq and allowing the solution to stand at 20° (Will, *B.* 24, 405). Amorphous, v. sol. water, but ppd. by alcohol. Reduces Fehling's solution and ammoniacal $AgNO_3$. Its solutions, and those of its salts, are slightly lævogyrate. Phenyl hydrazine forms the compound $C_{15}H_{14}N_4O_2$ or $(N_2HPh)CH.C(N_2HPh).CO_2H$, [205°], whence NaA′ [231°], KA′ [233°], NH_4A' [200°], CaA'_2, and EtA′ [149°].

Salts.—CaA'_2 8aq.—SrA'_2 4aq.—CdA'_2 4aq.

OXY-QUINALDINE *v.* OXY-METHYL-QUINOLINE.

OXY-QUINAZOLINE. *Dihydride* $C_6H_4<\begin{matrix}CH_2.NH\\NH.CO\end{matrix}$. '*Phenyldihydroacimiazine.*' [160°]. Formed from oxy-tolyl-urea and HCl (Söderbaum a. Widman, *B.* 22, 1669). Scales, insol. cold conc. KOHAq.—B′HCl.—$B'_2H_2PtCl_6$ 2aq. [205°].—$B'HAuCl_4$. [179°].

Oxy-quinazoline $C_6H_4<\begin{matrix}C(OH):N\\N{=\!=}CH\end{matrix}$. [212°]. Made by heating formyl-o-amido-benzamide [123°] for two hours at 180° (Knape, *J. pr.* [2] 43, 214). Thin needles.—$B'_2H_2PtCl_6$aq. [above 250°].

Methyl derivative [71°].

Di-oxy-quinazoline $C_6H_4<\begin{matrix}C(OH).NH\\N{=\!=}C.OH\end{matrix}$. '*Uramido-benzoyl.*' [above 350°]. Formed by passing cyanogen into an alcoholic solution of o-amido-benzoic acid and boiling the product with HClAq. Formed also by fusing *o*-amido-benzoic acid or o-amido-benzamide with urea, and by heating the product of the action of $ClCO_2Et$ on *o*-amido-benzamide (Griess, *B.* 2, 415; 11, 1985; Abt, *J. pr.* [2] 39, 140). Needles, sl. sol. hot water. With PCl_5 it yields di-chloro-quinazoline [115°].—$C_8H_5NaN_2O_2EtOH$: needles.

Di-methyl derivative $C_8H_4(OMe)_2N_2$. [66°]. Made from di-chloro-quinazoline and NaOMe. Needles, v. e. sol. alcohol.

OXY-*p*-QUINAZOLYL-BENZOIC ACID $C_6H_4<\begin{matrix}N:CH\\CO.N.C_6H_4.CO_2H\end{matrix}$. Made by oxidising *p*-tolyl-quinazoline dihydride with $KMnO_4$ (Paal a. Busch, *B.* 22, 2699). Small needles.—AgA′.

OXY-QUINHYDRONE $C_{12}H_{10}O_6$. Formed from oxyhydroquinone and HNO_3 (Barth a. Schreder, *M.* 5, 595). Dark greyish-blue crystals.

(*Py.* 1)-**OXY-QUINOLINE** $C_6H_4<\begin{matrix}CO.CH\\NH.CH\end{matrix}$. [235°]. Made by heating phenyl-β-amido-acrylic acid at 200° or oxanilic acid at 170° (Reissert, *B.* 20, 3109; *B.* 21, 1376). Long needles (from alcohol). Yields quinoline when distilled with zinc-dust.

Acetyl derivative. [228°]. Needles.

Phenyl hydrazide $C_{15}H_{13}N_3$. [168°].

(*Py.* 2)-**Oxy-quinoline.** This is probably the constitution of cynurine *v. infra.*

(*Py.* 3)-**Oxy-quinoline** $C_6H_4<\begin{matrix}CH:CH\\N{=}C.OH\end{matrix}$. *Carbostyril.* [199°].

Formation.—1. By reducing *o*-nitro-cinnamic acid (Chiozza, *A.* 83, 118; Tiemann, *B.* 13, 2070; Friedländer, *B.* 14, 1916).—2. By heating *o*-amido-cinnamic acid with HClAq (T.) or dilute H_2SO_4 (Feer a. Königs, *B.* 18, 2395).—3. By reducing tri-chloro-oxy-quinoline with HI.—4. By heating (*Py.* 3)-chloro-quinoline with water at 120° (Friedländer a. Ostermaier, *B.* 15, 335).—5. By the action of aqueous HOCl upon quinoline (Erlenmeyer a. Rosenhek, *B.* 18, 3295).—6. By heating quinoline on the water-bath with a conc. solution of bleaching-powder (E. a. R., *B.* 19, 489; Roos, *B.* 21, 619).

Properties.—Long thin feathery crystals (containing aq) (from water) or thick anhydrous prisms (from alcohol); v. sl. sol. cold water, insol. NH_3Aq.

Salts.—$Ba(C_9H_6NO)_2$: plates.—AgA′: pp.

Methyl ether MeA′. (247°). Oil.

Ethyl ether EtA′. (256°). Formed from (*Py.* 3)-chloro-quinoline and KOEt. Formed also by heating *o*-amido-cinnamic ether with alcohol and $ZnCl_2$ at 90° (Friedländer a. Weinberg, *B.* 15, 1424, 2103) and by ethylation of carbostyril. Pungent oil, solidifying below 0°. Yields a dihydride [199°] when reduced by sodium-amalgam.

Phenyl ether. [69°]. Plates.

Dihydride *v.* AMIDO-PHENYL-PROPIONIC ACID.

(*B.* 1)-**Oxy-quinoline** $\begin{matrix}CH:C(OH).C.CH:CH\\CH:CH{-\!-}C.\ N:CH\end{matrix}$. [224°]. Formed by potash-fushion from quinoline (*Py.* 1)-sulphonic acid (Riemerschmied, *B.* 16, 721; Lellmann, *B.* 20, 2174). Formed also from (*Py.* 1)-amido-quinoline by the diazo- reaction (Skraup, *M.* 5, 533). Silky needles or plates, sol. alcohol and aqueous Na_2CO_3, v. sl. sol. water.—Salts: B′HCl: yellow needles.—$B'_2H_2PtCl_6$ 4aq: orange tables.

Tetrahydride $C_6H_3(OH)<\begin{matrix}CH_2.CH_2\\NH.CH_2\end{matrix}$. [117°]. Made by reducing with tin and HCl. Needles, sol. water, alcohol, and ether. Yields a nitrosamine crystallising in tables, sol. alcohol.

(*B.* 2)-**Oxy-quinoline** $\begin{matrix}C(OH):CH.C.CH:CH\\CH:CH{-\!-}C{-}N:CH\end{matrix}$. [193°]. (above 360°). Formed by heating a mixture of *p*-amido-phenol, *p*-nitro-phenol, glycerin, and H_2SO_4 (Skraup, *B.* 15, 893; *M.* 3, 545). Formed also by heating its carboxylic acids (Weidel, *M.* 2, 575; Skraup, *M.* 4, 696) and by potash-fushion from its sulphonic acid (Fischer, *B.* 17, 440). Small prisms (from alcohol). Not coloured by ferric chloride solution $B'_2H_2PtCl_6$ 2aq [236°]. — $B'_2Cu(OAc)_2$. — $B'_3(H_2SO_4)_2$ 11aq.—B′HCl aq: prisms, v. e. sol.

water.—B'MeI aq. Crystalline (Claus a. Howitz, *J. pr.* [2] 42, 232; 43, 520).—B'MeCl. [c. 272°]. —$B'_2Me_2PtCl_6$.—$B'Me_2SO_4$ 5aq.—B'MeOH. [c. 200°]. — B'EtBr. [c. 242°]. — $B'C_7H_7Cl$ 1½aq. [237°].—$(B'C_7H_7Cl)_2PtCl_4$.

Methyl ether MeA'. *p-Quinanisole.* (305°). S.G. $\frac{0}{-}$ 1·665. Got by methylation, and also from *p*-anisidine, nitro-anisole, glycerin, and H_2SO_4 (Skraup, *M.* 6, 762). Oil. Solutions of its salts show blue fluorescence. Gives a green colour with chlorine-water and ammonia.—B'HCl 2aq. — $B'_2H_2PtCl_6$ 4aq. — $B'H_2SO_4$. — $B'_2H_2SO_4$. — $B'_2H_2Cr_2O_7$.—B'MeI. [235°]. Prisms.—Picrate [204°].

Acetyl derivative $C_9H_6(OAc)N$. [38°]. (298°). Crystals.—$B'_2H_2PtCl_6$. Prisms.

Benzoyl derivative. [231°]. Needles.

Tetrahydride of the methyl ether $C_9H_{10}(OMe)N$. *Thallin.* [43°]. (283°) at 735 mm. Got by reducing the methyl ether with tin and conc. HClAq. Prisms. $FeCl_3$ gives a golden colour, changing to emerald green.—Chlorine-water gives a green colour turned yellow by ammonia.—B'HCl.—$B'_2H_2SO_4$ 2aq.—B'HI. [155°]. —$B'C_4H_6O_6$: four-sided prisms. S. 10 at 15°.—Picrate. [162°].

Acetyl derivative $C_9H_9Ac(OMe)N$. [47°].

(B. 3)-Oxy-quinoline $\begin{matrix}CH & :CH-C.CH:CH \\ C(OH):CH & .\ C-N:CH\end{matrix}$. [c. 238°]. Formed by heating *m*-nitro-phenol with *m*-amido-phenol, glycerin, and H_2SO_4 (Skraup, *B.* 15, 893; *M.* 3, 559). Formed also by potash-fusion from quinoline (*B.* 3)-sulphonic acid (Fischer, *B.* 15, 1979). Silky needles, sol. alcohol, not volatile with steam. Its solutions show green fluorescence. $FeCl_3$ gives a brownish-red colour.—$B'_2H_2PtCl_6$ 2aq.—B'HCl 1½aq: prisms.—$B'Cu(OAc)_2$.—Picrate. [244°].

Benzoyl derivative. [86°]. Prisms.

Methyl ether $C_{10}H_9NO$. (275° at 720 mm.). Oil, volatile with steam.

(B. 4)-Oxy-quinoline $\begin{matrix}CH:CH-C.CH:CH \\ CH:C(OH).C-N:CH\end{matrix}$. [75°]. (267° cor.).

Formation.—1. By distilling its carboxylic acid (Weidel a. Cobenzl, *M.* 1, 862).—2. By soda fusion from its sulphonic acid (Bedall a. Fischer, *B.* 14, 443, 1366).—3. By heating o-amido-phenol with o-nitro-phenol, glycerin, and H_2SO_4 (Skraup, *B.* 15, 893; *M.* 3, 536).

Properties.—Prisms, sl. sol. water. May be distilled with steam. $FeCl_3$ gives a green colour. Gives quinolinic acid on oxidation with $KMnO_4$ (Fischer a. Renouf, *B.* 17, 756). Chlorine in HOAc forms mono-, di-, and tri-, chloro-derivatives (Zincke a. Hebebrand, *A.* 264, 198). Ethylene chlorhydrin forms crystalline $B'(C_2H_4OH)Cl$, whence $(C_{11}H_{12}NO_2Cl)_2PtCl_4$ (Wurtz, *C. R.* 96, 1269). $ClCO_2Et$ forms $C_{12}H_{11}NO_3$ [105°] whence $(C_{12}H_{11}NO_3)_2H_2PtCl_6$ (Lippmann, *M.* 8, 439). According to Lippmann (*M.* 10, 667), MeI in MeOH at 100° forms $(C_9H_6(OMe)N)(C_9H_6(OH)NMeI)HI$ 2aq, whence $C_{20}H_{19}ClN_2O_2HCl$ 5aq and $C_{20}H_{20}Cl_2N_2O_2PtCl_4$ 2aq. These bodies may perhaps be more simply formulated, as below. Chloroform and Na yield $CH(C_9H_6(OH)N)_3$ (Lippmann, *B.* 19, 2471).

Salts.—B'HCl aq.—$B'_2H_2PtCl_6$ 2aq: golden needles.—$B'H_2SO_4$ 2aq.—$B'C_6H_3N_3O_7$. [204°]. $Cu(C_9H_6NO)_2$: canary-yellow pp.—B'MeI aq. [c. 170°].—B'MeCl 2aq. [c. 260°].—$B'_2Me_2PtCl_6$ 2aq.

Acetyl derivative $C_9H_6(OAc)N$. (280°). Oil.—$B'_2H_2PtCl_6$ 2aq: yellow plates.

Benzoyl derivative. [120°]. Crystals.

Methyl ether $C_9H_6(OMe)N$. (268°). Got by methylation, and also from o-amido-anisole by Skraup's reaction. Oil.—$B'_2H_2PtCl_6$ 2aq.—B'HCl.—$B'C_6H_3N_3O_7$: yellow needles or plates. —B'MeI aq. [160°]. Leaflets (Claus a. Howitz, *J. pr.* [2] 42, 229).

Ethyl ether $C_9H_6(OEt)N$. (286°) at 718 mm. Needles (Fischer a. Renouf, *B.* 17, 759).—Picrate. [181°]. Yellow needles.

Tetrahydride $C_6H_3(OH):C_3H_7N$. [122°]. Made by reducing (*B.* 4)-oxy-quinoline with $SnCl_2$ (Fischer, *B.* 14, 1368; 14, 2571; 16, 713; 17, 759). Needles or prisms, sol. hot water. Yields a nitrosamine [68°]. The methyl ether $C_9H_{10}(OMe)N$ is oily and yields a crystalline hydrochloride and a nitrosamine [80°]. The ethyl ether is also liquid (275°) at 715 mm., and forms a crystalline nitrosamine [113°] and an oily acetyl derivative (307°).

Oxy-quinoline C_9H_7NO. *Cynurine.* [201°]. above 300°). S. ·477 at 15°. Probably (*Py.* 1)- or (*Py.* 2)-oxy-quinoline. Formed by heating its carboxylic acid (cynurenic acid) (Schmiedeberg a. Schultzen, *A.* 164, 158; Kretschy, *M.* 2, 68). Formed also by oxidising cinchonine or cinchonic acid (Skraup, *M.* 9, 821; 10, 729). Monoclinic prisms (containing 3aq), m. sol. hot water. Melts at 52° when hydrated. Tastes bitter. $KMnO_4$ oxidises it to cynuric acid. ICl gives a brownish pp. [275°] (Dittmar, *B.* 18, 1618). Distillation with zinc-dust forms quinoline. Ac_2O on heating forms an indigo-blue dye. Yields a tetrahydride.—B'_2HCl 2aq: monoclinic prisms. —B'HCl aq.—$B'_2H_2PtCl_6$ 2aq: orange needles.

(Py. 2, 3)-Di-oxy-quinoline $C_6H_4{<}\begin{matrix}CH:C(OH) \\ N{=\!=}C(OH)\end{matrix}$. *β-Oxy-carbostyril.* [above 300°]. Prepared by heating (*Py.* 2, 3)-chloro-oxy-quinoline (*β*-chloro-carbostyril) with fused KOH at 200° (Friedländer a. Weinberg, *B.* 15, 2681). Fine colourless needles. May be sublimed. Is a very weak base but a strong acid; it dissolves in concentrated HCl, but is reprecipitated on dilution. By PCl_5 it is converted into the di-chloro-quinoline [104°].—A'Ag: crystalline.

Di-oxy-quinoline $C_6H_4{<}\begin{matrix}C(OH):CH \\ N{=\!=\!=}C.OH\end{matrix}$. [above 320°].

Formation.—1. By the action of conc. H_2SO_4 on o-amido-phenyl-propiolic acid (Baeyer a. Bloem, *B.* 15, 2151).—2. By potash-fusion from (*Py.* 1, 3)-bromo-oxy-quinoline (Friedländer a. Weinberg, *B.* 15, 2683).—3. By reducing o-nitro-benzoyl-malonic ether with tin and HCl (Bischoff, *B.* 22, 387; *A.* 251, 377).—4. By boiling its carboxylic acid with conc. HClAq (B.).

Properties.—Needles, sol. Na_2CO_3 and in a mixture of alcohol and HClAq, insol. ordinary menstrua. Its ammoniacal solution turns blue in air. PCl_5 yields di-chloro-quinoline [67°].

Salt.—$C_9H_6AgNO_2$: needles.

Ethyl ether $C_6H_4{<}\begin{matrix}C(OH):CH \\ N{=\!=\!=}C(OEt)\end{matrix}$. [228°]. Formed by reducing o-nitro-benzoyl-malonic ether with tin and HCl (B.). Slender needles.

Dihydride $C_6H_4{<}\begin{matrix}CH(OH).CH_2 \\ N{=\!=\!=}C(OH)\end{matrix}$. [149°]. Formed by reducing o-nitro-*β*-oxy-phenyl-propi-

onic acid with $FeSO_4$ and NH_3 (Einhorn, *B.* 17, 2011). Needles (containing 2aq) melting at 96° when hydrated. Readily splits off water, yielding carbostyril.

(*B.* 1:4)-**Di-oxy-quinoline** $\begin{matrix}CH{:}C(OH).C.CH{:}CH\\CH{:}C(OH).C—N{:}CH\end{matrix}$. *Quinoline-hydroquinone.* Formed by reduction of quinoline-quinone by SO_2 (Fischer a. Renouf, *B.* 17, 1645). Thin needles. V. sol. water, sl. sol. cold benzene. Decomposes about 220°.

Salts.—The hydrochloride forms orange needles; the sulphate forms sparingly-soluble orange-yellow needles.

Di-oxy-quinoline $C_9H_5(OH)_2N$. *α-Oxyquinophenol.* [189°]. Got as a bye-product by fusing (*Py.* 1, 3)-bromo-oxy-quinoline with potash (Friedländer a. Weinberg, *B.* 15, 2684). Concentric needles, v. sol. most solvents. PCl_5 yields chloro-oxy-quinoline [180°].—AgA′: crystalline.

Di-oxy-quinoline $C_9H_5(OH)_2N$. *Oxycarbostyril.* [191°]. Got as a by-product in the preparation of carbostyril from o-nitro-cinnamic ether and alcoholic ammonium sulphide (Friedländer a. Ostermeyer, *B.* 14, 1916). Needles or plates, sl. sol. hot water. May be sublimed. Coloured red by HNO_3. Reduced by tin and HCl to carbostyril. Alkaline $KMnO_4$ oxidises it to o-nitro-benzoic acid.—BaA'_2: needles.

Ethyl ether $C_9H_6EtNO_2$. [73°]. Prisms, insol. water. May be distilled.—B′HCl: hygroscopic crystals.—$B'_2H_2PtCl_6$. Crystals.

Di-oxy-quinoline $C_9H_5(OH)_2N$. [130°–136°]. Formed from quinoline (α)-di-sulphonic acid by fusion with potash at 260° (La Coste a. Valeur, *B.* 19, 997; 20, 1821). Needles (from benzene), v. sol. ether. Oxidises in air.—B′HCl aq. [256°]. $B'_2H_2PtCl_6$ 2aq: yellow pp.—$B'C_6H_3N_3O_7$. [227°–237°]. Yellow needles, v. sol. warm water.

Mono-acetyl derivative $C_9H_6AcNO_2$. [117°]. White needles (from warm water).

Di-benzyl derivative $C_9H_5Bz_2NO_2$. [130°–134°]. Needles, v. sol. alcohol.

Mono-methyl ether $C_9H_5(OH)(OMe)N$. Formed by methylation. Liquid, sol. hot water. —B′HCl aq. [255°–259°]. Yellow needles.—$B'_2H_2PtCl_6$ 2aq: needles.—$B'C_6H_3N_3O_7$. [221°–226°]. Needles. sl. sol. cold water.

Di-methyl ether $C_9H_5(OMe)_2N$. Liquid, sl. sol. hot water.—B′HCl aq. [262°–266°].—$B'_2H_2PtCl_6$ 4aq: monoclinic. — $B'C_6H_3N_3O_7$. [104°].—B′MeI. [212°]. Monoclinic tables.—$(C_9H_5Me_2NO_2)(C_9H_7NO_2)MeI$. [207°]. Crimson needles. — $(C_9H_5Me_2NO_2)_4C_9H_7NO_2MeI$. [170°]. Lemon-yellow needles.

Di-oxy-quinoline $C_9H_5(OH)_2N$. [68°]. Made by potash-fusion from quinoline (β)-disulphonic acid (La Coste a. Valeur, *B.* 20, 3200). Needles.

Di-oxy-quinoline. *Di-methyl ether* $C_9H_5(OMe)_2N$. Got from veratric acid (derived from eugenol) by nitration and reduction, the resulting amido-veratric acid being heated with nitro-benzene, glycerin, and H_2SO_4 (Goldschmiedt, *M.* 8, 342). Oil. — Salts: B′HCl aq.—$B'_2H_2PtCl_6$ aq.—$B'C_6H_3N_3O_7$. [257°]. —$B'_2H_2Cr_2O_7$: yellow crystalline pp.

Di-oxy-quinoline $C_9H_5(OH)_2N$. Formed from quinoline (*B.* 1)-sulphonic acid by potash-fusion (Lellmann, *B.* 20, 2174). Needles, not melted at 320°.—$B'_2H_2PtCl_6$: needles.

Di-oxy-quinoline. *Acetyl derivative of the tetrahydride* $C_9H_9(OH)(OAc)N$. Formed by reducing (*Py.* 2)-nitroso-(*Py.* 3)-oxy-carbostyril with zinc-dust and HOAc (Baeyer a. Homolka, *B.* 16, 2217). Colourless needles, sl. sol. water, sol. HOAc. Forms a blue solution with alkalis.

(*B.* 2; *Py.* 3)-**Di-oxy-quinoline.** *Methyl derivative* $\begin{matrix}C(OMe){:}CH.C.CH{:}CH\\CH{:}CH——C.N{=}C.OH\end{matrix}$. [219°]. Got by the action of ammonia and $FeSO_4$ on [2:5:1]$C_6H_3(NO_2)(OMe).CH(OH).CH_2.CO_2H$ (Eichengrün a. Einhorn, *A.* 262, 179). Needles, v. sol. alcohol.

Tri-oxy-quinoline. *Dihydride of the methyl derivative* $C_6H_3(OMe)<\begin{matrix}CH(OH).CH_2\\N{=\!=}CH\end{matrix}$. [177°]. Got at the same time as the preceding body. Needles.

(*Py.* 1,2,3)-**Tri-oxy-quinoline** $C_6H_4<\begin{matrix}C(OH){:}C.OH\\N{=\!=}C.OH\end{matrix}$. Formed by reduction of (*Py.* 2)-nitroso-(*Py.* 3)-oxy-carbostyril with $SnCl_2$ (B. a. H.). Needles, v. sol. alcohol, v. sl. sol. water. Yields quinisatic acid $C_6H_4(NH_2).CO.CO.CO_2H$ on oxidation with $FeCl_3$.

References.—Di-bromo-, Chloro-, and Iodo-, oxy-quinoline.

DI-OXY-ISOQUINOLINE. *Di-methyl ether* $C_9H_5(OMe)_2N$. Formed, together with veratric acid, by fusing papaveraldine with potash. Formed also by heating its carboxylic acid, which is a product of the oxidation of papaverine (Goldschmiedt, *M.* 7, 494; 8, 510; 9, 344). Yields hemipic and cinchomeronic acids on oxidation.—B′HCl 3aq.—$B'C_6H_3N_3O_7$. [220°].—$B'_{12}H_2Cr_2O_7$.

(*Py.* 3)-**OXY-QUINOLINE (*P.* 1)-CARBOXYLIC ACID** $C_{10}H_7NO_3$ *i.e* $C_6H_4<\begin{matrix}C(CO_2H){:}CH\\N{=\!=}C.OH\end{matrix}$. *Oxycinchonic acid. Carbostyril carboxylic acid.* Mol. w. 189. [above 310°]. Got by fusing cinchonic acid with potash (Königs, *B.* 12, 99; 16, 2152). Needles, sl. sol. water. May be sublimed. Its Ag salt yields carbostyril on distillation.—CuA'_2.—AgA′: white pp.

Ethyl ether EtA′. [207°]. Needles.

Ethyl derivative $C_9H_5(OEt)(CO_2H)N$. [146°]. Made from chloro-quinoline carboxylic acid and NaOEt. Needles. Changes to the isomeric ethyl ether when heated above 146°.—$C_9H_5(OEt)(CO_2Et)N$. [86°]. Needles.

(*Py.* 3)-**Oxy-quinoline** (*Py.* 2)-**carboxylic acid** $C_6H_4<\begin{matrix}CH{:}C.CO_2H\\N\ \ {:}C.OH\end{matrix}$. [above 320°]. Made by heating o-amido-benzoic aldehyde with malonic acid at 120° (Friedländer a. Göhring, *B.* 17, 459), and also by reducing o-nitro-benzylidene-malonic acid (Stuart, *C. J.* 53, 143). Small needles, v. sl. sol. water, m. sol. HOAc. PCl_5 yields chloro-quinoline carboxylic acid [200°], whence KOEt forms the *ethyl derivative* $C_9H_5(OEt)(CO_2H)N$ [133°]. — BaA'_2. — AgA′: gelatinous pp.—$Ag_2C_{10}H_5NO_3$: needles.

(*B.* 4)-**Oxy-quinoline** (*Py.* 1)-**carboxylic acid** $C_{10}H_7NO_3$ *i.e.* $\begin{matrix}CH{:}CH—C.C(CO_2H){:}CH\\CH{:}C(OH).C——N{:}CH\end{matrix}$. (α)-*Oxycinchonic acid.* [256°]. Formed by fusing (α)-sulpho-cinchonic acid with potash (Weidel a. Cobenzl, *M.* 1, 855). Minute prisms

(containing aq), sl. sol. hot water, m. sol. hot alcohol. Gives a green colour with $FeCl_3$. Yields (*B.* 4)-oxy-quinoline on distillation, and pyridine (α)-tri-carboxylic acid on oxidation.—BaA'_2.—$BaC_{10}H_5NO_3$ aq.—$AgHA'_2$ aq.—AgA'.—HA'HCl: monoclinic needles.—$B'_2H_2PtCl_6$ 2aq: needles.

(*B.* 2)-**Oxy-quinoline carboxylic acid** $C_{10}H_7NO_3$. (β)-*Oxy-cinchonic acid.* [c. 320°], Made by potash-fusion from (β)-sulpho-cinchonic acid (Weidel, *M.* 2, 571). Tables (containing aq), sl. sol. water. Yields (*B.* 2)-oxy-quinoline on distillation, and a pyridine tricarboxylic acid on oxidation.—BaA'_2.—HA'HCl aq: needles.—$(HA')_2H_2PtCl_6$ 2aq: monoclinic tables, decomposed by water.

(*B.* 3)-**Oxy-quinoline-**(*Py.* 1?)-**carboxylic acid** $C_{10}H_7NO_3$. *Xanthoquinic acid.* [above 300°]. Possibly identical with the preceding acid. Got by heating quinic acid with conc. HClAq at 225° (Skraup, *M.* 2, 601; 4, 695). Yellow grains. Yields (*B.* 2)-oxy-quinoline on distillation.—Salts: BaA'_2 6aq. — CaA'_2 10aq. — CuA'_2 aq. — AgA' 2aq.— HA'HCl 2aq. — $H_2A'_2H_2PtCl_6$ 6aq. — $H_2A'_2H_2SO_4$ 3aq: golden prisms.

Methyl derivative $C_9H_5(OMe)(CO_2H)N$. *Quinic acid.* [280°]. Made by oxidising quinine or cinchonine with chromic acid (Skraup, *M.* 2, 589). Thin yellowish prisms, sl. sol. hot water and hot alcohol, nearly insol. ether. Its alcoholic solution shows blue fluorescence, destroyed by H_2SO_4. $KMnO_4$ oxidises it to pyridine tricarboxylic acid. — Salts: BaA'_2 4aq. — CaA'_2 2aq.—CuA'_2 $1\frac{1}{2}$aq.—AgA': pulverulent pp. HA'HCl 2aq: triclinic tables.—$H_2A'_2H_2PtCl_6$ 4aq: yellow crystals.

(*B.* 4)-**Oxy-quinoline carboxylic acid** $C_{10}H_7NO_3$. [280°]. Made by boiling *o*-oxy-quinoline with CCl_4, water, KOH, and alcohol (Lippmann a. Fleissner, *B.* 19, 2467; *M.* 8, 318). Minute prisms, v. sl. sol. hot water. Yields (*B.* 4)-oxy-quinoline on distillation, and pyridine dicarboxylic (quinolinic) acid [235°] on oxidation. $FeCl_3$ gives a green colour. Yields a di-bromo-derivative [193°].—$BaC_{10}H_5NO_3$ aq: needles.—$AgHA'_2$ (dried at 105°). Minute needles.

Tetrahydride $C_{10}H_{11}NO_3$. [265°]. Got by reduction with tin and HCl. Prisms, sl. sol. water, almost insol. ether. Reduces $AgNO_3$ in the cold. Gives a red colour with $FeCl_3$. EtI yields $C_{10}H_{10}EtNO_3HI$, whence $C_{10}H_{10}EtNO_3$ [220°] may be got. Nitrous acid forms a nitrosamine [195°].—$(C_{10}H_{11}NO_3)HCl$ aq: needles.—$B'_2H_2SO_4$ 3aq.—B'HOAc: pp.

(*B.* 4)-**Oxy-quinoline carboxylic acid** $C_{10}H_7NO_3$ aq. [250°]. Got from o-oxy-quinoline dithiocarboxylic acid $C_9H_5(OH)(CS_2H)N$ by warming with lead acetate and KOHAq (Lippmann a. Fleissner, *M.* 9, 300). Silky needles, sol. water. Coloured red by $FeCl_3$. Yields *o*-oxy-quinoline on distillation.—KA'.—BaA'_2 (dried at 130°).—AgA'.—$Hg_2A'_2Cl_2$.—$H_2A'_2H_2PtCl_6$ 4aq.—HA'HCl $2\frac{1}{2}$aq: trimetric crystals.

Tetrahydride $C_{10}H_{11}NO_3$. [222°]. Crystalline powder.—B'HCl: needles, v. sol. water.

(*B.* 4)-**Oxy-quinoline carboxylic acid** $C_9H_5(OH)(CO_2H)N$. Formed by heating sodium *o*-oxy-quinoline with liquid CO_2 in a closed vessel at 150° (Schmitt a. Engelmann, *B.* 20, 1217, 2690). Small yellow prisms (containing aq), m. sol. hot water and hot alcohol. Coloured red by $FeCl_3$. At 150° it splits up into CO_2 and *o*-oxy-quinoline. Yields $C_{10}H_6BrNO_3$ [235°].

Salts.—B'HCl: needles. — $B'HNO_3$. — NH_4A' aq.—BaA'_2 2aq: needles, sl. sol. water.—$BaC_{10}H_5NO_3$: amorphous, v. sl. sol. water.—AgA': amorphous powder.

Phenyl ether PhA': [226°]. Made by heating the acid with phenol and $POCl_3$ at 170°. Prisms.

Tetrahydride $C_9H_9(OH)(CO_2H)N$. Colourless prisms.—B'HCl: prisms. MeI and MeOH at 100° form $C_9H_8Me(OH)(CO_2H)N$ [211°], which crystallises with 2aq.

(*B.* 2)-**Oxy-quinoline carboxylic acid** $C_9H_5(OH)(CO_2H)N$. [204°]. Formed by boiling *p*-oxy-quinoline with NaOH, CCl_4, water, and alcohol (Lippmann a. Fleissner, *M.* 8, 324). Made also by heating potassium (not sodium) *p*-oxy-quinoline with liquid CO_2 at 170° (Schmitt a. Altschul, *B.* 20, 2695). Minute prisms, v. sl. sol. hot water and alcohol. Splits up at 200° into CO_2 and *p*-oxy-quinoline. Yields quinolinic acid on oxidation. — HA'HCl. — $HA'HNO_3$: needles. — $H_2A'_2H_2PtCl_6$ 2aq. — NH_4A' $\frac{1}{2}$aq: needles, v. sol. hot water. — BaA'_2 2aq. — CaA'_2 6aq.—$PbC_{10}H_5NO_3$ aq.—CaA'_2 6aq: small needles.—AgA'.

Oxy-quinoline carboxylic acid $C_{10}H_7NO_3$. *Cynurenic acid.* [258°]. S. ·9 at 100°. Occurs in the urine of dogs after a fat diet (Liebig, *A.* 86, 125; 108, 354; Voit a. Richter, *J.* 1865, 676; Schmiedeberg a. Schultzen, *A.* 164, 155; Hofmeister, *H.* 5, 70), or a diet of flesh only (Kretschy, *M.* 2, 57; 5, 16). Prisms (containing aq), insol. cold water. Decomposed by heat into CO_2 and oxy-quinoline. Yields quinoline on distillation with zinc-dust. Evaporation with $KClO_3$ and HCl leaves a residue which is turned emerald-green by ammonia (Jaffé, *H.* 7, 399).—HA'HCl. Decomposed by water (Brieger, *H.* 4, 92). — NH_4A'.—KA' 2aq. — BaA'_2 $4\frac{1}{2}$aq.—BaA'_2 3aq.—CaA'_2 2aq.—CuA'_2 2aq. —AgA' aq: thick white pp.

(*Py.* 3)-**Oxy-quinoline** (*B.* 3)-**carboxylic acid.** *Dihydride* $\begin{array}{l}CH{:}CH\text{———}C.CH_2.CH_2\\ C(CO_2H){:}CH.\ \ C.NH.CO\end{array}$. [above 280°]. Prepared by the reduction of [3:1:4] $C_6H_3(NO_2)(CO_2H).CH_2.CH_2.CO_2H$ with ammonia and $FeSO_4$ (Widman, *B.* 22, 2274). Yellow plates (from water), v. sl. sol. alcohol. Yields a *methyl ether* MeA' [192°] crystallising in tables.

Di-oxy-quinoline carboxylic acid. *Ethyl derivative of the ethyl ether* $C_6H_4{<}\begin{array}{l}C(OH){:}C.CO_2Et\\ N\text{——}C.OEt\end{array}$. [107°]. Got by the action of zinc, alcohol, and gaseous HCl on *o*-nitro-benzoyl-malonic ether (Bischoff, *B.* 22, 386). Small needles. Coloured violet by $FeCl_3$.

Tetra-oxy-quinoline carboxylic acid. *Lactone of the di-methyl derivative of the dihydride.* $C_{12}H_{11}NO_5$ *i.e.*

$$\begin{array}{l}CO.O\text{——}\diagdown\\ C_6H(OMe)_2{<}\begin{array}{l}CH.CH_2\\ NH.CO\end{array}\end{array}$$

[c. 256°]. Prepared by the reduction of *o*-nitro-meconin-acetic acid $C_6H(NO_2)(OMe)_2{<}\begin{array}{l}CO.O\\ CH.CH_2.CO_2H\end{array}$ with tin and HCl (Liebermann a. Kleemann, *B.* 19, 2296). Colourless needles (from water), v. sol. alcohol. Boiling baryta-water yields $Ba(C_{12}H_{12}NO_6)_2$ 6aq.

HI and HOAc at 120° form $C_{10}H_7NO_4$ [220°], a crystalline solid. PCl_5 yields $C_{12}H_{10}ClNO_4$ [218°].

DI-OXY-ISOQUINOLINE CARBOXYLIC ACID $C_{12}H_{11}NO_4$. [221°]. Formed by heating its di-methyl derivative with HIAq. Yellow powder. $FeCl_3$ gives a violet colour. When heated it yields a compound [230°] which gives isoquinoline on distillation with zinc-dust.

Di-methyl derivative $C_9H_4(OMe)_2(CO_2H)N$. [205°]. Got by oxidation of papaverine (Goldschmiedt, *M.* 6, 964; 8, 519; 9, 327). Yellow needles (containing 2aq).—HA'HCl 2aq: needles.

OXY-QUINOLINE SULPHONIC ACID $C_9H_5(OH)(SO_3H)N$. Formed by fusing quinoline (α)-disulphonic acid with potash (La Coste a. Valeur, *B.* 19, 997; 20, 100). Pale-yellow plates (containing aq), sl. sol. water.—KA' aq: prisms, v. e. sol. water. — BaA'_2 3aq. — CaA'_2 6aq. — CuA'_2 4aq: green needles.—$CaC_9H_5NSO_4$ 1½aq.—$BaC_9H_5NSO_4$ 3aq: yellow needles, sl. sol. water.

Oxy-quinoline sulphonic acid $C_9H_5(OH)(SO_3H)N$. [270°–275°]. Formed by potash-fusion from quinoline (β)-disulphonic acid (La Coste a. Valeur, *B.* 19, 998; 20, 3200). Yellow plates (containing aq), v. sol. hot water, insol. ether.

(*B.* 3)-**Oxy-quinoline sulphonic acid** $C_9H_5(OH)(SO_3H)N$. [c. 270°]. Made from *m*-oxy-quinoline and fuming H_2SO_4 (Riemerschmied, *B.* 16, 724). Yellow plates (containing aq), sl. sol. cold water.

(*Py.* 3)-**Oxy-quinoline sulphonic acid.** *Methyl derivative* $C_9H_5(OMe)NSO_3H$. Formed from the methyl derivative of carbostyril and fuming H_2SO_4 (Feer a. Königs, *B.* 18, 2395). Needles, sol. hot water.—AgA': needles.

(*B.* 4)-**Oxy-quinoline** (*B.* 1)-**sulphonic acid** $C_9H_5(OH)(SO_3H)N$. [270°]. Formed by sulphonating o-oxy-quinoline by H_2SO_4 in the cold (Claus a. Posselt, *J. pr.* [2] 41, 36). Needles (containing aq). $FeCl_3$ gives a green colour.

Salts. — NaA'aq. — $Na_2C_9H_5NSO_4$ 2aq. — KA' aq. — $K_2C_9H_5NSO_4$ 3aq. — BaA'_2 aq. — CaA'_2 aq: small needles, sl. sol. water.

(*B.* 4)-**Oxy-quinoline sulphonic acid** $C_9H_5(OH)(SO_3H)N$. Formed by heating o-oxy-quinoline with H_2SO_4 at 180° (Lippmann a. Fleissner, *M.* 10, 800). Crystals (containing 1½aq). Coloured green by $FeCl_3$.—KA'.—BaA'_2.—AgA'.

(*B.* 2)-**Oxy-quinoline sulphonic acid** $C_9H_5(OH)(SO_3H)N$. Made by sulphonating *p*-oxy-quinoline with fuming H_2SO_4 in the cold or at 100° (Claus a. Posselt, *J. pr.* [2] 41, 159). Yellow needles (containing ½aq), v. sl. sol. cold water. Decomposes at 270°.—NaA' aq.—KA' aq.

Oxy-quinoline sulphonic acid $C_{10}H_7NSO_4$. Formed by heating o-amido-phenyl-propiolic acid with H_2SO_4 at 210° (Baeyer a. Bloem, *B.* 15, 2152). M. sol. cold water.

(*B.* 4)-**Oxy-quinoline disulphonic acid** $C_9H_4(OH)(SO_3H)_2N$. Made by heating o-oxy-quinoline with H_2SO_4 and P_2O_5 at 200° (L. a. F.). Hygroscopic mass, decomposing at 200°. $FeCl_3$ gives a green colour.—KHA''.—$K_3C_9H_4NSO_7$.—BaA'' 3aq.—$Cu_3(C_9H_4NSO_7)_2$ 10aq: green pp.

OXY-QUINOLINE DITHIOCARBOXYLIC ACID $C_9H_5(OH)N.CS_2H$. [180°]. Made by heating o-oxy-quinoline with potassium xanthate and alcohol at 100° (Lippmann a. Fleissner, *M.* 9, 296). Small red crystals, nearly insol. water. $FeCl_3$ colours its aqueous solution brown. $KMnO_4$ yields quinolinic acid [231°].—NH_4A'. Tables, sl. sol. water.

(α)-**OXY-**(α)-**DIQUINOLYL** $C_{18}H_{12}N_2O$. [208°]. Made by fusing di-(*Py.* 3)-quinolyl sulphonic acid with potash (Weidel, *M.* 7, 312). Monoclinic needles (from xylene), insol. water, sl. sol. hot alcohol.—KA' aq.—PbA'_2 (dried at 100°).

Acetyl derivative [157°]. Needles.

Oxy-(*Py.* 3, *B.* 1)-**diquinolyl.** [187°]. Got by fusing (*Py.* 3, *B.* 1)-diquinolyl sulphonic acid with potash (Weidel, *M.* 8, 144). Crystalline powder (from alcohol), v. e. sol. alcohol.

(*B.* 2)-**Oxy-**(*Py.* 1, *B.* 1 or 3)-**diquinolyl.** *Methyl ether* $C_{19}H_{14}N_2O$ *i.e.*

$$C_6H_3(OMe){<}{\overset{\displaystyle C\text{——}}{N{:}CH.CH}}{>}C_6H_3{<}{\genfrac{}{}{0pt}{}{CH{:}CH}{N\ {:}CH}}.$$

Two isomerides of this formula are formed together by heating *m*-amido-(*Py.* 1)-phenyl-(*B.* 2)-methoxy-quinoline with o-nitro-phenol, glycerin, and H_2SO_4 (Miller a. Kinkelin, *B.* 20, 1924).

(α)-*Isomeride.* [151°]. Thin monoclinic tables, sol. alcohol and ether. Solutions of its salts exhibit blue fluorescence.—$B''H_2Cl_2$ 2aq.—B''HCl. — $B''H_2PtCl_6$ 2aq. — $B''_2H_4PtCl_8$: long needles.—B''MeI: yellow crystalline powder.

(β)-*Isomeride.* [120°]. Plates or flat monoclinic prisms. Its alcoholic and ethereal solutions show blue fluorescence.—$B''H_2PtCl_6$: amorphous pp. changing to a crystalline powder.

(α)-**Di-oxy-di-**(*Py.* 3)-**quinolyl** $C_{18}H_{12}N_2O_2$. [239°]. Made by potash-fusion from diquinolyl (α)-disulphonic acid (Weidel a. Gläser, *M.* 7, 320). Minute needles, insol. water and alcohol, sol. xylene. — B''HCl: yellow needles. — $B''H_2PtCl_6$: red plates.

Di-acetyl derivative $C_{18}H_{10}Ac_2N_2O_2$. [170°]. Rhombohedral crystals.

(β)-**Di-oxy-di-**(*Py.* 3)-**quinolyl.** [above 305°]. Made by potash-fusion from diquinolyl (β)-disulphonic acid (W. a. G.). Crystalline powder (from alcohol), v. sol. alkalis.

Di-acetyl derivative [216°]. Plates.

Tetra-oxy-diquinolyl. *Di-ethyl derivative of the anhydride* $C_{22}H_{18}N_2O_3$ *i.e.* $O(C_9H_4(OEt)N)_2$. A base which apparently has this constitution is prepared by heating $C_{12}H_4(NH_2)_2(OEt)_4$ (*cf.* p. 667) with o-nitro-phenol, glycerin, and H_2SO_4. It crystallises from ether, gives a green colour with $FeCl_3$, and forms $B''H_2PtCl_6$ 2aq (Colson, *C. R.* 107, 1003).

(*Py.* 3)-**OXY-**(*Py.* 2)-**QUINOLYL METHYL KETONE** $C_{11}H_9NO_2$ *i.e.* $C_6H_4{<}{\genfrac{}{}{0pt}{}{CH{:}C.CO.CH_3}{N{=}C.OH}}$. [232°]. Made by heating a mixture of o-amido-benzoic aldehyde and acetoacetic ether at 160° (Friedländer, *B.* 16, 1838). Needles, sl. sol. Aq.

OXY-QUINOLYL PHENYL KETONE $C_6H_4{<}{\genfrac{}{}{0pt}{}{CH{:}C.CO.C_6H_5}{N{=}C.OH}}$. [above 270°]. Made by heating o-amido-benzoic aldehyde with benzoyl-acetic ether (Friedländer a. Göhring, *B.* 16, 1838). Sl. sol. most solvents.

α-**OXY-**(*Py.* 3)-**QUINOLYL-PROPIONIC ACID** $C_{12}H_{11}NO_3$ *i.e.* $(C_9H_6N)CH_2.CH(OH).CO_2H$. [125°]. Formed from $(C_9H_6N)CH_2.CH(OH).CCl_3$ by heating with alcoholic NaOH (Einhorn, *B.* 18, 3465; 19, 906). Orange crystals, sol. water and ppd. by alcohol. Yields $(C_9H_6N)CHO$ on

oxidation by $KMnO_4$.—NaA′ 3aq.—AgA′: yellow pp.—$H_2A'_2H_2PtCl_6$ 5aq.

β-**Oxy-**(*Py.* 3)-**quinolyl-propionic acid** $C_6H_4\left\langle\begin{matrix}CH:CH \\ N{=}C.CH(OH).CH_2.CO_2H\end{matrix}\right.$ [176°]. Got from its amide, or by the action of Na_2CO_3Aq on bromo-quinolyl-propionic acid in the cold (Einhorn, *A.* 246, 176). Colourless prisms, v. sol. alcohol and HOAc, insol. chloroform.—NaA′.—AgA′.—HA′HCl. [188°]. White prisms.—$H_2A'_2H_2PtCl_6$. [218°]. Yellowish-red prisms.

Methyl ether MeA′. [62°]. Prisms.

Amide. [152°]. Made by dissolving the hydrobromide of bromo-quinolyl-propionic acid in ammonia in the cold. White crystals (from alcohol).

Lactone $(C_9H_6N).CH\left\langle\begin{matrix}O \\ CH_2\end{matrix}\right\rangle CO$. [82°]. Made by adding an equivalent quantity of Na_2CO_3 to the hydrobromide of bromo-quinolyl propionic acid suspended in water (Einhorn, *A.* 246, 169). Needles.—$C_{12}H_9NO_3HCl$. [138°].—$B'C_6H_3N_3O_7$. Golden plates (from alcohol).

OXY-QUINONE. *Methyl ether* $C_6H_3O_2(OMe)$. [140°]. Prepared by oxidation of *o*-anisidine with $K_2Cr_2O_7$ and dilute H_2SO_4 (Mühlhäuser, *B.* 13, 923; *A.* 207, 251; Will, *B.* 21, 605). Got in like manner from the methyl ether of amido-resorcin (Bechhold, *B.* 22, 2381). Yellow needles, with pleasant smell, sol. alcohol, m. sol. ether and water. Conc. H_2SO_4 forms a deep-blue solution. The vapour colours filter-paper red. Reduced by SO_2 to $C_6H_3(OH)_2(OMe)$. With aniline it forms $C_6H(NHPh)_2(OMe)O_2$, crystallising in coppery needles, and forming a dark-blue solution in H_2SO_4 (Schweitzer, *C. C.* 1888, 1434). o-Toluidine, o-xylidine, and diphenylamine form corresponding bodies melting at 239°, 228°, and 120° respectively.

Ethyl ether $C_6H_3O_2(OEt)$. [117°]. Made by oxidation of $C_6H_3(NH_2)(OEt)_2$ with $K_2Cr_2O_7$ and dilute H_2SO_4 at 15° (Will a. Pukall, *B.* 20, 1128). Yellow needles (by sublimation), m. sol. warm water, decomposed by hot water.

Dioxy-quinone $C_6H_2(OH)_2O_2$ [5:2:4:1].

Formation.—1. By boiling the basic sodium salt of dioxyquinone dicarboxylic acid with HCl or H_2SO_4 (Loewy, *B.* 19, 2387).—2. From di-amido-resorcin by oxidation to di-imido-resorcin and treatment of this body with dilute (10 p.c.) KOH at 70° (Nietzki, *B.* 21, 2374; Böniger, *B.* 22, 1288).—3. By heating $C_6H_2(NHPh)(OH)O_2$ or tetra-methyl-di-amido-quinone with KOHAq (Kehrmann, *B.* 23, 904).

Properties. — Dark - yellow needles, almost insol. cold water, v. sol. alcohol. Its alkaline solutions are red. Not melted at 180°. May be sublimed. Forms a dioxim. Conc. HNO_3 forms nitranilic acid. — $Na_2C_6H_2O_4$. — $BaC_6H_2O_4$aq: bluish-black needles.

Di-methyl ether Me_2A''. [c. 220°]. Obtained by methylation. Prepared also from $C_6H_2(NO_2)_2(OMe)_2$ by reduction followed by oxidation with $FeCl_3$ (Nietzki a. Rechberg, *B.* 23, 1216). Got also by oxidation of acetyl-di-methyl pyrogallol $C_6H_3(OMe)_2(OAc)$ (Hofmann, *B.* 11, 332). Yellow needles. Yields, on reduction, colourless $C_8H_{10}O_4$ [166°].

Di-ethyl ether $C_6H_2(OEt)_2O_2$. [183°]. Got by oxidising the di-ethyl ether of diamido-hydroquinone with $FeCl_3$ (N. a. R.). Sulphur-yellow plates (from water). Yields a crystalline dioxim $C_6H_2(OEt)_2(NOH)_2$, which may be reduced by $SnCl_2$ to $C_6H_2(OEt)_2(NH_2)_2$.

Di - oxy - quinone. *Di-methyl ether* $C_6H_2(OMe)_2O_2$. [249°]. A product of the oxidation of $C_6H_3(OMe)_3$[1:2:3] by nitric acid (Will, *B.* 21, 608). Prisms, v. sol. hot HOAc. May be sublimed. Reduced by $SnCl_2$ to $C_6H_2(OH)_2(OMe)_2$ [158°]. Gives $C_6Br_2(OMe)_2O_2$ [175°].

Tri-oxy-quinone $C_6H(OH)_3O_2$. Made from tri-amido-resorcin by the action of $FeCl_3$, the resulting amido-di-imido-resorcin being heated with HClAq at 150° (Merz a. Zetter, *B.* 12, 2035). Nearly black powder, insol. water, sl. sol. alcohol. Yields a crystalline tri-acetyl derivative.—$Ba_3A'''_2$: nearly black pp.—$Pb_3A'''_2$.—Ag_3A''': black pp.

Tetra-oxy-quinone $C_6(OH)_4O_2$. '*Dihydro-carboxylic acid.*' Formed by the action of alcohol, air, and HCl on the black mass containing $C_6(OK)_6$ got by combination of potassium with CO (Lerch, *A.* 124, 20). Formed also by atmospheric oxidation of a solution of hexa-oxy-benzene (Nietzki a. Benckiser, *B.* 18, 507, 1836, 1855). It is also a product of the action of HNO_3 on inosite (Maquenne, *A. Ch.* [6] 12, 112). Steel-blue monoclinic needles and plates, v. sol. alcohol and hot water, sl. sol. ether. Oxidised in alkaline solution by the air to croconic acid. Nitric acid forms C_6O_6. Aniline forms the compound $C_6(OH)_2O_3(NPh)NH_2Ph$, crystallising in red needles, with green lustre. Phenylene-o-diamine yields $C_{12}H_8N_2O_4$, sol. HClAq (Kehrmann, *B.* 23, 2448). o-Tolylene-diamine forms black crystals of $C_6O(OH)_3\left\langle\begin{matrix}N \\ NH\end{matrix}\right\rangle C_7H_6$ (Nietzki a. Kehrmann, *B.* 20, 3150).—$K_2C_6H_2O_6$: stable in the air.—$K_4C_6O_6$. Readily oxidised by air to $C_6(OK)_2O_4$. — $Na_2C_6H_2O_6$: dark needles with metallic lustre. Sl. sol. water, forming a dark-yellow solution. — $BaC_6H_2O_6$ (dried at 100°): dark-red pp.

Di-acetyl derivative $C_6(OH)_2(OAc)_2O_2$[2:5:3:6:4:1]. [205°]. Yellow plates, sl. sol. water.

Tetra-benzoyl derivative $C_6(OBz)_4O_2$. Yellow needles, sol. hot BzCl (Maquenne, *Bl.* [2] 48, 64; *C. R.* 104, 1719).

Anilide $C_6(OH)_4O(NPh)$. Made from $C_6(OH)_6$, aniline, and alcohol. Red plates with golden lustre, v. sl. sol. ordinary solvents.

References.—Di-bromo- and Di-chloro-, *di-oxy-quinone.*

OXY-QUINONE OXIM *v.* Nitroso-resorcin.

DI-OXY-QUINONE DICARBOXYLIC ETHER $C_6O_2(OH)_2(CO_2Et)_2$. [151°]. Formed by passing dry nitrous acid gas into an ethereal solution of di-oxy-terephthalic ether (Hantzsch a. Loewy, *B.* 19, 26, 2393; 20, 1306, 1311). Got also by dissolving $C_6Cl_2O_2(CO_2Et)_2$ in NaOHAq, and by atmospheric oxidation of tetra-oxy-terephthalic ether in presence of NaOHAq (Böniger, *B.* 22, 1284). Greenish-yellow monoclinic prisms (from alcohol) or yellow triclinic plates (from xylene), sl. sol. cold water. Acid to litmus. Its solutions are yellow. Has no action on phenyl cyanate (Goldschmidt, *B.* 23, 265). SO_2 yields $C_6(OH)_4(CO_2Et)_2$. Hydroxylamine produces $C_6O_2(ONH_3.OH)_2(CO_2Et)_2$ [170°]. Phenyl-hydrazine forms $C_6O_2(ON_2H_4Ph)_2(CO_2Et)_2$ [134°]. Hot NaOHAq yields an amorphous sodium salt

$Na_7C_{12}HO_{10}$ 2aq, decomposed by hot HClAq yielding $C_6H_2(OH)_2O$.—$Na_2C_{12}H_{10}O_8$ 2aq: heavy yellow powder.—$Na_2C_{12}H_{10}O_8$EtOH.—$MgC_{12}H_{10}O_8\frac{1}{2}$aq: orange pp.—$MnC_{12}H_{10}O_8\frac{1}{2}$aq.—$Ag_2C_{12}H_{10}O_8\frac{1}{2}$aq.

Acetyl derivative $C_6O_2(OAc)_2(CO_2Et)_2$. [174°]. Needles (from HOAc) (Böniger, *B.* 22, 1284).

OXY-QUINOXALINE. *Dihydride* $C_6H_4<\begin{matrix}NH.CH_2\\N{=}COH\end{matrix}$. [c. 130°]. Made by reduction of *o*-nitro-phenyl-amido-acetic acid with tin and HCl (Plöchl, *B.* 19, 8). Prisms (containing aq), sol. alcohol, ether, acids, and alkalis. Melts at 94° when hydrated.

Di-oxy-quinoxaline $C_8H_6N_2O_2$ *i.e.* $C_6H_4<\begin{matrix}N:C.OH\\N:C.OH\end{matrix}$. Formed by heating with HCl at 150° the compound of phenylene-*o*-diamine and cyanogen (Bladin, *B.* 18, 674; *Bl.* [2] 42, 104). Needles (containing aq), sl. sol. water. Not melted at 290°.

DI-OXY-DIQUINOYL $C_6H_2O_6$ *i.e.* $C_6(OH)_2O_4$. *Rhodizonic acid.* '*Carboxylic acid.*' Formed by treatment of $C_6(OK)_6$ with dilute alcohol and air (Heller, *A.* 24, 1; 34, 232; Lerch, *A.* 124, 32; Will, *A.* 118, 189). Formed also by atmospheric oxidation of $C_6O_2(OK)_4$, and by reduction of C_6O_6 with SO_2 (Nietzki a. Benckiser, *B.* 18, 513, 1838; 20, 323; 23, 3136). The hydroxyls are probably in the o- position. Colourless crystals, forming a colourless aqueous solution.

Reactions.—1. Oxidised by HNO_3 to triquinoyl C_6O_6.—2. Air and Na_2CO_3Aq yield croconic acid.—3. *Phenylene-o-diamine* forms red-brown needles of the azine $C_6H_4:N_2:C_6(OH)_2O_2$ (Nietzki a. Schmidt, *B.* 21, 1227).—4. *Tolylene-o-diamine* forms $C_6(OH)_2O_2:N_2:C_7H_6$, which crystallises from HOAc in yellowish-brown needles.

Salts.—$Na_2C_6O_6$: violet needles, forming an orange aqueous solution.—$K_2C_6O_6$: red powder, or small blue-black needles.

DI-OXY-RICINOLEIC ACID $C_{18}H_{34}O_5$. *Trioxyoleic acid.* [64°]. Made from ricinoleic acid and H_2SO_4 (Liechti a. Suida, *B.* 16, 2455). Insol. water, v. e. sol. alcohol.

OXY-SALICYLIC ACID *v.* DI-OXY-BENZOIC ACID.

OXYSALTS. This name is sometimes used to distinguish salts which contain O from those which do not; *i.e.* it is applied to salts which are not haloid salts (including cyamides), thio- (or sulpho-) salts, nor salts of acids composed of H, halogen, and metal or non-metal (*v.* SALTS in vol. iv.). M. M. P. M.

OXY-SEBACIC ACID $C_{10}H_{16}O_5$. [143°]. Made by boiling di-bromo-sebacic acid with water (Claus. a. Steinkauler, *B.* 20, 2886). Granules, m. sol. cold water.—Na_2A'': crystalline powder, v. e. sol. water.

Di-oxy-sebacic acid $C_{10}H_{16}O_6$. [130°]. Made from di-bromo-sebacic acid, water, and Ag_2O (C. a. S.). Nodules, v. e. sol. water.—Na_2A'': v. e. sol. water.

DI-OXY-SHIKIMIC ACID. *Dihydride* $CH(OH)<\begin{matrix}CH(OH).CH(OH)\\CH_2\text{———}CH(OH)\end{matrix}>C(OH).CO_2H$. [156°]. $[\alpha]_D = -28°$. Formed from bromo-shikimolactone and baryta (Eykman, *B.* 24, 1294). Long needles, m. sol. cold water.

OXY-SORBIC ACID $C_6H_8O_3$. [85°]. Made from pyridine (α)-carboxylic acid by treatment with sodium-amalgam (Weidel, *B.* 12, 2001). Very deliquescent needles. Reduces Fehling's solution.—BaA'_2.—CdA'_2.

α-OXY-STEARIC ACID $C_{18}H_{36}O_3$ *i.e.* $C_{16}H_{33}.CH(OH).CO_2H$. [81°] (G.); [85°] (S.). S. (alcohol) 9·63 at 20°; 2·3 at 20° (S.).

Formation.—1. A mixture of H_2SO_4 (1 mol.) with oleic acid (1 mol.) at 0° yields $C_{16}H_{33}.CH(SO_4H)CO_2H$, a liquid acid soluble in ether, water, and alcohol, and forming the salts K_2A'', Na_2A'', $(NH_4)_2A''$, $Ba(HA'')_2$, and $Cu(HA'')_2$. This acid is decomposed by boiling dilute acids into H_2SO_4 and α-oxy-stearic acid (Geitel, *J. pr.* [2] 37, 74; *cf.* Fremy, *A.* 33, 15; Ssabanejeff, *B.* 19, 239 Ref.; Saytzeff, *J. pr.* [2] 35, 369).—2. By the action of moist Ag_2O on iodo-stearic acid prepared from oleic acid, P, and I (Saytzeff, *J. pr.* [2] 33, 310; 35, 378; *Bl.* [2] 47, 169).

Preparation.—H_2SO_4 (32g.) is gradually added to olive oil (88 pts.) in the cold, and the mixture boiled with alcoholic potash. The product is acidified by hydrogen chloride, and the separated acids crystallised from ether (Geitel). In this preparation there is also formed the acid $(C_{16}H_{33}.CH(CO_2H))_2SO_4$ [24°], which yields α-oxy-stearic acid on boiling with dilute acids.

Properties.—White six-sided plates, m. sol. alcohol, v. sol. ether. At 200° it forms a syrupy anhydride, which is also formed by heating with fuming HClAq at 100° for 12 hours. Does not unite with Br. Reduced by HI to stearic acid.

Salts.—NaA'.—CaA'_2: small crystals (G.).—CaA'_2 aq (C. a. S.).—BaA'_2.—ZnA'_2.—CuA'_2: green powder.—PbA'_2.—AgA'.

γ-Oxy-stearic acid $C_{14}H_{29}.CH(OH).CH_2.CH_2.CO_2H$. The lactone $C_{18}H_{34}O_2$ [48°] is one of the products of the action of H_2SO_4 on oleic acid. After boiling with potash it yields $Ca(C_{18}H_{35}O_3)_2$ and $Pb(C_{18}H_{35}O_3)_2$, whence acids at once set free the lactone.

Di-oxy-stearic acid $C_{18}H_{36}O_4$. [136°]. S. (alcohol) ·6 at 19°. S. (ether) ·19 at 18° (Spiridonoff, *J. pr.* [2] 40, 243). Formed from di-bromo-stearic acid (oleic acid dibromide) by treatment with moist Ag_2O (Overbeck, *A.* 140, 72). Got also by boiling oxyoleic acid with potash (O.). Prepared by oxidising oleic acid with alkaline $KMnO_4$ (Saytzeff, *J. pr.* [2] 31, 541; 33, 304; *Bl.* [2] 45, 255). Probably identical with a di-oxy-stearic acid [131°] got by oxidising tallow with $KMnO_4$ (Gröger, *B.* 22, 620). Tables, insol. water, v. sol. hot alcohol, v. sl. sol. ether. Converted by HI into iodo-stearic acid. Reduced by alcohol and zinc to stearic acid. Distilled under 100 mm. it gives an acid [c. 79°], which may be its anhydride $C_{18}H_{34}O_3$. This acid forms the salts $C_{18}H_{33}AgO_3$ and $C_{18}H_{33}NaO_3$. Yields octoic, sebacic, and azelaic acids on oxidation by $KMnO_4$.

Salts.—NaA'.—KA'.—CaA'_2 aq.—BaA'_2. ZnA'_2.—AgA'.

Di-acetyl derivative. Syrup, sol. ether.

Methyl ether. [106°]. S. (alcohol) 3·45 at 18·5°. S. (ether 1·04 at 19°. Plates.

Ethyl ether. [100°]. S. (alcohol) 4·8 at 16°; 4·95 at 18°. S. (ether) 1·78 at 18°. Plates.

Di-oxy-stearic acid $C_{18}H_{36}O_4$. [100°]. Formed by oxidising elaidic acid with alkaline $KMnO_4$ (Saytzeff, *J. pr.* [2] 33, 315). More sol. alcohol

and ether than the preceding isomeride.—NaA'.—AgA'.

Di-oxy-stearic acid $C_{18}H_{36}O_4$. [78°]. Got by the action of Ag_2O on the dibromide of iso-oleic acid [45°], which is formed from iodo-stearic acid and alcoholic potash (Saytzeff, *J. pr.* [2] 37, 276). Crystalline powder, v. sol. alcohol and ether. HI yields an iodo-stearic acid reduced by tin and HCl to stearic acid.

Tri-oxy-stearic acid $C_{18}H_{36}O_5$. '*Ricinolic acid.*' [141°]. Occurs among the products of the oxidation of castor oil with alkaline $KMnO_4$ (Hazura a. Grüssner, *M.* 9, 476).—KA'.—NaA' $\frac{1}{2}$aq.

Tri-oxy-stearic acid $C_{18}H_{36}O_5$. '*Ricinisolic acid.*' [111°]. Occurs together with the preceding isomeride, among the products of oxidation of castor oil by $KMnO_4$ (H. a. G.).

Tri-oxy-stearic acid $C_{18}H_{36}O_5$. [115°]. Formed by oxidising ricinelaidic acid with alkaline $KMnO_4$ (Hazura a. Grussner, *M.* 10, 199). Trimetric prisms, insol. cold water, v. sol. HOAc and ether.

Tetra-oxy-stearic acid $C_{18}H_{36}O_6$ *i.e.* $C_{18}H_{32}(OH)_4O_2$. *Sativic acid.* [173°]. A product of the oxidation of linoleic acid by alkaline $KMnO_4$ (Hazura, *M.* 9, 190). Long prisms. Converted by HI into $C_{18}H_{31}I_2O_2$ and finally into stearic acid.

Hexa-oxy-stearic acid $C_{18}H_{36}O_8$. *Linusic acid.* [203°]. Got by oxidising linoleic acid with alkaline $KMnO_4$, being derived from linolenic acid, which is present in linoleic acid (Hazura, *M.* 7, 637; 8, 155, 267). Minute needles (from water). More sol. water and less sol. alcohol than sativic acid. Yields a hexa-acetyl derivative.

Hexa-oxy-stearic acid $C_{18}H_{36}O_8$. *Isolinusic acid.* [175°]. Occurs in small quantity, together with sativic and linusic acids, in the product of the oxidation of linoleic acid by alkaline $KMnO_4$. Needles, insol. ether, v. sol. hot water. Forms a hexa-acetyl derivative, sl. sol. ether.

OXY-STILBENE *v.* OXY-DI-PHENYL-ETHYLENE.

DI-o-OXY-DI-STYRYL DIKETONE $C_{17}H_{14}O_3$ *i.e.* $CO(CH:CH.C_6H_4OH)_2$. [160°]. Got by heating the glucoside with dilute H_2SO_4. Brownish powder, sol. alcohol.

Glucoside $CO(CH:CH.C_6H_4.OC_6H_{11}O_5)_2$. [257°]. Formed, together with the compound $CH_3.CO.CH:CH.C_6H_4.OC_6H_{11}O_5$, by condensation of helicin with acetone in presence of a little alkali (Tiemann a. Kees, *B.* 18, 1967). Colourless crystals (containing aq), sl. sol. alcohol, nearly insol. water, insol. ether.

Tetra-oxy-di-styryl ketone. *Di-methylene derivative* $CO(CH:CH.C_6H_3:O_2CH_2)_2$. [185°]. Made from piperonal, acetone, and NaOHAq (Haber, *B.* 24, 617). Yellow needles, insol. water, m. sol. alcohol. Colours H_2SO_4 a deep blue.

o-OXY-STYRYL METHYL KETONE $C_{10}H_{10}O_2$ *i.e.* $C_6H_4(OH).CH:CH.CO.CH_3$. [139°]. Got by hydrolysis of its glucoside by emulsin (Tiemann a. Klees, *B.* 18, 1964). Formed also from salicylic aldehyde, acetone, and dilute NaOH (Harries, *B.* 24, 3180). Long needles (from alcohol), sl. sol. water. $FeCl_3$ colours its aqueous solution blue. Sodium-amalgam reduces it to $C_6H_4(OH).CH:CH.CH(OH).CH_3$ [48°]. Yields a benzoyl derivative $C_6H_4(OBz).CO.CH_3$ [88°], an oxim $C_6H_4(OH).C(NOH)CH_3$ [85°], and a phenyl-hydrazide [160°].

Glucoside $CH_3.CO.C_2H_2.C_6H_4.O(C_6H_{11}O_5)$. [192°]. Made by adding a few drops of caustic soda solution to a mixture of acetone and helicin $C_6H_4(OC_6H_{11}O_5).CHO$. Slender needles (containing aq), v. sol. hot water. Lævorotatory. Yields an oxim [173°].

p-Oxy-styryl methyl ketone. *Methyl derivative* $C_6H_4(OMe).CH:CH.CO.CH_3$. [73°]. Made by allowing anisic aldehyde, acetone, and aqueous NaOH to stand in the cold (Einhorn a. Grabfield, *A.* 243, 363). Plates, v. sol. alcohol.

Di-oxy-styryl methyl ketone. *Methyl derivative* $CH_3.CO.CH:CH.C_6H_3(OH)(OMe)$ [1:4:3]. Got from its glucoside by the action of emulsin. Yellow needles, v. sol. alcohol.

Glucoside $CH_3.CO.CH:CH.C_6H_3(OMe)(O.C_6H_{11}O_5)$. [207°]. Got by heating the glucoside of vanillin with acetone and NaOHAq (Tiemann, *B.* 18, 3491). Pale-yellow needles (containing 2aq), m. sol. water. Lævorotatory.

Methylene derivative $CH_3.CO.CH:CH.C_6H_3:O_2CH_2$. [107°]. Made from piperonal, acetone, and NaOHAq (Haber, *B.* 24, 618). Prisms, sl. sol. warm water. Changed by steam into an isomeride (?) [111°]. Yields a yellow oxim [186°] and phenyl-hydrazide [160°]. The isomeride [111°] yields a colourless oxim [183°] and phenyl-hydrazide [163°].

DI-OXY-STYRYL-m-PYRAZOLE $C_{11}H_{10}N_2O_2$ *i.e.* $CO<\begin{matrix}NH.CO\\NH.CH.CH:CHPh\end{matrix}$. *Di-oxy-styryl-glyoxaline. Styryl hydantoïn.* [172°]. Made by the action of boiling dilute hydrogen chloride upon $CHPh:CH.CHCy.NH.CO.NH_2$, which is got from cinnamic aldehyde cyanhydrin, and urea (Pinner a. Lifschütz, *B.* 20, 2353; 22, 685). White plates, changing on fusion to an isomeride [195°].

Reactions.—1. On heating with alcoholic potash it yields the isomeric $C(NH)<\begin{matrix}NH.CO\\O-CH.C_2H_2Ph\end{matrix}$ which decomposes at 300° and, with KOH and EtBr, yields $C(NH)<\begin{matrix}NEt.CO\\O-CH.C_2H_2Ph\end{matrix}$ [280°]. 2. Alcoholic potash and EtBr at 100° from $CO<\begin{matrix}NEt.CO\\NH.CH.C_2H_2Ph\end{matrix}$ [162°].—3. *Bromine* in $CHCl_3$ forms $C_{11}H_{10}N_2O_2Br_2$ [200°]. *Bromine water* produces $CO<\begin{matrix}NH.CO\\NH.CH.CH(OH).CHBrPh\end{matrix}$ [220°], whence NaOHAq forms tri-oxy-styryl-metapyrazole $CO<\begin{matrix}NH.CO\\NH.CH.CO.CH_2Ph\end{matrix}$, a crystalline powder [185°].

Acetyl derivative $CO<\begin{matrix}NAc.CO\\NH.CH.C_8H_7\end{matrix}$. [185°]. Small white prisms.

o-OXY-STYRYL-PYRIDINE $C_{13}H_{11}NO$ *i.e.* $C_6H_4(OH).CH:CH.C\begin{matrix}CH:CH\\N\ .CH\end{matrix}CH$. [132°]. Formed by heating (α)-methyl-pyridine (10 g.) with salicylic aldehyde (13 g.) and water (7 g.) at 140° (Butter, *B.* 23, 2697). Small crystals (from dilute alcohol). Yields a dibromide. Reduced by Na and alcohol to $C_6H_4(OH).C_2H_4.C_5H_{10}N$ [94°]. Salts.—$B'_2H_2PtCl_6$. [188°].—$B'HHgCl_3$. [c. 170°]. Salts of the ethyl derivative

$(C_{13}H_{10}(OEt)N)_2H_2HgCl_4$. [92°]. Light-yellow needles.—$(C_{13}H_{10}(OEt)N)_2H_2PtCl_6$. [183°].

Ethylo-iodide of the ethyl derivative $C_{13}H_{10}(OEt)NEtI$. [218°]. Golden crystals.

Oxy-styryl-pyridine. *Methyl derivative* $C_6H_4(OMe)CH:CH.C_5H_4N$. [97°]. Formed from anisic aldehyde and methyl-pyridine (Schuften, *B.* 23, 2719). Plates. — $B'_2H_2PtCl_6$. [184°]. Yellow plates.

***p*-OXY-(*Py.* 3)-STYRYL-QUINOLINE**

$C_{17}H_{13}NO$ *i.e.* $C_6H_4<\begin{matrix}CH:CH\\N=C.CH:CH.C_6H_4.OH\end{matrix}$ [253°]. Formed from *p*-amido-styryl-quinoline by the diazo-reaction (Bulach, *B.* 22, 286). Formed also from *p*-oxybenzoic aldehyde, quinaldine, and $ZnCl_2$ (Wallach, *B.* 16, 2009). Yellow plates.

o-Oxy-(*Py.* 1)-styryl-quinoline. [215°]. Made from salicylic aldehyde, lepidine, and $KHSO_4$ (Heymann a. Königs, *B.* 21, 1429, 2172). Yellow crystals.

***m*-Oxy-(*Py.* 1)-styryl-quinoline.** [255°]. Got from *m*-amido-styryl-quinoline. Brownish-yellow crystals (from alcohol).

***p*-Oxy-(*Py.* 1)-styryl-quinoline** [249°]. Got from *p*-oxy-benzoic aldehyde, lepidine, and $KHSO_4$ (H. a. K.). Yellow crystals (from alcohol).

OXYSUBERANIC ACID $C_8H_{14}O_3$ *i.e.* $C_7H_{12}(OH).CO_2H$. [90°]. Made from suberone cyanhydrin and conc. HClAq (Spiegel, *A.* 211, 118). Tables (containing ½aq). Melts at 50° when hydrated. V. e. sol. alcohol and hot water.

OXYSUBERIC ACID $C_8H_{14}O_5$. [112°]. Made by boiling bromo-suberic acid with NaOHAq (Hell a. Rempel, *B.* 15, 149; 18, 817). Nodules (from ether). HNO_3 oxidises it to adipic and oxalic acids.—MgA″ aq.—CuA″.—ZnA″ 2½aq.—Ag_2A'': crystalline pp.

Ethyl derivative $C_6H_{11}(OEt)(CO_2H)_2$. Made from bromo-suberic acid and alcoholic potash. Syrup, v. sol. water and alcohol.—BaA″.—ZnA″.—PbA″.—Ag_2A'': amorphous pp.

Oxy-isosuberic acid $C_8H_{14}O_5$. A sticky mass got by saponification of its ether, which is a product of the action of silver on bromo-butyric ether (Hell a. Mühlhäuser, *B.* 13, 477). HIAq at 160° reduces it to *β*-isosuberic acid.—Ag_2A''.

Di-oxy-suberic acid $C_8H_{14}O_6$. Made from di-bromo-suberic acid and KOH (Gay a. Gay-Lussac, *A.* 155, 251). Amorphous.

Di-ethyl derivative $C_6H_{10}(OEt)_2(CO_2H)_2$. Made from di-bromo-suberic acid and alcoholic potash (H. a. R.). Syrup, v. sol. water, alcohol, and ether.—Ag_2A'': amorphous pp.

OXY-SUCCINIC ACID *v.* MALIC ACID.

Di-oxy-succinic acid *v.* TARTARIC ACID.

Tetra-oxy-succinic acid

$C_4H_6O_8$ *i.e.* $CO_2H.C(OH)_2.C(OH)_2.CO_2H$ or $CO_2H.CO.CO.CO_2H$ 2aq. *Di-oxy-tartaric acid. Carboxytartronic acid.* [98°]. Formed by passing nitrous acid into an ethereal solution of protocatechuic acid (Grüber, *B.* 12, 514), of pyrocatechin (Barth, *M.* 1, 869), of guaiacol (Herzig, *M.* 3, 825), or of 'nitro'-tartaric acid (Kekulé, *A.* 221, 240). The free acid is got by decomposing the dry sodium salt in dry ether with HCl gas (W. L. Miller, *B.* 22, 2015). White crystals, v. sol. water. The salt $Na_2C_4H_4O_8$ 2aq is nearly insol. water. It splits up on heating into CO_2 and sodium tartronate. With $NaHSO_3$ at 90° it yields glyoxal (Hinsberg, *B.* 24, 3235). The salt $Ba_3(C_4H_3O_8)_2$ aq is a crystalline pp. HClAq and zinc reduce it to a mixture of racemic and inactive tartaric acids. Yields hydantoïn when the Na salt is rubbed up with urea and dilute HClAq at 55° (Anschütz, *A.* 254, 258).

Ethyl ether. Thick liquid (Anschütz, *A.* 261, 130). Converted by urea into the ureïde $C_{10}H_{14}N_4O_6$, which crystallises in needles, sl. sol. cold water, decomposing at 245°.

(*β*)-*Oxim* $CO_2H.C(NOH).C(NOH).CO_2H$. [145°–150°]. Got from the Na salt, hydroxylamine and HCl. Colourless prisms, v. e. sol. water and alcohol, insol. benzene (Müller, *B.* 16, 2985; Söderbaum, *B.* 24, 1223). After crystallisation from water it melts at 70°–75°. It yields the salts CaA″ 4aq and Ag_2A'' and a crystalline diacetyl derivative, v. sol. water. Conc. HClAq converts the oxim into an isomeride [145°–150°] crystallising in nodules, which are v. e. sol. water and yield the salts CaA″ 3aq and Ag_2A'' aq. Ac_2O decomposes this (*α*)-oxim into cyanogen and CO_2.

Phenyl hydrazide $C_{10}H_8N_2O_5$ *i.e.* $CO_2H.CO.C(N_2HPh).CO_2H$. *Monophenylizine dioxytartaric acid.* [218°]. Made by mixing a solution of the acid (1 mol.) with phenyl-hydrazine (1 mol.) dissolved in HClAq (Ziegler a. Locher, *B.* 20, 835). Feathery needles, insol. cold water, v. sol. hot alcohol. Coloured red by $FeCl_3$. — $BaC_{10}H_8N_2O_6$ 3aq. — Na_2A''. — Ag_2A'': orange-yellow pp.

Di-phenyl-di-hydrazide $CO_2H.C(N_2HPh).C(N_2HPh).CO_2H$. *Diphenylizine dioxytartaric acid.* [above 200°]. Made from tetra-oxy-succinic acid (1 mol.) and phenyl-hydrazine (2 mols.). Orange-yellow powder, v. sl. sol. water, v. sol. warm alcohol. On heating with Ac_2O it yields $O<\begin{matrix}CO.C:N_2HPh\\CO.C:N_2AcPh\end{matrix}$ [c. 234°], which crystallises in red needles, v. sol. Ac_2O.—$(NH_4)_2A''$: colourless plates.—$(NH_4)HA''$: brick-red needles. With silver nitrate it gives $AgN<\begin{matrix}CO.C:N_2HPh\\CO.C:N_2HPh\end{matrix}$ of a vermilion colour. Na_2A'': lemon-yellow plates.—NaHA″: brick-red needles.—The ethyl ether $C_{20}H_{22}N_4O_4$ [121°] is got from phenyl-hydrazine and tetra-oxy-succinic ether (A. a. G.); it forms canary-yellow crystals.

Di-p-sulpho-di-phenyl-di-hydrazide $CO_2H.C(N_2H.C_6H_4.SO_3H).C(N_2H.C_6H_4.SO_3H).CO_2H$. Formed from sodium tetra-oxy-succinate, sodium phenyl-hydrazine *p*-sulphonate, and HClAq. The Na salt is an orange-yellow powder, v. sol. water, insol. alcohol, and is used as a yellow dye (*tartrazine*).

Di-phenyl-hydrazide. [158°]. Made from the acid and $N_2H_2Ph_2$. Yellow pp., turning blue in the air.

Tetra-phenyl-di-hydrazide $CO_2H.C(N_2Ph_2).C(N_2Ph_2).CO_2H$. [177°]. Made from the acid (1 mol.) and diphenylhydrazine (2 mols.) (Ziegler a. Locher, *B.* 20, 841). Yellowish plates (from hot alcohol), insol. water. Conc. H_2SO_4 forms a red solution, becoming green. On fusion with resorcin it gives a crimson mass, coloured blue by NaOH; hydroquinone and pyrogallol give green and blue masses respectively. Bromine gives a crystalline bromo-

derivative. Ac_2O forms $O<\genfrac{}{}{0pt}{}{CO.C:N_2Ph_2}{CO.C:N_2Ph_2}$ [222°] crystallising in ruby-red prisms with green lustre. Converted into the imide $NH<\genfrac{}{}{0pt}{}{CO.C:N_2Ph_2}{CO.C:N_2Ph_2}$ [192°] by NH_3.—Na_2A'': rosettes of needles (from water) or plates (from alcohol).—CuA''.—PbA'': white pp.

m-Nitro-phenyl-hydrazide. [175°]. Made by using *m*-nitro-phenyl-hydrazine (Bischler a. Brodsky, *B.* 22, 2814). Sl. sol. hot water and alcohol.

Di-m-nitro-di-phenyl-dihydrazide. [c. 200°]. Made from *m*-nitro-phenyl-hydrazine (2 mols.) and tetra-oxy-succinic acid (1 mol.). Sl. sol. hot water.

OXYSULPHIDES. Compounds of an element, or positive compound radicle, with O and S. The term is generally restricted to compounds of metals with O and S. Oxysulphides of metals are not numerous, and they have not been much studied. They are produced in various reactions, of which the following are the chief: by acting on the sulphide with water, *e.g.* oxysulphide of Ba; by heating the oxide with S, *e.g.* Bi oxysulphide; by boiling the oxide and sulphide with water, *e.g.* Ca oxysulphide; by partially reducing the sulphate by H, *e.g.* oxysulphides of Co and Mn; by heating the oxide in H_2S, or by passing H_2S into an aqueous solution of the oxide, *e.g.* oxysulphides of Fe and Os; by adding a little alkali sulphide to the solution of a salt, *e.g.* Cu oxysulphide. M. M. P. M.

OXY-SULPHO-BENZOIC ACID $C_7H_6SO_6$ *i.e.* $C_6H_3(OH)(SO_3H).CO_2H$. *Sulphosalicylic acid.* [120°]. Made by sulphonation of salicylic acid (Mendius, *A.* 103, 45; Remsen, *A.* 179, 107). Long thin needles, v. e. sol. water and alcohol. Gives a reddish-violet colour with $FeCl_3$. Yields phenol and salicylic acid on fusion with potash. — $NaHA''$ 2aq. — Na_2A'' 3aq. — KHA'' 2aq. — K_2A'' 2aq.—$K_3HA''_2$ aq.— $KNaA''$ 4aq.—CaA''aq. — $Ba(HA'')_2$ 4aq. —MgA'' 3aq. — ZnA'' 3aq. — PbA''. — CuA''. — $Cu_2A''(OH)_2$ aq. —Ag_2A'' aq: crystalline powder, v. sol. hot water.

Ethyl ether. Et_2A''. [58°]. Crystals.

Oxy-sulpho-benzoic acid $C_6H_3(OH)(SO_3H)(CO_2H)$ [4:3:1]. Made from *p*-oxy-benzoic acid by treatment with SO_3 (Kölle, *A.* 164, 150) or by digesting with H_2SO_4 at 100° (Klepl, *J. pr.* [2] 28, 196). Deliquescent needles, v. e. sol. water and alcohol, insol. ether. $FeCl_3$ gives a red colour. Potash-fusion yields protocatechuic acid.—KHA'' aq: crystals, sl. sol. water (Klepl).—K_2A'' aq (Kölle).—$K_3C_7H_3SO_6$ 2aq (Kölle).—BaA'' 4aq.—$Ba_3(C_7H_3SO_6)_2$: amorphous (Kölle).—CdA'' 3aq.—Ag_2A'': small prisms.

Methyl derivative $C_6H_3(OMe)(SO_3H)(CO_2H)$. Made from fuming H_2SO_4 and anisic acid at 160° (Zervas, *A.* 103, 338; Limpricht, *Gm.* 13, 128). Needles, insol. ether.—BaA'' aq.—PbA'' aq: needles, sl. sol. Aq.

Oxy-sulpho-benzoic acid $C_6H_3(OH)(SO_3H)(CO_2H)$ [4:2:1]. Formed by the diazo-reaction from (4,2,1)-amido-sulpho-benzoic acid (Hedrick, *Am.* 9, 416). Crystalline, sol. water, alcohol, and ether.—$Ba(HA'')_2$: insol. dilute HOAc. — BaA''. — CaA'' 5aq: triclinic prisms, sol. hot water.—CoA''7aq.—CdA'' 8aq.—ZnA'' 3aq (Pisanello).

Imide of the ethyl derivative $C_6H_3(OEt)<\genfrac{}{}{0pt}{}{CO}{SO_2}>NH$. [258°]. Made by oxidising $C_6H_3Me(OEt).SO_2NH_2$ with $KMnO_4$ and ppg. with HCl (Remsen a. Palmer, *Am.* 8, 227). Concentric groups of needles.—$KC_9H_8NSO_4$.—$AgC_9H_8NSO_4$: lustrous needles, sl. sol. water.

Oxy-sulpho-benzoic acid $C_6H_3(OH)(SO_3H)(CO_2H)$ [3:4?:1]. Formed from *m*-oxy-benzoic acid and SO_3 (Barth, *A.* 148, 38; Senhofer, *A.* 152, 102). Yellowish-green needles (containing $1\frac{1}{2}$aq), v. sol. alcohol. Coloured red by $FeCl_3$. Yields protocatechuic acid and an acid [189°] when fused with potash.—BaA'' $4\frac{1}{2}$aq. —$Cd(HA'')_2$ 2aq.—$Pb_3(C_7H_3SO_6)_2$: reddish amorphous mass.

Oxy-sulpho-benzoic acid $C_6H_3(OH)(SO_3H).CO_2H$. Got by dissolving *m*-diazo-benzoic acid in warm H_2SO_4 (Griess, *Z.* 1864, 538). White laminæ (from water). Perhaps identical with the preceding acid.—BaA''.

Oxy-disulpho-benzoic acid $C_6H_2(OH)(SO_3H)_2CO_2H$. [146°]. Made from salicylic acid and $ClSO_3H$ at 180° (Pisanello, *G.* 18, 346). Deliquescent needles (containing 4aq). Gives a red colour with $FeCl_3$.—Na_3A''' 3aq.—K_3A''' 3aq.—$Ca_3A'''_2$ 12aq.—$Ba_3A'''_2$ $6\frac{1}{2}$aq: prisms, sl. sol. water.—$Pb_3A'''_2$ 10aq.—$Cd_3A'''_2$ 18aq.—$Cu_3A'''_2$ 12aq.—$Zn_3A'''_2$ 15aq: plates.

Oxy-disulpho-benzoic acid $C_7H_6S_2O_9$. Got by boiling trisulpho-*m*-oxy-benzoic acid with $BaCO_3$ (Kretschy, *B.* 11, 862).—$Ba_3A'''_2$ 8aq.

Oxy-trisulpho-benzoic acid $C_6H(OH)(SO_3H)_3CO_2H$. Made by heating *m*-oxy-benzoic acid with H_2SO_4, SO_3, and P_2O_5 at 250° (Kretschy, *B.* 11, 858). Hygroscopic syrup (containing 4aq at 100°). $FeCl_3$ gives a red colour.—$K_5C_7HS_3O_{12}$ 2aq: monoclinic prisms.—K_4A^{iv} 2aq. $Pb_5(C_7HS_3O_{12})_2$ 6aq.—Pb_2A^{iv} 8aq.—Cd_2A^{iv} 3aq.—Ba_2A^{iv} 4aq: colourless plates.

Di-oxy-sulpho-benzoic acid $C_6H_2(OH)_2(SO_3H)CO_2H$. Formed from (4, 2, 1)-di-oxy-benzoic acid and H_2SO_4 (Zehenter, *M.* 2, 468). Hygroscopic needles (containing 2aq). $FeCl_3$ colours its aqueous solution red. — Salts. — K_2A'' $3\frac{1}{2}$aq. — BaA'' 2aq.—PbA'' 2aq.—$Cu_3(C_7H_3SO_7)_2$ 5aq. — Ag_2A'' 2aq: needles.

Di-oxy-sulpho-benzoic acid $C_6H_2(OH)_2(SO_3H)(CO_2H)$[5:2:*x*:1]. Made by heating (5, 2, 1)-di-oxy-benzoic acid with H_2SO_4 and P_2O_5 at 130° (Senhofer a. Sarlay, *M.* 2, 454). Needles.—K_2A'' aq.—$Ba(HA'')_2$ $8\frac{1}{2}$aq.—BaA'' 2aq. —PbA'' 2aq: crystalline powder.

OXY-SULPHO-ISOCUMINIC ACID $CMe_2(OH).C_6H_3(SO_3H)(CO_2H)$. Made by oxidising the sulphonic acids of cymene and *m*-isocymene by $KMnO_4$ (R. Meyer, *A.* 220, 7, 29).—K_2A'' 5aq.—BaA'' aq: minute plates.—PbA''.

OXY - SULPHOCYANO - ACETOACETIC ETHER. *Anhydride* $O(CAc(SCy).CO_2Et)$. [c. 163°]. Made by heating equivalent weights of barium sulphocyanide and dichloro-acetoacetic ether (207°) (Zürcher, *A.* 250, 293). Yellow crystalline powder (from alcohol), insol. ether.

OXY-SULPHO-NAPHTHOIC ACID $C_{10}H_5(OH)(SO_3H).CO_2H$. Made from (α)-oxy-naphthoic acid and H_2SO_4 at 60° (König, *B.* 22, 787; 23, 806). Needles (containing 5aq), v. sol. water and alcohol. Its alkaline solutions fluoresce blue. HNO_3 yields di-nitro-naphthol [138°]. Diazobenzene chloride forms the azo-compound

$C_{10}H_5(OH)(N_2Ph)SO_3H$.—NaHA″: needles, v. sol. water.—Na_2A'' $x$aq.—$Ba(HA'')_2$.

Oxy-di-sulpho-naphthoic acid $C_{10}H_4(OH)(SO_3H)_2CO_2H$. Formed from ($a$)-oxy-naphthoic acid and fuming H_2SO_4 (K.). Stellate groups of needles (containing 4aq).—K_2A''.—$Ba_3(C_{11}H_5S_2O_9)_2$: needles, m. sol. water.

OXY-SULPHYDRO-ALLYL-QUINAZOLINE $C_6H_4<\begin{smallmatrix}CO.N.C_3H_5\\NH.CS\end{smallmatrix}$. *Allylthiobenzoylurea.* [199°]. Formed from o-amido-benzamide and allyl thio-carbimide (Stewart, *J. pr.* [2] 44, 416). Needles. Its benzene solution fluoresces blue.

OXY-SULPHYDRO-DI-METHYL-GLYOXALINE. *Di-methyl derivative* $NMe<\begin{smallmatrix}C(OMe):CMe\\C(SMe):N\end{smallmatrix}$. Formed from di-methyl-thio-hydantoïn [167°], alcoholic potash, and MeI (Marckwald, *B.* 24, 3293). Syrup.—B′HCl: syrup.—$B'H_2SO_4$: crystalline.—$B'_2H_2PtCl_6$.

The isomeride $NMe<\begin{smallmatrix}CO——CMe_2\\C(SMe):N\end{smallmatrix}$ formed from tri-methyl-thiohydantoïn, alcoholic potash, and MeI yields the crystalline salts $B'H_2SO_4$ [138°] and $B'_2H_2PtCl_6$ [150°].

OXY-SULPHYDRO-PHENYL-METHYL-GLYOXALINE. *Di-methyl derivative* $NPh<\begin{smallmatrix}C(OMe):CMe\\C(SMe):N\end{smallmatrix}$. [90°]. Formed from phenyl-methyl-thiohydantoïn, alcoholic KOH, and MeI (Marckwald, *B.* 24, 3290). Crystals.—B′HCl. [140°]. — $B'_2H_2PtCl_6$. [213°]. — $B'C_6H_3N_3O_7$. [192°].

The isomeric compound $NPh<\begin{smallmatrix}CO——CMe_2\\C(SMe):N\end{smallmatrix}$ (223°) from phenyl-di-methyl-thiohydantoïn [67°] forms the salts B′HCl, $B'_2H_2PtCl_6$ [132°] and $B'C_6H_3N_3O_7$ [174°].

OXY-SULPHYDRO-PHENYL-QUINAZOLINE $C_6H_4<\begin{smallmatrix}CO.NPh\\NH.CS\end{smallmatrix}$. [199°]. Formed from o-amido-benzamide and phenyl thiocarbimide (Stewart, *J. pr.* [2] 44, 416). Satiny tables.

OXY-SULPHYDRO-QUINAZOLINE $C_6H_4<\begin{smallmatrix}CO.NH\\NH.CS\end{smallmatrix}$. [281°]. Formed from o-amido-benzamide and thio-urea (Stewart, *J. pr.* [2] 44, 416). Nodules (from alcohol).

OXY-SULPHYDRO-THIAZOLE $C_3H_3NS_2O$ *i.e.* $NH<\begin{smallmatrix}CS.S\\CO.CH_2\end{smallmatrix}$. [167°]. Formed by heating $NH<\begin{smallmatrix}C(NH).S\\CO——CH_2\end{smallmatrix}$ with CS_2 in alcohol at 160° (Miolati, *A.* 262, 84). Formed also from chloro-acetic ether, ammonium dithiocarbamate, and alcoholic HCl; and from sulphocyanoacetic ether by successive treatment with H_2S and HCl.

OXY-SULPHYDRO-o-TOLYL-METHYL GLYOXALINE. *Di-methyl derivative* $C_6H_4MeN<\begin{smallmatrix}C(OMe):CMe\\C(SMe):N\end{smallmatrix}$. [120°]. Got from o-tolyl-methyl-thiohydantoïn, alcoholic potash, and MeI (Marckwald, *B.* 24, 3292). Plates, v. sol. alcohol. Yields the following salts: B′HCl [120°], $B'_2H_2PtCl_6$, $B'H_2SO_4$ [205°], $B'HNO_3$, and the picrate $B'C_6H_3N_3O_7$ [200°].

The isomeric $C_6H_4MeN<\begin{smallmatrix}C(SMe):N\\CO——CMe_2\end{smallmatrix}$ from o-tolyl-di-methyl-thiohydantoïn yields the salts B′HCl [118°], $B'_2H_2PtCl_6$, $B'H_2SO_4$ [208°], and $B'C_6H_2N_3O_7$ [212°].

Oxy-sulphydro-*p*-tolyl-methyl-glyoxaline. *Di-methyl derivative.* [109°]. Plates. Yields B′HCl [123°], $B'_2H_2PtCl_6$, and $B'C_6H_3N_3O_7$ [180°].

The isomeric $[4:1]C_6H_4MeN<\begin{smallmatrix}C(SMe):N\\CO——CMe_2\end{smallmatrix}$ yields $B'H_2SO_4$ [210°], $B'_2H_2PtCl_6$ [152°], and $B'C_6H_3N_3O_7$, decomposing at 190°.

DI-OXY-TARTARIC ACID *v.* TETRA-OXY-SUCCINIC ACID.

OXY-TEREBIC ACID $C_7H_{10}O_5$. [100°–120°]. Made by boiling chloro-terebic acid with water and $CaCO_3$ (W. Roser, *A.* 220, 264). Syrup, crystallising with difficulty, v. sol. water.—CaA'_2.—AgA′: needles, v. sol. water.

OXY-TEREPHTHALIC ACID $C_8H_6O_5$ *i.e.* $C_6H_3(OH)(CO_2H)_2$. Formed by the diazo- reaction from amido-terephthalic acid (De la Rue a. Müller; Burkhardt, *B.* 10, 144, 1273). Prepared also by potash-fusion from bromo-terephthalic acid (Fischli, *B.* 12, 621), from oxy-aldehydo-benzoic acid (Tiemann a. Landshoff, *B.* 12, 1335), from *p*-xylenol, from carvacrol, and thymol (Jacobsen, *B.* 11, 570), from oxy-*p*-toluic acid (Hall a. Remsen, *B.* 12, 1433), and from rufi-gallic acid (Schreder, *M.* 1, 439).

Properties.—Crystalline powder, sl. sol. water, v. sol. alcohol. Not melted at 300°. $FeCl_3$ colours its solution reddish-violet. Yields CO_2 and phenol when strongly heated. On fusion with NaOH it gives salicylic acid and some *p*-oxy-benzoic acid (Barth a. Schreder, *B.* 12, 1260). Yields *m*-oxy-benzoic acid on heating with HClAq at 120°. Forms a di-nitro- derivative [179°].

Salts.—BaA″ 3½aq: laminæ (from water).—Ag_2A'': white pp., insol. water.

Methyl ether Me_2A''. [94°]. Leaflets. Yields an acetyl derivative $C_6H_3(OAc)(CO_2Me)_2$ [76°].

Methyl derivative $C_6H_3(OMe)(CO_2H)_2$. [279°]. Got by oxidation of methoxy-toluic acid and of methyl-thymol. Small prisms.

Methyl ether of the methyl derivative $C_6H_3(OMe)(CO_2Me)_2$. [65°]. Concentric needles.

Ethyl derivative $C_6H_3(OEt)(CO_2H)_2$. [254°]. Got by oxidation of the ethyl ether of thymol (Paterno a. Canzoneri, *G.* 9, 460). Stellate groups of minute crystals, insol. water.

Benzyl derivative $C_6H_3(OCH_2Ph)(CO_2H)_2$. [230°–240°]. Made from $C_6H_3(ONa)(CO_2Me)_2$ and benzyl chloride, the product being saponified (Baeyer a. Tutein, *B.* 22, 2188). Slender needles.

Tetrahydride $C_6H_7(OH)(CO_2H)_2$. Got by reducing the acid with sodium-amalgam (Baeyer a. Tutein, *B.* 22, 2180). Yellowish-white needles, sl. sol. cold water. Coloured bluish-violet by $FeCl_3$. Its methyl ether forms feathery needles [77°]. Hydroxylamine converts the tetrahydride into $C_7H_{10}O_2(NOH)$ [170°], while phenyl-hydrazino forms $C_7H_{10}O_2(N_2HPh)$ [125°] converted by HClAq into $\begin{smallmatrix}NH\\C_6H_4\end{smallmatrix}>C_6H_7.CO_2H$, a crystalline body [230°] giving off a fæcal odour when heated. The tetrahydride, heated at 120°, loses CO_2 and forms $C_6H_9O(CO_2H)$, whence NaA′ and $C_6H_9(OH)Cy.CO_2H$ [130°–140°] may be prepared; the latter body yielding the crystalline acid $C_6H_9(OH)(CO_2H)_2$ on saponification.

Di - oxy - terephthalic acid $C_8H_6O_6$ *i.e.* $C_6H_2(OH)_2(CO_2H)_2$[5:2:4:1] or

$$CH\left\langle\begin{array}{c}CO.CH(CO_2H)\\ \hline CH(CO_2H).CO\end{array}\right\rangle CH.$$

Quinone hydro-dicarboxylic acid. Hydroquinone dicarboxylic acid. [above 300°].

Formation.—1. By passing a current of air through a solution of the dihydride of its ether (succinyl-succinic ether) containing excess of alkali (Herrmann, *B.* 10, 107; *A.* 211, 335).—2. By the oxidising action of $KMnO_4$ on $C_6H_2Me(C_3H_7)(OPO_3K)_2$, a derivative of thymoquinone, and on $C_6H_2Me_2(OPO_3K)_2$, a derivative of hydro-*p*-xyloquinone (Heymann a. Königs, *B.* 20, 2392).—3. By the action of PCl_5 on succinyl-succinic ether (Levy a. Curchod, *B.* 22, 2108).—4. By saponifying its ether.

Properties.—Interlaced needles (containing 2aq) (from water) or yellow plates (from alcohol), sl. sol. alcohol and ether, v. sl. sol. water. Its alcoholic solution shows blue fluorescence. $FeCl_3$ gives a deep-blue colour. When distilled it yields hydroquinone. Bromine-water yields tetrabromoquinone. Chlorine passed into its alcoholic solution forms tetra-chloro-quinone (Loewy, *B.* 19, 2394).

Salts.—K_2A'': yellow needles, forming a solution with green fluorescence. — KHA''. — Na_2A'' 2aq. — $NaHA''$ 2aq. — $Na_4A''(OH)_2$ 10aq: crystals ppd. by conc. NaOHAq.—$(NH_4)_2A''$ 2aq (Duisberg, *A.* 213, 162).—BaA''.—CaA'' 5aq.—$Ca(HA'')_2$ 5aq.—PbA''.—Ag_2A'': green-yellow pp.

Mono-ethyl ether $EtHA''$. [184°]. Made by the action of dilute KOH on the di-ethyl ether in the cold. Pale-yellow needles (from water), sl. sol. water, alcohol, and ether. — $Ba(EtA'')_2$ 5aq.—$Ca(EtA'')_2$ 5aq: greenish-yellow needles.

Di-ethyl ether Et_2A''. [133°]. S. (ether) 1·6 at 20°. Prepared by adding bromine to a solution of its dihydride in CS_2 or to the dihydride suspended in water (Herrmann, *A.* 211, 327; *B.* 19, 2229). Formed also by the action of sodium on di-bromo-acetoacetic ether dissolved in ether (Wedel, *A.* 219, 74).

Properties.—Greenish-yellow trimetric tables (from benzene) or needles (from ether). May be sublimed. Its alcoholic solution shows blue fluorescence. $FeCl_3$ gives a bluish-green colour. Does not react with phenyl cyanate (Goldschmidt a. Meissler, *B.* 23, 259). Does not react with phenyl-hydrazine or hydroxylamine. Sol. alkalis, forming a yellow liquid, from which it is ppd. by CO_2, and, as a scarlet pp., $Na_2C_{12}H_{12}O_6$, by conc. NaOHAq. Ac_2O has no action at 510°.

Reactions.—1. Reduced to its dihydride by *zinc* and HClAq (Baeyer, *B.* 19, 428).—2. *Bromine-vapour* forms $C_6H_2Br_2O_2(CO_2Et)_2$ [157°] and afterwards $C_6Br_2O_2(CO_2Et)_2$ (Hermann, *B.* 19, 2234; Böniger, *B.* 21, 1758).—3. Dry *nitrous acid gas* passed into its solution in absolute ether oxidises it to di-oxy-quinone dicarboxylic ether (Hantzsch a. Loewy, *B.* 19, 26); an intermediate crystalline powder $C_{24}H_{25}NO_{16}$ or $C_{24}H_{23}NO_{16}$ [148°] giving a violet colour with alkalis being first formed (Loewy, *B.* 19, 2393).

Hydrate of the ether $C_{12}H_{18}O_8$ *i.e.*

$$CO_2Et.C\left\langle\begin{array}{c}C(OH)_2.CH_2\\ \hline C(OH)_2.CH_2\end{array}\right\rangle C.CO_2Et. \qquad [113°].$$

Formed, together with the ether, by the action of bromine on the dihydride (succinyl-succinic ether) (Hantzsch a. Zeckendorf, *B.* 20, 2800). Yellow needles. On boiling with alcohol it changes to the ether $C_{12}H_{14}O_6$ [133°]. Hydroxylamine reduces it to $C_{12}H_{18}O_6$ [128°].

Di-acetyl derivative of the ether $C_6H_2(OAc)_2(CO_2Et)_2$. [154°]. Got by the action of AcCl on the ether or on $C_6H_2(ONa)_2(CO_2Et)_2$ (Wedel, *A.* 219, 81; Nef, *A.* 258, 306). Monoclinic crystals. Not attacked by Br. Its alcoholic solution is not fluorescent.

Di-benzoyl derivative of the ether $C_6H_2(OBz)_2(CO_2Et)_2$. [174°]. Made from the ether, NaOHAq, and BzCl. Colourless needles (from alcohol). Not attacked by Br in $CHCl_3$. Conc. H_2SO_4 sets free $C_6H_2(OH)_2(CO_2Et)_2$. Zinc-dust and conc. HClAq form three isomeric dihydrides $C_6H_4(OBz)_2(CO_2Et)_2$ melting at 165°, 85°–95°, and 100°–110°.

Di-methyl derivative $C_6H_2(OMe)_2(CO_2H)_2$. [265°]. Formed by saponification of $C_6H_2(OMe)_2(CO_2Et)_2$ (*v. infra*) with alcoholic potash (Nef, *A.* 258, 298). Colourless needles. Its aqueous solution shows bluish-violet fluorescence.—$(NH_4)_2A''$: sol. water. Not fluorescent.

Di-methyl derivative of the ethyl ether $C_6H_2(OMe)_2(CO_2Et)_2$. [101·5°]. Made from $C_6H_2(ONa)_2(CO_2Et)_2$ and MeI at 100° (Nef, *A.* 258, 297). Colourless tables. Its solutions show bluish-violet fluorescence. Not reduced by zinc-dust and HOAc.

Di-benzyl derivative of the ethyl ether $C_6H_2(OCH_2Ph)_2(CO_2Et)_2$. [96·5°]. Monoclinic needles (from alcohol), insol. KOHAq.

Oxy-amide $C_6H_2(OH)_2(CO.NH.OH)_2$. Formed by the action of hydroxylamine on the ether (Jeaurenaud, *B.* 22, 1278). Prisms (containing 2aq), sol. water and alcohol.

Dioxyterephthalic acid dihydride $C_8H_8O_6$. *Succinyl-succinic acid.* S. ·015 at 19·5°. Got from its ether and the calculated quantity of cold NaOHAq. Minute needles, decomposed by heat, yielding $C_6H_8O_2$ [78°] and CO_2. $FeCl_3$ colours its solution violet (Baeyer a. Noyes, *B.* 22, 2168).—BaA'' 2½aq.—$(NH_4)_2A''$ 2aq.

Methyl ether Me_2A''. [132°]. Made by the action of sodium on methyl succinate (Ebert, *A.* 229, 50). Got also from bromo-acetoacetic ether and ammonia (Geuther, *A.* 244, 204). Sol. alcohol and ether.

Mono-ethyl ether $EtHA''$. [98°]. Got from the di-ethyl ether and cold NaOHAq (Herrmann). Yellowish prisms (from ether). Its alcoholic solution shows blue fluorescence. $FeCl_3$ gives a violet colour. Decomposed by boiling water into CO_2 and $C_7H_7EtO_4$.

Di-ethyl ether Et_2A'' *i.e.*

$$CO_2Et.CH\left\langle\begin{array}{l}CH_2.CO\\ CO\;.CH_2\end{array}\right\rangle CH.CO_2Et \text{ or}$$

$$CO_2Et.CH\left\langle\begin{array}{l}CH{=\!=}C(OH)\\ C(OH):CH\end{array}\right\rangle CH.CO_2Et. \qquad [127°].$$

S.G. $\frac{18}{4}$ 1·41. S. (ether) 1·6 at 17°.

Formation.—1. By the action of K or Na on ethyl succinate (Fehling, *A.* 49, 186; Herrmann, *A.* 211, 306; Duisberg, *B.* 16, 133).—2. By the action of NaOEt (free from alcohol) on succinic ether (Volhard, *B.* 16, 134).—3. From bromo-acetoacetic ether by the action of alcoholic NH_3 (Duisberg, A. 213, 133) or of NaOEt

(Wedel, *A.* 219, 92).—4. By reducing di-oxy-terephthalic ether with zinc and HClAq (Baeyer, *B.* 19, 428).

Properties.—Green triclinic crystals with blue fluorescence (from ether), v. sl. sol. hot water. Insol. NH_3Aq, but forms a yellow solution in NaOHAq. Its alcoholic solution shows blue fluorescence. $FeCl_3$ gives a red colour. Decomposed by excess of KOHAq, yielding black products containing syrupy 'succinyl-propionic' acid $C_7H_8O_4$ and a crystalline acid $C_8H_{16}O_6$ [139°], which forms BaA″ 2aq. The alkaline solution is turned brown by oxygen. Does not react with phenyl cyanate (Goldschmidt a. Meissler, *B.* 23, 258).

Reactions.—1. Converted by *bromine* into di-oxy-terephthalic ether. Bromine and potash yield brominated quinones.—2. *Nitrous acid* forms a di-nitroso- derivative $C_{12}H_{14}N_2O_8$ [114°], a white powder, insol. water and alcohol, decomposed by boiling alcohol with formation of di-oxy-terephthalic ether, and by boiling water with formation of the oxim of pyruvic ether.—3. *Hydroxylamine* in presence of NaOHAq form $C_6H_3(NOH)_2CO_2Et$, crystallising from alcohol in plates which begin to decompose at 160° (Jeaurenaud, *B.* 22, 1282). An alcoholic solution of phenyl-hydrazine forms the white hydrazo- compound $C_6H_4(NH.NHPh)_2(CO_2Et)_2$ [165°] whence bromine produces the disazo compound $C_6H_4(N_2Ph)_2(CO_2Et)_2$ [126°], which on saponification yields the acid $C_6H_4(N_2Ph)_2(CO_2H)_2$ [over 250°]. The white hydrazo- compound is accompanied by $C_6H_4(NH.NHPh)_2(CO_2Et)_2$ [208°], a yellow isomeride identical with Knorr's body [206°] (Baeyer, *B.* 24, 2690).—4. *Phenyl hydrazine* (2 mols.) forms in presence of toluene and some glacial acetic acid, the four following compounds $C_6H_6O(N_2HPh)(CO_2Et)_2$ [160°], $C_6H_8(N_2HPh)_2(CO_2Et)_2$ [206°], $C_{22}H_{22}N_4O_3$ [212°], and $C_{20}H_{16}N_4O_2$, decomposing above 300° (Knorr a. Bülow, *B.* 17, 2054). The last body yields a di-methyl derivative $C_{20}H_{14}Me_2N_4O_2$ and is converted by nitrous acid into a blue substance $C_{26}H_{14}N_4O_2$.—5. PCl_5 forms the chlorides of di-chloro-dihydroterephthalic and dioxyterephthalic acids (Levy a. Curchod, *B.* 22, 2106).

Salts.—$Na_2Et_2C_8H_4O_6 2EtOH$. Got from the ether by ppg. with alcoholic soda (Remsen, *B.* 8, 1409). Red; on drying it changes to colourless $Na_2Et_2C_8H_4O_6$ (Hantzsch a. Herrmann, *B.* 21, 1756).—$KC_8H_5O_6Et_2$. Colourless.—$K_2Et_2C_8H_4O_6$: orange.—$MgEt_2C_8H_4O_6$ 2aq: dark-red amorphous mass.—$BaC_{12}H_{14}O_6$ aq: red pp.—$CaC_{12}H_{14}O_6$ aq.

Di-acetyl derivative of the ether $C_6H_4(OAc)_2(CO_2Et)_2$. [171°]. Made from the ether and AcCl. Needles (by sublimation). Its solutions are not fluorescent.

Di-benzoyl derivative of the ether $C_6H_4(OBz)_2(CO_2Et)_2$. [165°]. Formed from $C_6H_4(ONa)_2(CO_2Et)_2$ and BzCl (Nef, *A.* 258, 310). Formed also, together with two isomerides [138°] and [102·5°], by reducing the di-benzoyl derivative of di-oxy-terephthalic ether with zinc and HClAq The three isomerides may be separated by crystallisation from ether-ligroïn. The three compounds are converted into $C_6H_4(OH)_2(CO_2Et)_2$ by H_2SO_4, and into $C_6H_2(OBz)_2(CO_2Et)_2$ by Br in CS_2.

(α)-*Di-benzyl derivative of the ether* $C_6H_4(OCH_2Ph)_2(CO_2Et)_2$. [169°]. Made in small quantity (5 p.c.) from $C_6H_2(OCH_2Ph)_2(CO_2Et)_2$ by reducing with Zn and HCl (Nef, *A.* 258, 301). Colourless needles. May be sublimed.

(β)-*Di-benzyl derivative of the ether* $C_6H_4(OCH_2Ph)_2(CO_2Et)_2$. [148·5°]. Made, together with a (γ)-isomeride [140·5°], by the action of benzyl chloride on $C_6H_4(ONa)_2(CO_2Et)_2$ at 100°. Less sol. alcohol than the (γ)-isomeride. H_2SO_4 converts it into a crystalline polymeride [272°]. Hydroxylamine and phenyl-hydrazine have no action.

Di-ethyl derivative $C_6H_4(OEt)_2(CO_2H)_2$. [126·5°]. Got, with EtBr, by heating bromo-ethyl-acetoacetic ether at 100° (Wedel, *A.* 219, 104). Trimetric octahedra; $a:b:c = \cdot245:1:\cdot641$. Sol. water and alcohol, forming acid solutions, coloured red by $FeCl_3$.—$(NH_4)_2A''$.—Na_2A'' 2aq.—K_2A''aq. — BaA″ 2aq.— CaA″aq.—MgA″ 2½aq.—ZnA″ 2½aq.—MnA″ 4aq.—PbA″.—Et_2A''.

Di-oxy-terephthalic acid tetrahydride $C_8H_{10}O_6$ *i.e.* $C_6H_6(OH)_2(CO_2H)_2$. [191°]. Made by the action of hydroxylamine on dioxyterephthalic ether (Jeaurenaud, *B.* 22, 1279). Prisms, sl. sol. cold water, v. e. sol. alcohol and ether. $FeCl_3$ gives a brown colour.—$(NH_4)_2A''$: needles. —BaA″: white powder.—Ag_2A'' 2aq: needles.

Ethyl ether Et_2A''. [128°]. Made by the action of hydroxylamine on the hydrate of di-oxyterephthalic ether [113°] (Hantzsch a. Zeckendorf, *B.* 20, 2801). Yellow crystalline body.

Di-oxy-terephthalic acid hexahydride $C_6H_8(OH)_2(CO_2H)_2$. *Di-oxy-hexamethylene dicarboxylic acid.* The salt BaA″3½aq is got by saponifying the nitrile with baryta-water (Baeyer a. Noyes, *B.* 22, 2177). Thick prisms or needles, v. sl. sol. water.

Nitrile $C_6H_{10}O_2(CN)_2$. [180°]. Made from quinone tetrahydride (diketohexamethylene) and HCy. Colourless, v. sol. hot water and alcohol.

c-**Di-oxy-terephthalic acid** $C_6H_2(OH)_2(CO_2H)_2$ [1:2:3:4]. [290°]. Formed from sodium pyrocatechin and CO_2 (Schmitt a. Hähle, *J. pr.* [2] 44, 1). Thin needles (containing aq) forming solutions with deep-blue fluorescence. $FeCl_3$ gives a blue colour.—Na_2A'' 2aq: fluorescent prisms.—$Pb_2C_8H_2O_6$.—Ag_2A''.

Methyl ether Me_2A''. [145°]. Needles.

Ethyl ether Et_2A''. [90°]. Tables.

Tetra-oxy-terephthalic acid $C_8H_6O_8$ *i.e.* $C_6(OH)_4(CO_2H)_2$. *Ethyl ether* Et_2A''. [178°]. Formed by passing SO_2 into a feebly-alkaline solution of di-oxy-quinone dicarboxylic ether (Loewy, *B.* 19, 2388). Golden plates (from chloroform), v. sl. sol. water, alcohol, and ether. In presence of NaOHAq it is oxidised by air to di-oxy-quinone dicarboxylic ether (Böniger, *B.* 22, 1284). Phenyl cyanate (4 mols.) and some chloroform at 170° yield $C_6(O.CO.NHPh)_4(CO_2Et)_2$ [260°], an orange powder, insol. most solvents (Goldschmidt a. Meissler, *B.* 23, 266). Ac_2O yields the tetra-acetyl derivative $C_6(OAc)_4(CO_2Et)_2$ [202°], a colourless crystalline powder (Hantzsch a. Zeckendorf, *B.* 20, 2798). Hydroxylamine forms $C_6O_2(O.NH_3OH)_2(CO_2Et)_2$ [170°]. Alcoholic phenyl-hydrazine forms, on boiling, the corresponding salt $C_6O_2(O.N_2H_4Ph)_2(CO_2Et)_2$ [134°] (Böniger).

Reference. — DI-CHLORO-DI-OXY-TEREPHTHALIC ACID.

DI-OXY-TETRADECANE *v.* BUTYRO-PINACONE and DI-ISOBUTYL-PINACONE.

DI-OXY-TETRADECOIC ACID $C_{14}H_{26}(OH)_2O_2$. [60°]. A product of oxidation of oil of millet by $KMnO_4$ (Kassner, *Ar. Ph.* [3] 25, 1081). Insol. water, v. sol. alcohol and ether.

OXYTETRIC ACID, formed by heating methyl-acetoacetic ether with bromine and a little water, is identical with MESACONIC ACID (Cloez, *Bl.* [3] 3, 598 ; *C. R.* 110, 583 ; Walden, *B.* 24, 2033 ; Gorboff, *J. R.* 1887, 605).

α-OXY-THIENYL-ACETIC ACID $C_4H_3S.CH(OH).CO_2H$. [115°]. Formed by reducing thienyl-glyoxylic acid with sodium-amalgam (Ernst, *B.* 19, 3280). Needles (from benzene), v. sol. water, alcohol, and ether. Yields thiophenic aldehyde on boiling with MnO_2. Reduced by HI and P to thienyl-acetic acid.—BaA'_2 $x$aq.—CaA'_2 $x$aq : v. sol. water.—Ag_2A'' : white pp.

o-OXY-THIOBENZOIC ACID $C_7H_6SO_2$ *i.e.* $C_6H_4(OH).CO.SH$. Made from *o*-oxy-benzoyl chloride and KSH (Carius, *A.* 129, 11). Brownish-yellow amorphous mass, insol. water.—BaA'_2.

Methyl derivative of the ethyl ether $C_6H_4(OMe).CO.SEt$. (198° at 80 mm.). Made from $C_6H_4(OMe).CO.OPh$ and NaSEt in ether (Seifert, *J. pr.* [2] 31, 475). Oil, smelling like mercaptan.

o-Oxy-thiobenzoic acid $C_6H_4(OH).CS.OH$. *Amide* $C_6H_4(OH).CS.NH_2$. [118°]. Made by fusing salicylamide with P_2S_5 (Spilker, *B.* 22, 2767). Colourless needles, v. sol. alcohol. $FeCl_3$ colours its aqueous solution violet. Slowly converted into $C_6H_4(OH).CO.NH_2$ by boiling water.

Di-oxy-dithio-benzoic acid $C_6H_3(OH)_2.CS_2H$. [4:2:1]. Made by heating resorcin with potassium xanthate at 100° (Lippmann, *M.* 10, 618). Yellow needles (containing aq). Melts at 131° when hydrated, but decomposes at 124° when anhydrous. Potash-fusion yields (4,2,1)-di-oxy-benzoic acid.

Tri-oxy-di-thio-benzoic acid $C_6H_2(OH)_3.CS_2H$ [4:3:2:1]. [154°]. Made by heating pyrogallol with potassium xanthate and alcohol (L.). Yellow crystals (containing aq), v. sol. alcohol and ether. Yields *c*-tri-oxy-benzoic acid when fused with potash.

OXY-THIONAPHTHENE C_8H_6SO *i.e.* $CH{<}{\scriptstyle CH.C.C(OH):CH \atop \scriptstyle S-C---CH:CH}$ [72°]. Made by heating thiophenic aldehyde with sodium succinate and Ac_2O at 135° (Biedermann, *B.* 19, 1618). Needles (by sublimation), sl. sol. water, v. sol. NaOHAq. Gives the indophenine reaction. Chloroform and KOHAq give a bluish-green colour on warming.

OXY-THYMOQUINONE $C_{10}H_{12}O_3$ *i.e.* $C_6HMe(C_3H_7)(OH)O_2$ [1:4:6:2:5]. [165°].

Formation.—1. By the oxidising action of $FeCl_3$ on di-amido-thymol (Carstanjen, *J. pr.* [2] 15, 399 ; Ladenburg a. Engelbrecht, *B.* 10, 1218). 2. By dissolving bromo-thymoquinone in KOHAq (Carstanjen, *J. pr.* [2] 3, 57).—3. By the action of H_2SO_4 or HClAq on methylamidothymoquinone (Zincke, *B.* 14, 97) or dimethylamidothymoquinone (Schulz, *B.* 16, 898).

Properties.—Yellow needles, sol. alcohol, ether, and hot water. Forms a violet-red solution in alkalis. May be sublimed.

Reactions.—1. EtI at 100° forms $C_{10}H_{11}EtO_3$ which sublimes in golden plates.—2. *Aniline* in alcohol forms $C_6Me(C_3H_7)(OH)O_2(NHPh)$ [135°], crystallising in violet-black needles, and forming a bluish-violet solution in NH_3Aq.—3. *p-Toluidine* yields the corresponding *p*-toluide [165°].

(β)-Oxy-thymoquinone $C_6HMe(C_3H_7)(OH)O_2$ [1:4:3:2:5]. [183°]. Made from di-nitro-carvacrol by reduction and subsequent oxidation with $FeCl_3$ (Mazzara, *B.* 23, 1390). Orange prismatic tables, volatile with steam. Na_2CO_3Aq forms a violet solution.

Di-oxy-thymoquinone $C_6Me(C_3H_7)(OH)_2O_2$. [213°]. Formed by boiling chloro-oxy-thymoquinone with KOHAq (E. a. L.) and by boiling dimethylamido-thymoquinone with alcohol and H_2SO_4 or KOH (Zincke, *B.* 14, 95). Red needles or prisms, forming a violet solution in alkalis. Phenylene-phenyl-o-diamine, in presence of alcohol and HOAc, forms oxythymophenindulone $C_6H_4{<}{\scriptstyle N \atop \scriptstyle NPh}{>}C_6Me(C_3H_7)(OH)O$ as ruby-red crystals [175°] (Kehrmann a. Messinger, *B.* 24, 590).—BaA'' aq.—PbA'': green pp.

Di-acetyl derivative. [81°]. Needles.

Di-benzoyl derivative. [163°].

Reference.—CHLORO-OXY-THYMOQUINONE.

DI-OXY-DITHYMYL-ETHANE $C_{22}H_{30}O_2$ *i.e.* $CH_3.CH(C_{10}H_{12}OH)_2$. [185°]. Formed by reducing $CCl_3.CH(C_{10}H_{12}OH)_2$ with zinc-dust and alcohol (Jäger, *C. J.* 31, 262) and also by adding a mixture of chloroform and $SnCl_4$ to a cooled mixture of paraldehyde and thymol (Steiner, *B.* 11, 287). Efflorescent plates (from alcohol).

Di-acetyl derivative. [100°]. Needles.

Di-benzoyl derivative. [191°]. Needles.

Di-ethyl ether $C_{22}H_{28}Et_2O_2$. [72°].

DI-OXY-DI-THYMYL-ETHYLENE $CH_2:C(C_{10}H_{12}.OH)_2$. [171°]. Formed, together with the preceding body, by boiling the compound $CCl_3.CH(C_{10}H_{12}.OH)_2$ with zinc-dust and alcohol (Jäger, *C. J.* 31, 263). Needles (from HOAc). K_3FeCy_6 oxidises it, in alcoholic solution, to $C_{24}H_{54}O_4$ [215°], crystallising in green needles. Alkaline K_3FeCy_6 forms $C_{22}H_{26}O_2$ [215°], which forms dark-red crystals.

DI-OXY-DI-THYMYL SULPHIDE $(C_{10}H_{12}.OH)_2S$. [152°]. Formed from thymol and SCl_2 (Tassinari, *G.* 17, 92).

OXY-TOLUAMIDOXIM [3:6:1] $C_6H_3Me(OH).C(NOH).NH_2$. [124°]. Formed from the thioamide in alcohol by treatment with hydroxylamine hydrochloride and NaOHAq (Goldbeck, *B.* 24, 3662). Yellowish plates (from benzene), v. sol. hot water. Coloured cherry-red by $FeCl_3$.—B'HCl. [215°].

Acetyl derivative. Plates (from benzene) gives $C_7H_6(OH).C{<}{\scriptstyle N.O \atop \scriptstyle N}{>}CMe$ [45°] on heating with water in a sealed tube.

Benzoyl derivative $C_7H_6(OH).C(NOBz).NH_2$. [182°]. Plates, sl. sol. alcohol. Coloured green by $FeCl_3$ in acetone.

Di-benzoyl derivative. [143°].

c-Oxy-toluamidoxim [3:2:1] $C_6H_3Me(OH).C(NOH).NH_2$ [126·5°]. Formed from the nitrile and hydroxylamine (Paschen, *B.* 24, 3670). Tables, v. sol. alcohol and hot water. Yields a dibenzoyl derivative $C_6H_3Me(OBz).C(NOBz).NH_2$ [164°], whence KOH forms $C_6H_3Me(OH){<}{\scriptstyle N.O \atop \scriptstyle N}{>}CPh$ [150°]

OXY-TOLUENE *v.* Cresol and Benzyl alcohol.

Di-oxy-toluene $C_7H_8O_2$ *i.e.* $C_6H_3Me(OH)_2$[1:2:4]. *Cresorcin. Lutorcin.* Mol. w. 124. [104°]. (c. 269°). Formed from amido-*p*-cresol and from amido-o-cresol [161°] by the diazo- reaction (Knecht, *A.* 215, 92; *B.* 15, 298; Wallach, *B.* 15, 2835). Formed also by potash-fusion from the corresponding toluene disulphonic acid (Nölting, *B.* 19, 136) and from bromo-*p*-cresol (Vogt a. Henninger, *C. R.* 94, 650). Spherical crystalline groups, v. sol. water, alcohol, and ether, sl. sol. benzene and ligroïn. $FeCl_3$ colours its solutions blue. NH_3 with damp air turns it brown, green, and finally blue. Bleaching-powder gives a yellow colour. Its solution in NaOHAq is turned brown by air. On heating with chloroform and NaOHAq it gives a rose-red colour. On heating with phthalic anhydride it forms the phthaleïn $C_{22}H_{16}O_5$, which is a brick-red powder, exhibits green fluorescence in alkaline solution, and yields $C_{22}H_{14}Ac_2O_5$ [260°]. Unlike resorcin, cresorcin gives no colour when the product got by heating with H_2SO_4 and nitro-benzene is diluted and made alkaline.

Di-acetyl derivative $C_7H_6(OAc)_2$. [c. 160°].

Di-oxy-toluene $C_6H_3Me(OH)_2$[1:2:6]. [63°–66°]. Made by the diazo- reaction from amido-cresol [124°–128°] (Ullmann, *B.* 17, 1960). Needles, v. sol. water and alcohol. Coloured red by bleaching powder. With phthalic anhydride it gives a compound analogous to fluoresceïn. Reduces cold ammoniacal $AgNO_3$.

Iso-orcin $C_7H_6(OH)_2$. [87°]. (260°). Made by potash-fusion from toluene (γ)-disulphonic acid (Senhofer, *A.* 164, 131). Needles (containing aq). Sol. water, alcohol, and ether. Tastes sweet. $FeCl_3$ gives a brownish-green colour. Reduces cold ammoniacal $AgNO_3$.

Other **di-oxy-toluenes** are described as Hydrotoluquinone, Isohydrotoluquinone, Orcin, and Methyl-pyrocatechin.

ω-OXY-TOLUENE PHOSPHINIC ACID $C_6H_5.CH(OH).P(OH)_2$. [90°]. Formed, together with $(C_6H_5.CH(OH))_2PO.OH$ [165°] by heating benzoic aldehyde with hypophosphorous acid (Ville, *C. R.* 107, 659; 110, 348). Plates, decomposing at 140° with formation of benzoic aldehyde. Reduces $AgNO_3$.—$Ba(HA'')_2$ ½aq: small plates.

Acetyl derivative $CHPh(OAc).P(OH)_2$.

ω-OXY-TOLUENE PHOSPHONIC ACID $C_6H_5.CH(OH).PO(OH)_2$. [173°]. Made from benzoic acid by successive treatment with PCl_3 and water (Fossek, *M.* 7, 34). Hard crusts (from benzene and HOAc).—BaA''.—$Ba(HA'')_2$.

OXY-TOLUENE SULPHONIC ACID *v.* Cresol sulphonic acid.

OXY-o-TOLUIC ACID $C_8H_8O_3$ *i.e.* $C_6H_3Me(OH).CO_2H$[2:3:1]. *Oxy-methyl-benzoic acid.* Mol. w. 152. [183°]. Formed by the diazo- reaction from amido-o-toluic acid [191°], and by potash-fusion from sulpho-*o*-toluic acid (Jacobsen, *B.* 16, 1963; 17, 163). Needles, sol. cold water, alcohol, and ether, sl. sol. chloroform. Volatile with steam. $FeCl_3$ gives a brown pp.

Methyl derivative $C_6H_3Me(OMe).CO_2H$. [146°]. Needles, sl. sol. cold water.—CaA'_2 2aq.

Oxy-o-toluic acid $C_6H_3Me(OH).CO_2H$[2:4:1]. [179°]. *Formation.*—1. By potash-fusion from the corresponding aldehyde (Tiemann a. Schotten, *B.* 11, 778), and from the corresponding $C_6H_3Me(SO_2NH_2).CO_2H$ (Jacobsen, *B.* 14, 40).—2. By heating *m*-cresol with CCl_4 and alcoholic NaOH (Schall, *B.* 12, 819).—3. From amido-o-toluic acid [c. 165°] by the diazo- reaction (Jacobsen, *B.* 17, 164).

Properties.—Needles (containing ½aq), v. sol. hot water, alcohol, and ether, insol. cold chloroform. Not coloured by $FeCl_3$. Yields *m*-cresol on distillation.—CaA'_2 2aq: crystals, v. sol. water.

Methyl derivative $C_6H_3Me(OMe).CO_2H$. [176°]. Needles (from water).

Oxy-o-toluic acid $C_6H_3Me(OH).CO_2H$[2:5:1]. [172°]. Formed by potash-fusion from the corresponding $C_6H_3Me(SO_2NH_2)CO_2H$, and also from amido-*o*-toluic acid [196°] by the diazo- reaction (Jacobsen, *B.* 14, 41; 17, 163). Prisms, sol. alcohol, ether, and hot water, v. sl. sol. chloroform. Volatile with steam. $FeCl_3$ gives a brown pp. The Cu salt forms bluish-green plates.

Oxy-o-toluic acid $C_6H_3Me(OH).CO_2H$[2:6:1]. [168°]. S. ·143 at 25°. Formed by potash-fusion from bromo-o-toluic acid (Jacobsen, *B.* 16, 1962). Long needles, v. sol. hot water, alcohol, and ether. Volatile with steam. At 200° it yields *m*-cresol. $FeCl_3$ gives a bluish-violet colour.

Oxy-*m*-toluic acid $C_6H_3Me(OH).CO_2H$[3:2:1]. *Homosalicylic acid.* (β)-*Cresotic acid.* [164°].

Formation.—1. By the action of CO_2 on sodium-o-cresol (Engelhardt a. Latschinoff, *Z.* 1869, 623; Kekulé, *B.* 7, 1006; Ihle, *J. pr.* [2] 14, 456).—2. By heating o-cresol with CCl_4 and NaOH at 100° (Schall, *B.* 12, 816).—3. By means of potash-fusion from the corresponding $C_6H_3Me(SO_2NH_2)CO_2H$ (Jacobsen, *B.* 11, 902).—4. From *c*-amido-toluic acid (Jacobsen, *B.* 14, 2354).

Properties.—Long needles, sl. sol. cold water, v. sol. chloroform. Volatile with steam. $FeCl_3$ gives a violet colour. Poisonous (Dunstan a. Black, *Ph.* [3] 21, 429).

Methyl derivative $C_7H_6(OMe).CO_2H$. [81°]. Feathery needles.

Methyl ether MeA'. (235°). S.G. $\frac{23}{23}$ 1·1444 (Pinner, *B.* 23, 2938).

Ethyl ether EtA'. (248°). S.G. $\frac{23}{23}$ 1·1020. With benzamidine it forms $C_{22}H_{17}N_3O$ crystallising in yellowish needles, insol. acids and alkalis (Pinner, *B.* 23, 2939).

Nitrile $C_7H_6(OH).CN$. [88·5°]. Got from its acetyl derivative, which is formed by the action of Ac_2O on the oxim of *c*-toluic aldehyde (Paschen, *B.* 24, 3669). Tables, v. sol. alcohol.

Oxy-*m*-toluic acid $C_6H_3Me(OH)CO_2H$[3:4:1]. [173°]. *Formation.*—1. By potash-fusion from the corresponding $C_6H_3Me(SO_2NH_2)CO_2H$ (Jacobsen, *B.* 11, 897; Remsen a. Iles, *Am.* 1, 37; *B.* 11, 462; Mahon, *Am.* 4, 186), from bromo-*m*-toluic acid and from chloro-*m*-toluic acid [210°] (Jacobsen, *B.* 14, 2351; 18, 1761).—2. By heating *o*-cresol with CCl_4 and NaOH; the yield being 40 p.c. (Schall, *B.* 12, 816).—3. By the diazo-reaction from amido-*m*-toluic acid (Remsen a. Kuhara, *Am.* 3, 428).—4. By oxidation of the corresponding aldehyde (Tiemann a. Schotten, *B.* 11, 777).

Properties.—Long needles (containing ½aq), sol. hot water, alcohol, and ether, insol. cold chloroform. Gives no colour with $FeCl_3$. Yields o-cresol when heated with HClAq at 180°. Gives a nitro- compound [85°].

Salts. — CaA'_2 3aq: minute needles.—BaA'_2 3aq.—CuA'_2 $1\frac{1}{2}$aq: blue flocculent pp.

Methyl derivative $C_6H_3Me(OMe).CO_2H$. [193°]. Minute needles. Got by saponifying $C_6H_3Me(OMe).CO_2Me$ [67°] (Schall). The amide $C_6H_3Me(OMe).CONH_2$ [144°] is prepared from $C_6H_4Me(OMe)$ [1:2], $ClCONH_2$, and $AlCl_3$ (Gattermann, *A.* 244, 64).

Ethyl derivative $C_6H_3Me(OEt).CO_2H$. [199°]. Obtained by saponification of the amide $C_6H_3Me(OEt).CONH_2$ [167°] which is got from $C_6H_3Me(OEt)$ and $ClCONH_2$ (G.).—CaA'_2 2aq (Brown, *Am.* 4, 375).

s-Oxy-*m*-toluic acid $C_6H_3Me(OH).CO_2H$ [3:5:1]. [208°]. Formed from *m*-toluic acid by sulphonation followed by potash-fusion, the resulting acid being freed from its isomeride by steam distillation (Jacobsen, *B.* 14, 2357). Formed also by the action of baryta-water on $C_{12}H_{16}O_8$ [90°], which is obtained from acetyl-pyruvic ether and NaOHAq (Claisen, *B.* 22, 3271). Needles or prisms, v. sol. hot water, not volatile with steam.—CaA'_2 2aq: prisms.—SrA'_2.

Methyl ether MeA'. [93°]. Needles.

Oxy-*m*-toluic acid $C_6H_3Me(OH).CO_2H$ [3:6:1]. *p-Homosalicylic acid.* (α)-*Creosotic acid.* [151°].

Formation.—1. By passing CO_2 over *p*-cresol in which sodium has been dissolved (Engelhardt a. Latschinoff, *Z.* 1869, 622, 712; Kolbe a. Lautemann, *A.* 115, 203; Ihle, *J.pr.* [2] 14, 455). 2. By heating *p*-cresol with CCl_4 and NaOH (Schall, *B.* 12, 816).—3. By potash-fusion from chloro-*m*-xylene sulphonic acid (Voigt, *Z.* [2] 5, 577; *B.* 2, 284), from *m*-xylene sulphonic acid (E. a. L.), from (1,3,4)-xylenol or its (β)-sulphonic acid, from bromo-*m*-toluic acid, and from sulpho-*m*-toluic acid (Jacobsen, *B.* 11, 374; 14, 2352; Staedel a. Hölz, *B.* 18, 2919).—4. By oxidation of the corresponding aldehyde (Tiemann a. Schotten, *B.* 11, 778).—5. From amido-toluic acid [172°] by the diazo- reaction (Panaotovic, *J. pr.* [2] 33, 64).

Properties.—Colourless trimetric prisms (from water), sl. sol. water, v. sol. alcohol, ether, and chloroform. Volatile with steam. Its aqueous solution is turned violet by $FeCl_3$. Conc. HClAq at 180° yields *p*-cresol $POCl_3$, forming various dehydration-products (Schiff, *A.* 245, 43). Distillation with Ac_2O yields $C_{15}H_{12}O_2$ [143°] (Kostanecki, *B.* 18, 1988).

Salt.—BaA'_2 2aq: leaflets.

Methyl ether MeA'. (242°). S.G. $\frac{23}{23}$ 1·1438. Liquid (Pinner, *B.* 23, 2938).

Ethyl ether EtA'. (251°). S.G. $\frac{23}{23}$ 1·1037. Reacts with benzamidine, forming $C_{22}H_{17}N_3O$ crystallising in yellowish needles (P.).

Amide $C_6H_3Me(OH).CONH_2$. [178°]. Got from the acid by treatment with $POCl_3$ at 60° followed by alcoholic NH_3 at 160° (Schiff, *G.* 17, 559; *A.* 245, 43), and from the ether and NH_3 (Goldbeck, *B.* 24, 3659). Needles (from alcohol). P_2S_5 forms $C_7H_6(OH).CS.NH_2$ [127°].

Anilide $C_7H_6(OH).CONHPh$. [53°]. Plates.

Nitrile $C_7H_6(OH).CN$. V. sol. alcohol. Its acetyl derivative [57°] is got by the action of Ac_2O on the oxim of toluic aldehyde.

Methyl derivative $C_6H_3Me(OMe).CO_2H$. [70°] (L.); [67°] (Schall, *B.* 22, 749). Long needles.—AgA'.

Amide of the methyl derivative $C_6H_3Me(OMe).CONH_2$. [163°]. Made from $C_6H_4Me(OMe)$ and $ClCONH_2$ in presence of $AlCl_3$ (Gattermann, *A.* 244, 66). Needles (from hot Aq).

Nitrile of the methyl derivative $C_6H_3Me(OMe).CN$. (270° uncor.). Made by warming diazotised amido-*p*-cresol with $CuCy_2$ (Limpach, *B.* 22, 351). Oil.

Amide of the ethyt derivative $C_6H_3Me(OEt).CONH_2$. [152°]. Made from $C_6H_4Me(OEt)$, $ClCONH_2$, and $AlCl_3$ (G.). Silky needles (from dilute alcohol).

Oxy-*p*-toluic acid $C_6H_3Me(OH).CO_2H$ [4:2:1]. (γ)-*Cresotic acid. m-Homosaticylic acid.* [177° cor.]. *Formation.*—1. By passing CO_2 into *m*-cresol in which sodium has been dissolved (E. a. L.; Biedermann a. Pike, *B.* 6, 323).—2. By oxidation of the corresponding aldehyde (Tiemann a. Schotten, *B.* 11, 777).—3. By heating *m*-cresol with CCl_4 and NaOHAq (Schall, *B.* 12, 816).—3. By potash-fusion from *p*-xylenol (Jacobsen, *B.* 11, 570).

Properties.—Needles (from water) or monoclinic prisms (from alcohol), m. sol. hot water, v. sol. alcohol and chloroform. Volatile with steam. $FeCl_3$ gives a red colour. HClAq at 170° yields *m*-cresol.

Salts.—CaA'_2 3aq.—BaA'_2 3aq: prisms.

Methyl ether MeA'. (243°). S.G. $\frac{23}{23}$ 1·1395 (Pinner, *B.* 23, 2938).

Ethyl ether EtA'. (254°). S.G. $\frac{23}{23}$ 1·0973. Converted by benzamidine into $C_{22}H_{17}N_3O$ crystallising in needles [235°].

Methyl derivative $C_6H_3Me(OMe).CO_2H$. [104°]. Leaflets, sol. hot water (Schall).

Ethyl derivative $C_6H_3Me(OEt).CO_2H$. [109°]. Got by oxidising the ethyl derivative of thymol (Paterno, *J.* 1879, 519).

Oxy-*p*-toluic acid $C_6H_3Me(OH).CO_2H$ [4:3:1]. [207° cor.].

Formation.—1. By potash-fusion from sulpho-*p*-toluic acid or its mono-amide (Flesh, *B.* 6, 481; Remsen a. Hall, *Am.* 2, 54; Weinreich, *B.* 20, 981), and from chloro- or bromo- *p*-toluic acid (Gerichten, *B.* 11, 368).—2. From nitro-toluic acid [190°] by reduction, followed by the diazo- reaction (Fittica, *B.* 7, 927).

Properties.—Needles; sol. hot water, alcohol, and ether, insol. chloroform. Volatile with steam. Not coloured by $FeCl_3$. Gives o-cresol on distillation with lime.

Salts.—CaA'_2 4aq.—PbA'_2 2aq: needles.

Ethyl ether EtA'. [75°]. Prisms.

Methyl derivative $C_6H_3Me(OMe).CO_2H$. [156°]. Needles (by sublimation).—BaA'_2 4aq.

ω-Oxy-o-toluic acid $CH_2(OH).C_6H_4.CO_2H$. [118°]. Made by dissolving phthalide in boiling NaOHAq (Hessert, *B.* 10, 1446; 11, 237). Powder, v. sl. sol. cold water, v. sol. alcohol and ether. Changes on fusion, and on boiling with water, into its anhydride.—BaA'_2.—AgA': octahedra.

Anhydride v. PHTHALIDE.

ω-Oxy-*p*-toluic acid $CH_2(OH).C_6H_4.CO_2H$. *Oxymethyt-benzoic acid.* [181°]. Formed, together with terephthalic acid and $C_6H_4(CH_2.OH)_2$, by boiling terephthalic aldehyde with NaOHAq (Löw, *A.* 231, 373). Formed also by boiling $CH_2Br.C_6H_4.CO_2H$ with baryta-water (Kekulé a. Dittmar, *A.* 162, 342). Plates or needles, v. sol. water and ether. Not reddened or resinified by H_2SO_4.—AgA'.

Di-oxy-o-toluic acid $C_6H_2Me(OH)_2CO_2H$ [2:5:3:1]. *Cresorsellic acid.* Mol. w. 168. [245°]. S. ·86 at 0°. Formed by fusing di-sulpho-*o*-toluic acid with potash (Jacobsen, *B.* 16, 1960). Long needles, v. sol. alcohol and boiling water. $FeCl_3$ gives a brownish-black colour. Reduces alkaline Ag and Cu solutions. Conc. H_2SO_4 gives a bright-red colour on heating.—NH_4A' 2aq: prisms.

Di-oxy-toluic acid. *Methyl derivative* $C_6H_2Me(OMe)(OH).CO_2H$ [1:3:4:5]. *Creosol-carboxylic acid.* [182°]. Obtained by the action of CO_2 upon sodium creosol (Wende, *B.* 19, 2324). Concentric needles. Sublimable. V. sol. alcohol, ether, and chloroform, sl. sol. water, nearly insol. benzene. Gives a blue colouration with $FeCl_3$.

Salts. — NH_4A': needles. — KA': small readily soluble needles.—BaA'_2: small needles. —PbA'_2: white pp.—CuA'_2: yellow powder.

Methyl ether MeA': [92°]; small colourless trimetric crystals, $a:b:c = \cdot 5285:1:0\cdot 7334$. Gives a bluish-green colour with $FeCl_3$.

Ethyl ether EtA': [77°]; small needles.

Di-oxy-*m*-toluic acid $C_6H_2Me(OH)_2.CO_2H$ [1:2:4:3or5]. *Cresorcin carboxylic acid.* [208°]. Made by boiling cresorcin (di-oxy-toluene) (1 pt.) with $NaHCO_3$ (4 pts.) and water (8 pts.) (Kostanecki, *B.* 18, 3203). Prisms (containing aq), v. e. sol. water.—KA' 2aq: prisms, v. sol. water.

Di-oxy-*p*-toluic acid $C_6H_2Me(OH)_2CO_2H$ [4:5:3:1]. [176°]. Formed by heating disulpho-*p*-toluic acid with KOH (Weinreich, *B.* 20, 981). Needles, v. sol. water, alcohol, and ether.

Di-oxy-toluic acid $C_6H_2Me(OH)_2CO_2H$. *Hydrotoluquinone carboxylic acid.* [206°–210°]. S. ·07 at 8°. Formed by heating hydrotoluquinone with $KHCO_3$ and conc. K_2SO_3Aq at 160° (Brunner, *M.* 2, 458). Trimetric plates (from alcohol) or indistinct crystals (containing $\frac{1}{2}$aq) (from water), m. sol. hot water and alcohol. $FeCl_3$ gives a blue colour. Reduces ammoniacal $AgNO_3$ in the cold. Yields hydrotoluquinone on fusing. Conc. H_2SO_4 at 160° yields tetra-oxy-di-methyl-anthraquinone, a dark-red powder.— CaA'_2 2aq.—BaA'_2 2aq.—PbA'_2 2aq: crystalline.

Ethyl ether EtA'. [98°]. Needles.

Di-oxy-*p*-toluic acid $C_6H_2Me(OH)_2CO_2H$. *Orsellic acid. Orsellinic acid. Orsellesic acid.* [176°]. S. (ether) 22 at 20°. Formed by boiling lecanoric acid or erythrin with lime water, baryta-water, or NaOHAq (Stenhouse, *P.M.* [3] 32, 300; *Pr.* 12, 263; *A.* 68, 61; Hesse, *A.* 117, 312; 139, 35). Prisms (containing aq), v. e. sol. alcohol, sol. water. Splits up on fusion, or on boiling with water, into CO_2 and orcin. $FeCl_3$ gives a purple colour. Bromine gives tri-bromo-orcin. $POCl_3$ acting on the anhydrous acid at 90° forms a blue liquid which, when poured into water, ppts. $C_{40}H_{30}P_4O_{21}$, a blue substance with coppery lustre resembling indigo. The solutions of this 'phosphorsellic acid' in water and alcohol are intensely blue, and it is ppd. from aqueous solution by HCl, by H_2SO_4, and by NaCl. Phosphorsellic acid forms $C_{40}H_{22}Pb_7P_4O_{24}$ and $C_{40}H_{24}Pb_{11}P_4O_{34}$, an anilide $C_{40}H_{31}(NHPh)_2P_4O_{22}$ which gives $C_{80}H_{50}Pb_9(NHPh)_4P_8O_{44}$, and an acetyl derivative $C_{40}H_{33}Ac_3P_4O_{24}$ as a dark-violet mass which gives $C_{40}H_{25}(PbOH)_8Ac_3P_4O_{24}$ (Schiff, *A.* 228, 56).

Salt.—$Ba(C_8H_7O_4)_2$ *x*aq: prisms.

Methyl ether MeA'. Made by boiling lecanoric acid or erythrin with MeOH. Silky needles (from boiling water).

Ethyl ether EtA'. [132°]. Got in like manner (Heeren, *Schw. J.* 59, 341; Liebig, *P.* 21, 32; Kane, *Tr.* 1840, 237, 279; Schunck, *A.* 41, 160; 61, 72; Rochleder a. Heldt, *A.* 48, 5; Stenhouse, *C. J.* 20, 224; Strecker, *A.* 68, 111; Hesse, *A.* 117, 297). May be prepared by repeatedly exhausting *Roccella tinctoria* with boiling alcohol and evaporating the extract. Thin needles, nearly insol. cold water, v. sol. alcohol and alkalis. Yields $C_6Cl_2Me(OH)_2CO_2Et$ [162°] on chlorination.

Isoamyl ether $C_5H_{11}A'$. [76°]. Prisms.

Di-oxy-o-toluic acid $C_6H_2Me(OH)_2CO_2H$ [6:4:2:1]. *Paraorsellic acid.* [172°]. S. ·17 in the cold. Formed by heating orcin with a solution of ammonium carbonate, $KHCO_3$, or $NaHCO_3$ (Senhofer a. Brunner, *M.* 1, 236; Bistrzycki a. Kostanecki, *B.* 18, 1986), or by heating potassium orcin in a current of CO_2 at 250° (Schwarz, *B.* 13, 1643). Needles (containing aq), sl. sol. water, v. sol. alcohol and ether. $FeCl_3$ gives a blue colour. Boiling water decomposes it into CO_2 and orcin. $POCl_3$ followed by water gives $P_2(C_8H_6O_4)_5$, a chrome-green powder (Schiff, *A.* 228, 56).—KA'.—$BaA'_2$6aq.—$Ba_3(C_8H_5O_4)_2$8aq.— CuA'_2 4aq.—AgA': nearly insol. water.

Di-oxy-*m*-toluic acid $CH_2(OH).C_6H_3(OH).CO_2H$[3:2:1]. [142°]. Formed by reduction of aldehydo-o-oxy-benzoic acid with sodium-amalgam (Reimer, *B.* 11, 792). Prisms, v. sol. water, alcohol, and ether. $FeCl_3$ gives a violet colour. H_2SO_4 gives a red colour. Boiling HClAq resinifies it.

Di-oxy-*m*-toluic acid $CH_2(OH).C_6H_3(OH).CO_2H$[5:2:1]. [above 270°]. Formed by reduction of aldehydo-*p*-oxy-benzoic acid (R.). White powder, sl. sol. water. Not coloured by $FeCl_3$ or by H_2SO_4.

Di-oxy-*m*-toluic acid $CH_2(OH).C_6H_3(OH).CO_2H$[3:6.1]. Made by reducing aldehydo-o-oxy-benzoic acid (R.). Prisms (from ether), sl. sol. water, m. sol. alcohol and ether. $FeCl_3$ gives a violet colour. Oxidised by $KMnO_4$ to oxy-isophthalic acid, and by aqueous $K_2Cr_2O_7$ to aldehydo-oxy-benzoic acid.

References.—DI-BROMO-OXY-TOLUIC ACID and DI-IODO-ORSELLIC ACID.

OXY-o-TOLUIC ALDEHYDE $C_8H_8O_2$ *i.e.* $C_6H_3Me(OH).CHO$[2:4:1]. [110°]. Prepared, together with the (4,2,1)-isomeride, by heating *m*-cresol with chloroform and NaOHAq (Tiemann a. Schotten, *B.* 11, 773). Flat leaflets (from water), not volatile with steam. $FeCl_3$ gives a red colour.

Phenyl hydrazide $C_6H_3Me(OH).CH:N_2HPh$. [151°] (Paschen, *B.* 24, 3671).

Oxy-*m*-toluic aldehyde $C_6H_3Me(OH).CHO$ [3:4:1]. [115°]. Formed, together with the (3,2,1)-isomeride, by the action of chloroform and potash on *o*-cresol (Tiemann a. Schotten, *B.* 11, 772). Long prisms (from water), not volatile with steam. $FeCl_3$ gives a bluish-violet colour. Yields a nitro- derivative [152°].

Acetyl derivative $C_7H_6(OAc).CHO$. [40°]. (275°). Needles (Staats, *B.* 13, 138; Barbier, *Bl.* [2] 33, 52; *C. R.* 90, 37).

Oxy-*m*-toluic aldehyde $C_6H_3Me(OH).CHO$ [3:2:1]. [17°]. (209°). Formed as above (T. a. S.).

Crystals, volatile with steam. $FeCl_3$ gives a bluish colour. Forms a yellow solution in NH_3Aq.

Acetyl derivative $C_{10}H_{10}O_3$. (267°) (B.).

Oxim. [99°] (Paschen, *B.* 24, 3668).

Phenyl hydrazide. [95°]. Tables.

Oxy-*m*-toluic aldehyde $C_6H_3Me(OH).CHO$ [3:6:1]. [56°]. (218°). Formed by the action of $CHCl_3$ and KOH on *p*-cresol (T. a. S.). White leaflets. $FeCl_3$ gives a green colour. Yields a nitro- derivative [141°].

Acetyl derivative $C_6H_3Me(OAc).CHO$. [57°]. Long needles. Made by the action of Ac_2O on the ethereal solution of the K salt. Combines with $NaHSO_3$. With Ac_2O it unites in the cold, forming $C_6H_3Me(OAc).CH(OAc)_2$, which crystallises in prisms [94°] and does not combine with $NaHSO_3$.

Methyl derivative $C_6H_3Me(OMe).CHO$. (254°). Colourless liquid.

Oxim $C_6H_3Me(OH).CH:NOH$. [105°]. Needles (Goldbeck, *B.* 24, 3658).

Oxy-*p*-toluic aldehyde $C_6H_3Me(OH).CHO$ [4:2:1]. [54°]. (223°). Made, together with the (2,4,1)-isomeride, by the action of chloroform and potash on *m*-cresol (T. a. S.). Crystals, volatile with steam. $FeCl_3$ gives a violet colour.

Di-oxy-o-toluic aldehyde $C_6H_2Me(OH)_2CHO$ [6:4:2:1]. *Orcyl aldehyde.* [178°]. Formed by heating orcin with chloroform and potash (Tiemann a. Helkenberg, *B.* 12, 999), and also by potash-fusion from methyl-umbelliferone (Pechmann a. Welsh, *B.* 17, 1646). Needles, sol. alcohol and hot water. $FeCl_3$ gives a reddish-brown colour. Aniline forms the compound $C_6H_2Me(OH)_2CH:NPh$ [126°], crystallising in yellow prisms.

Di-oxy-*m*-toluic aldehyde. *Methyl derivative* $C_6H_2Me(OH)(OMe)CHO$ [5:2:3:1]. (270°–275°). Formed by the action of chloroform and NaOHAq upon creosol (Tiemann a. Koppe, *B.* 14, 2026). Oil, sol. alcohol. $FeCl_3$ colours its alcoholic solution green.

OXY-TOLUIDINE *v.* Amido-cresol.

OXY-TOLUQUINOLINE *v.* Oxy-methyl-quinoline.

DI-OXY-TOLUQUINONE $C_6HMe(OH)_2O_2$. [177°]. Made by digesting oxy-phenylamido-toluquinone anilide with dilute KOHAq (Hagen a. Zincke, *B.* 16, 1562). Brownish-yellow plates, v. sol. most solvents. May be sublimed.

Tri-oxy-toluquinone $C_6Me(OH)_3O_2$. Formed from tri-amido-orcin by treatment with $FeCl_3$, the resulting amido-diimido-orcin being heated with HClAq at 150° (Merz a. Zetter, *B.* 12, 2044). Dark crystals, nearly insol. cold alcohol. Yields a crystalline tri-acetyl derivative.

Reference.—Di-bromo- and Di-chloro- oxy-toluquinone.

OXY-TOLUQUINOXALINE

$\left[1^{3}_{4}\right]C_6H_3Me\Big<\begin{matrix}N:CO.H\\N:CH\end{matrix}$. [267°]. Formed by oxidation of its dihydride [c. 127°], which is got by condensing tolylene-diamine with chloro-acetic ether (Hinsberg, *B.* 18, 2870; *A.* 248, 75), or by reducing nitro-tolyl-amido-acetic acid (Plöchl, *B.* 19, 6). Yields a methyl derivative [71°], and an ethyl derivative [67°].

Isomeride *v.* Oxy-methyl-quinoxaline.

Di-oxy-toluquinoxaline $C_6H_3Me\Big<\begin{matrix}N:C.OH\\N:C.OH\end{matrix}$. [above 300°]. Formed by heating tolylene-o-diamine with oxalic acid at 150° (Hinsberg, *B.* 15, 2690; *A.* 237, 348) by reducing nitro-tolyl-oxamic acid, and by heating tolylene-diamine dicyanide with HClAq at 150° (Bladin, *B.* 18, 670). Needles.—$NaHA''$.—Ag_2A''.—H_2A'' HOAc. Plates.

DI-OXY-DITOLYL

[3:4:1] $C_6H_3Me(OH).C_6H_3Me(OH)$ [1:3:4]. *o-Di-cresol.* [157°] (H.); [161°] (G.). Made from di-amido-ditolyl by the diazo- reaction (Gerber, *B.* 21, 749; Hobbs, *B.* 21, 1067). Needles, sl. sol. hot water, v. sol. alcohol and ether. Yields a di-nitro- derivative [273°].

Di-acetyl derivative $C_{14}H_{12}(OAc)_2$. [131°].

Di-benzoyl derivative [185°]. Needles.

Di-ethyl ether $C_{14}H_{12}(OEt)_2$. [156°]. Made, together with ditolyl, by the action of alcohol on di-amido-ditolyl (Schultz, *B.* 17, 468). White plates, sol. hot alcohol.

Di-propyl ether. [115°]. Leaflets.

Di-isoamyl ether. [69°].

Tetra-oxy-ditolyl $C_{14}H_{14}O_4$ *i.e.* [1:2:5:6]$C_6H_2Me(OH)_2.C_6H_2Me(OH)_2$[6:1:2:5]. [202° uncor.]. Formed by oxidising hydrotoluquinone, dissolved in HOAc with MnO_2 and H_2SO_4 in the cold (Brunner, *M.* 10, 174). $FeCl_3$ oxidises it to the quinhydrone $C_{28}H_{24}O_8$, crystallising in violet scales [220° uncor.], and finally to the quinone $C_{14}H_{10}O_4$ [163°], crystallising in yellow prisms.

Tetra-acetyl derivative $C_{14}H_{10}(OAc)_4$. [135°]. Made by heating with NaOAc and Ac_2O at 160°. Needles.

Anhydride $C_{12}H_4Me_2(OH)_2O$. [232°]. Got by heating $C_{12}H_4Me_2(OMe)_2O_2$ with HClAq at 180° (Nietzki, *B.* 11, 1281). Colourless plates (containing aq) (from dilute alcohol).

Di-methyl ether $C_{12}H_4Me_2(OMe)_2(OH)_2$. [173°]. Formed by partial methylation. Colourless needles, quickly oxidised in alcoholic solution by air. Yields a di-acetyl derivative $C_{12}H_4(Me(OMe)(OAc)[6:1:2:5])_2$, crystallising in needles [123°] (Noelting a. Werner, *B.* 23, 3248).

Dehydride of the di-methyl ether $C_{16}H_{16}O_4$ *i.e.* $C_{12}H_4Me_2(OMe)_2O_2$. [153°]. Formed by oxidation of the di-methyl ether of hydrotoluquinone by chromic acid mixture (Nietzki, *A.* 215, 161). Dark-red needles (from alcohol).

Tetra-methyl ether $C_{14}H_{10}(OMe)_4$. [129°].

Di-ethyl ether $C_{14}H_{10}(OEt)_2(OH)_2$. [133°]. Formed by the action of alcoholic ammonium sulphide on the dehydride (or quinone) $C_{14}H_{10}(OEt)_2O_2$, which crystallises in green-black needles [139°], and is made by oxidising $C_6H_3Me(OEt)_2$ with chromic acid mixture (Noelting, *B.* 23, 3247; *Bl.* [3] 4, 805). White needles.

α-OXY-*m*-TOLYL-ACETIC ACID $C_9H_{10}O_3$ *i.e.* [1:3]$C_6H_4Me.CH(OH).CO_2H$. *m-Methyl-mandelic acid.* [84°]. Formed from *m*-toluic aldehyde, KCy, and HCl (Bornemann, *B.* 17, 1469). Small plates (from benzene), v. sol. water.

α-Oxy-*p*-tolyl-acetic acid [1:4]$C_6H_4Me.CH(OH).CO_2H$. [146°]. Made by reduction of *p*-tolyl-glyoxylic acid by zinc-dust and ammonia (Claus a. Kroseberg, *B.* 20, 2050). Tables (from water).—NaA'.—KA' ½aq.—CaA'_2.—BaA'_2 ½aq.

Ethyl ether EtA'. [77°]. Needles.

ω-OXYTOLYL-ALLYL-THIO-UREA

[1:2]$C_6H_4(CH_2OH).NH.CS.NH.C_3H_5$.

Formed from *o*-amido-benzyl alcohol and allyl

thiocarbimide in benzene. Oil, changed by warming with HClAq to $C_6H_4<\begin{smallmatrix}CH_2.NC_3H_5\\NH.CS\end{smallmatrix}$. [91°]. Converted by HgO in alcohol to oxy-allyl-quinazoline dihydride $C_6H_4<\begin{smallmatrix}CH_2.NC_3H_5\\NH.CO\end{smallmatrix}$, which crystallises in four-sided prisms [78°], and yields $B'_2H_2PtCl_6$ [171°] (Söderbaum a. Widmann, *B.* 22, 1670, 2937).

OXY-TOLYL-BENZYLIDENE-TOLYLENE-DIAMINE $C_{21}H_{20}N_2O$ *i.e.* $C_7H_7.NH.C_7H_6.N:CH.C_6H_4.OH$. [160°]. Made from o-amido-di-*p*-tolyl-amine and salicylic aldehyde (O. Fischer a. Sieder, *B.* 23, 3801). Yellow crystals, sl. sol. water, v. sol. benzene.

OXY-*p*-TOLYL-BENZYL-METHYL-PYRIMIDINE $C_6H_4Me.C<\begin{smallmatrix}N.CMe\\N:C(OH)\end{smallmatrix}>C.CH_2Ph$. [240°]. Made from *p*-tolenyl-amidine hydrochloride and benzyl-aceto-acetic ether (Pinner, *B.* 23, 3826). Slender needles (from pyridine), insol. water, v. sl. sol. hot alcohol.

OXY-TOLYL-CARBINOL $C_6H_3Me(OH).CH_2OH$[5:2:1]. [105°]. S. 6·7 at 15°. Made by reduction of (2,5,1)-oxytoluic aldehyde with sodium amalgam (Schotten, *B.* 11, 784). Colourless leaflets.

TRI-OXY-TRI-TOLYL-CARBINOL. *Anhydride* $C_{22}H_{20}O_3$ *i.e.* $(C_6H_3Me(OH))_2C<\begin{smallmatrix}C_6H_3Me\\O\end{smallmatrix}$. *Cresaurin.* Formed by heating *p*-cresol with formic acid and $ZnCl_2$ at 110° (Nencki, *J. pr.* [2] 25, 275). Red amorphous powder, insol. water, v. sol. HOAc. Forms a crimson solution in alkalis.

DI-OXY-DITOLYL DICARBOXYLIC ACID $C_{16}H_{14}O_6$. Made by heating sodium di-oxy-ditolyl with CO_2 in a closed vessel at 160° (Deninger, *B.* 21, 1639). Crystals, insol. water, sl. sol. alcohol and ether. Not melted at 290°. $FeCl_3$ gives a blue colour. Yields a di-acetyl derivative $C_{20}H_{18}O_8$ [163°].

OXY-TOLYL-CROTONIC ACID. *Anhydride v.* DI-METHYL-COUMARIN.

Di-oxy-tolyl-crotonic acid. *Anhydride* $C_6H_2Me(OH)<\begin{smallmatrix}CMe:CH\\O—CO\end{smallmatrix}$. *Di-methyl-umbelliferone.* [250°]. Made by the action of H_2SO_4 on a mixture of acetoacetic ether and orcin (Pechmann a. Cohen, *B.* 17, 2188). Needles (from alcohol), nearly insol. water. On boiling with $NaHSO_3$ it forms a solution coloured red by $FeCl_3$.

Acetyl derivative $C_{11}H_9AcO_3$. [195°]. Needles, v. sol. alcohol.

TRI-OXY-TRI-TOLYL-ETHANE $C_6H_3Me(OH).CH_2.CH(C_6H_3Me.OH)_2$. Three isomerides with this formula are got by warming di-chloro-ethyl ether with o-, *m*-, and *p*- cresol respectively (Brückner, *A.* 257, 322). They are amorphous powders, v. sol. alcohol and ether, insol. water, and yield tri-acetyl derivatives which are oxidised by $FeCl_3$ to anhydrides $[C_6H_3Me(OH).CH_2.C(C_6H_3Me(OH))_2]_2O$.

OXY-TOLYL-HYDRAZINE. *Methyl derivative* [1:4:3] $C_6H_3Me(OMe).NH.NH_2$. [45°]. Got from the methyl ether of amido-*p*-cresol by treatment with nitrous acid and subsequent reduction (Limpach, *B.* 22, 351). Crystalline.

Oxy-o*m*-di-tolyl-hydrazine. *Ethyl derivative* [2:1]$C_6H_4Me.NH.NH.C_6H_3Me(OEt)$[1:3:4]. [78°]. Made by reducing the azo- compound with alcoholic ammonium sulphide (Noelting a. Werner, *B.* 23, 3260; *Bl.* [2] 4, 796). White crystals, insol. water, sol. alcohol.

The isomerides [2:1]$C_6H_4Me.NH.NH.C_6H_3Me(OEt)$[1:5:2] [138°], [4:1]$C_6H_4Me.NH.NH.C_6H_3Me(OEt)$[1:3:4] [87°], and [4:1]$C_6H_4Me.NH.NH.C_6H_3Me(OEt)$[1:5:2] [153°] are formed in like manner.

DI-OXY-DI-TOLYL KETONE $C_{15}H_{14}O_3$ *i.e.* $C_6H_3Me(OH).CO.C_6H_3Me(OH)$. [138°]. Got by potash-fusion from o-cresol-benzeïn, which is a product of the action of benzotrichloride on o-cresol (Schroeter, *A.* 257, 74). Colourless needles, v. sol. alcohol and ether.

Di-oxy-di-tolyl ketone $CO(C_6H_3Me.OH)_2$. [104°]. Made from *p*-cresol-phthaleïn $C_{22}H_{16}O_3$ by potash-fusion (Drewson, *A.* 212, 344). Yellow needles (from alcohol), insol. water, v. sol. alkalis.

OXY-*p*-TOLYL-METHYL-ETHYL-PYRIMIDINE $C_6H_4Me.C<\begin{smallmatrix}N.CMe\\N:C(OH)\end{smallmatrix}>CEt$. [218°]. Made from *p*-tolenyl-amidine and ethyl-acetoacetic ether (Pinner, *B.* 23, 3826). Hair-like needles, m. sol. hot alcohol.

OXY-TOLYL METHYL KETONE $C_9H_{10}O_2$ *i.e.* [1:2:5]$C_6H_3Me(OH).CO.CH_3$. [104°]. Formed from amido-*m*-tolyl methyl ketone by the diazo-reaction (Klingel, *B.* 18, 2699). Flat white prisms, v. sol. alcohol and hot water. $FeCl_3$ gives a yellowish-brown colour.

Di-oxy-tolyl methyl ketone $C_6H_2Me(OH)_2.CO.CH_3$. [146°]. Made from orcin, HOAc, and $POCl_3$ (Rasinsky, *J. pr.* [2] 26, 59). Needles, v. sol. alcohol, ether, and HOAc. $FeCl_3$ colours its aqueous solution black.

OXY-o-TOLYL-METHYL-PYRAZOLE $C_{11}H_{12}N_2O$ *i.e.* $C_6H_4Me.N<\begin{smallmatrix}CO.CH_2\\N=CMe\end{smallmatrix}$. [183°]. Formed by heating o-tolyl-hydrazine with aceto-acetic ether at 140° (Knorr, *B.* 17, 549). Colourless crystals. With KOH and MeI it yields $C_{11}H_{11}MeN_2O$ [97°].

Oxy-*p*-tolyl-methyl-pyrazole $C_{11}H_{12}N_2O$. [140°]. From *p*-tolyl-hydrazine and acetoacetic ether (K.). Yields a methyl derivative [137°]. The compound $C_7H_7.N<\begin{smallmatrix}CO.C:N.NHC_7H_7\\N=CMe\end{smallmatrix}$ [217°] is formed, together with $C_{22}H_{22}N_4O_2$ by heating *p*-tolyl-hydrazine with thio-acetoacetic ether (Buchka a. Sprague, *B.* 22, 2555; *C. J.* 59, 340).

OXY-TOLYL-METHYL-PYRIMIDINE $C_6H_4Me.C<\begin{smallmatrix}N.CMe\\N:C(OH)\end{smallmatrix}>CH$. [216°]. Made from tolenyl-amidine and acetoacetic ether (Glock, *B.* 21, 2658). Long white needles, m. sol. hot alcohol. — Salts: $B'_2H_2PtCl_6$ 2aq. [241°]. — $B'_2H_2Cr_2O_7$ 7aq. [c. 170°]. Yellow plates. — $B'C_6H_3N_3O_7$. [196°]. Yellow needles.

β-OXY-TOLYL-DIPHENYL-ETHYLIDENE-AMINE $C_7H_7N:CPh.CHPh.OH$. [141°]. Made by heating benzoïn with o-toluidine at 150° (Bandrovski, *M.* 9, 693). Canary-yellow needles.

OXY-TOLYL-PROPIONIC ACID $C_{10}H_{12}O_3$ *i.e.* $CH_3.C(C_7H_7)(OH).CO_2H$. Got from di-bromo-oxy-tolyl-propionic acid $CHBr_2.C(C_7H_7)(OH).CO_2H$ by reducing with sodium-amalgam (Bottinger, *B.* 14, 1598). Long four-sided tables, v. sol. water.

OXY-DI-*p*-TOLYL-PYRAZINE. *Tetrahydride* $C_6H_4Me.N\langle{}^{CH_2.CH_2}_{CH_2.CO}\rangle N.C_6H_4Me$. '*Ditolylmonoacipiperazine.*' [168·5°]. Made from *p*-toluidine by successive treatment with ethylene bromide and a mixture of chloro-acetic acid and NaOAc (Bischoff, *B.* 22, 1785; 23, 2035). Crystals, v. sol. water and ether.

Di-oxy-di-o-tolyl-pyrazine. *Dihydride* $C_6H_4Me.N\langle{}^{CH_2.CH_2}_{CO\ .CO}\rangle N.C_6H_4Me$. *Ditolyldiacipiperazine.* [184°]. Formed from di-*o*-tolyl-ethylene-diamine and oxalic acid at 200° (Bischoff, *B.* 22, 1805; 23, 2034).

Di-oxy-di-*p*-tolyl-pyrazine dihydride. [263°]. Made by dissolving oxy-di-*p*-tolyl-pyrazine tetrahydride in HOAc and oxidising with nitrous or chromic acid (B.). Colourless plates, v. sol. aniline and alcohol, sl. sol. ether and hot water. Alcoholic potash yields di-tolyl-ethylene-diamine [97°] and oxalic acid.

Di-oxy-*s*-di-o-tolyl-pyrazine. *Dihydride* $C_6H_4Me.N\langle{}^{CO\ .CH_2}_{CH_2.CO}\rangle N.C_6H_4Me$. [160°]. Formed by heating o-tolyl-amido-acetic acid at 220° (Bischoff a. Nastvogel, *B.* 22, 1787) and by the action of potash on the product of the action of chloro-acetyl chloride on o-toluidine (Widman, *J. pr.* [2] 38, 299, 305). Rectangular plates (from alcohol), insol. water, sol. conc. HClAq.

Reactions.—1. PCl_5 forms the compound $C_7H_7.N\langle{}^{CO.CCl—}_{—CCl.CO}\rangle N.C_7H_7$ crystallising from alcohol in white needles [201°].—2. *Alcoholic potash* forms $C_7H_7N(CH_2.CO_2H).CO.CH_2.NHC_7H_7$, a white crystalline solid [129°] decomposed by conc. HClAq at 160° into MeCl, o-toluidine, and $C_7H_7NH.CH_2.CO_2H$.

Salt.—$(C_{18}H_{18}N_2O_2)_2H_2PtCl_6$ 4aq. [176°].

Di-oxy-di-*p*-tolyl-pyrazine. *Dihydride.* [253°]. Formed from oxalic acid and *p*-tolyl-amido-acetic *p*-toluide (B. a. N.). Made also by boiling the bromo-acetyl derivative of *p*-toluidine with alcoholic potash, or by heating *p*-tolyl-amido-acetic acid at 200° (Abenius, *J. pr.* [2] 40, 433). Long white needles, insol. water, m. sol. alcohol.

Di-oxy-*op*-di-tolyl-pyrazine. *Dihydride* $[1:2]C_6H_4Me.N\langle{}^{C(OH):CH}_{CH:C(OH)}\rangle N.C_6H_4Me[1:4]$. [180°]. Made by heating *p*-toluidine with the chloro-acetyl derivative of o-tolyl-amido-acetic acid at 140° (Abenius, *J. pr.* [2] 40, 443). White matted needles, v. sol. hot alcohol, insol. ether.

Tetra-oxy-di-phenyl-pyrazine. *Dihydride of the di-ethyl derivative* $[1:4]C_6H_4(OEt).N\langle{}^{CH_2.CO}_{CO\ .CH_2}\rangle N.C_6H_4(OEt)[4:1]$. [265°]. Slender needles.

OXY-*p*-TOLYL-QUINAZOLINE $C_{15}H_{12}N_2O$ *i.e.* $C_6H_4\langle{}^{N\ :CH}_{CO.N.C_6H_4Me}$. [146°]. Made by oxidising *p*-tolyl-quinazoline dihydride with $KMnO_4$ (Paal a. Busch, *B.* 22, 2698). Plates (from dilute alcohol) or needles (from ether), sl. sol. hot water. Does not react with hydroxylamine or phenyl-hydrazine.—B'HCl. [214°]. Needles.—$B'_2H_2PtCl_6$. [above 300°]. Golden plates, sol. alcoholic HCl.

OXY-(*Py.* 3)-TOLYL-QUINOLINE $C_{16}H_{13}NO$ *i.e.* $C_6H_4\langle{}^{CH:CH}_{N\ :C.C_6H_3Me(OH)}$. *ψ-Flavenol.* [196°]. Got by the diazo- reaction from (4,3,1)-amido-tolyl-quinoline (Weidel a. Bamberger, *M.* 9, 104). Small plates (from alcohol). Yields (*Py.* 3)-tolyl-quinoline on distillation with zinc-dust. Reduction followed by potash-fusion yields oxy-isophthalic acid.—B'HCl 2aq.—$B'_2H_2PtCl_6$ (dried at 105°). Yellow needles.

Acetyl derivative $C_{18}H_{15}NO_2$. [106°].

Di-oxy-tolyl-quinoline $C_{16}H_{13}NO_2$. [89°]. Formed, as well as oxy-tolyl-quinoline, by the above method of preparation. Plates (from alcohol), sol. benzene.

DI-OXY-DI-o-TOLYL SULPHIDE $C_{14}H_{14}SO_2$ *i.e.* $S(C_6H_3Me(OH)[2:1:4])_2$. *Dioxythiotoluene.* [135°]. Formed from di-amido-di-tolyl sulphide by the diazo- reaction (Truhlar, *B.* 20, 676). Amorphous, sl. sol. water, alcohol, and ether.

Di-oxy-di-tolyl sulphide. [210°–215°]. Formed from *m*-cresol by treatment with SCl_2 in CS_2 (Tassinari, *G.* 17, 92; *C. C.* 1888, 1354). Yields an acetyl derivative [44°], which forms, on oxidation, the corresponding sulphone [263°], which on saponification gives $SO_2(C_7H_6OH)_2$ [133°].

Di-oxy-di-tolyl sulphide. [118°]. Formed from *p*-cresol and SCl_2. Yields an acetyl derivative [84°] which is oxidised by $KMnO_4$ to a sulphone [209°], which on saponification gives $SO_2(C_7H_6OH)_2$ [209°] (Tassinari, *Rend. Accad. Linc.* [4] 4, 47).

ν-OXY-o-TOLYL-THIO-UREA $C_8H_{10}N_2SO$ *i.e.* $C_6H_4Me.NH.CS.NH.OH$. [92°]. Formed from o-tolyl-thiocarbimide and hydroxylamine in chloroform solution (Tiemann, *B.* 22, 1939; Voltmer, *B.* 24, 381). Slender needles, almost insol. chloroform and water, sol. alcohol, ether, and KOHAq. $FeCl_3$ colours its alcoholic solution violet. Yields o-tolyl-cyanamide on long standing.

Benzyl ether $C_6H_4Me.NH.CS.NH.OCH_2Ph$. [125°]. Made from benzyl-hydroxylamine and o-tolyl-thiocarbimide.

ω-OXY-o-TOLYL-UREA $C_8H_{10}N_2O_2$ *i.e.* $CH_2(OH).C_6H_4.NH.CO.NH_2$. [c. 180°]. Formed from amido-benzyl alcohol, potassium cyanate, and HCl (Söderbaum a. Widman, *B.* 22, 1668). Tables or prisms, m. sol. boiling water, v. sl. sol. alcohol. Decomposes on fusion, yielding di-oxy-di-tolyl-urea $CO(NH.C_6H_4.CH_2OH)_2$ [108°], which crystallises in needles.

OXYTROPINE $C_8H_{15}NO_2$. [242°]. A base occurring in crude belladonnine (Merling, *B.* 17, 384; Ladenburg, *B.* 17, 153). Crystalline.—$B'_2H_2PtCl_6$ *x*aq: red prisms.

OXY-TRUXILLIC ACID $(C_6H_4(OH).CH:CH.CO_2H)_x$. [273°]. Formed by potash-fusion from (α)-sulpho-truxillic acid (Liebermann a. Bergami, *B.* 22, 783). Prisms, m. sol. cold water. Probably a polymeride of *p*-coumaric acid. An isomeric acid, formed from the amido- acid by the diazo- reaction, does not melt at 360°. It yields an acetyl derivative [244°] (Homans, *B.* 24, 2591).

OXY-URAMIDO-BENZOIC ACID. *Methyl derivative* $NH_2.CO.NH.C_6H_3(OMe).CO_2H$. *Anisuramic acid.* S. ·05 at 100°. Formed from potassium cyanate and a solution of the hydrochloride of amido-anisic acid (Menschutkin, *A.* 153, 99). Needles (from water).—CaA'_2 7aq.

OXY-UREA $NH_2.CO.NH.OH$. [130°]. Formed from aqueous hydroxylamine nitrate and potas-

sium cyanate in the cold (Dressler a. Stein, *Z.* [2] 5, 202). Needles (from alcohol) v. e. sol. Aq. Decomposed by heating, yielding urea. Reduces $AgNO_3$. $FeCl_3$ gives a blue-violet colour.—$KH(CH_3N_2O_2)_2$: crystalline pp., got by adding alcoholic potash to the alcoholic solution (Hodges, *A.* 182, 214).—$(Pb_2H(OAc)_2(CH_3N_2O_2)_3$: crystals.—$(CuCH_2N_2O_2)_4HOAc$: green mass.

Benzyl ether $NH_2.CO.NH.OCH_2Ph$. [138°]. Formed from (α)-benzyl hydroxylamine hydrochloride and potassium cyanate (Behrend a. Leuchs, *A.* 257, 203). Needles.

Oxy-biuret $C_2H_5N_3O_3$. [134°]. Formed from conc. hydroxylamine sulphate and potassium cyanate, the mixture being evaporated with alcohol. Minute four-sided prisms, sol. water and alcohol. Gives a white pp. with $AgNO_3$. Reduces warm ammoniacal $AgNO_3$. $FeCl_3$ gives no colour.—$KC_4H_9N_6O_6$: minute needles.

(α) - OXY - UVITIC ACID $C_9H_8O_5$ *i.e.* $C_6H_2Me(OH)(CO_2H)_2$ [1:2:3:5]. *Cresol dicarboxylic acid.* [285°] (B.); [295°] (H. a. R.); [278°] (J.). Formed from (α)-amido-uvitic acid by the diazo- reaction (Böttinger, *B.* 9, 804; 13, 1934; *A.* 189, 177) and by potash-fusion from sulpho-uvitic acid (Jacobsen, *A.* 206, 187; Hall a. Remsen, *Am.* 2, 137). Needles (from alcohol), v. sol. alcohol, insol. chloroform. Decomposes on fusion. Conc. HClAq at 200° yields o-cresol. $FeCl_3$ gives a purple colour.—$Ca(HA'')_2$ 2aq.—CaA'' 2aq.—CaA'' 4aq.—$Ca_3(C_9H_5O_5)_2$.—Ag_2A''.

Methyl ether Me_2A''. [128°]. Needles.

Mono-ethyl ether EtHA''aq. Needles.

(β)-Oxy-uvitic acid $C_6H_2Me(OH)(CO_2H)_2$ [1:4:3:5]. [225°–235°] (J.); [220°] (B.). S. ·13 at 12°; 5·2 at 100° (J.). Formed by the action of nitrous acid on (β)-amido-uvitic acid (Böttinger). Formed also by potash-fusion from *s*-mesitol $C_6H_2Me_3.OH$ and from oxy-mesitylenic acid (Jacobsen, *A.* 195, 285). Needles (from water), v. sol. alcohol and ether. $FeCl_3$ gives a red colour. HClAq at 200° forms *p*-cresol (J.).—Ag_2A'': prisms.

Methyl ether Me_2A''. [79°]. Needles.

Oxy-*i*-uvitic acid $C_6H_2Me(OH)(CO_2H)_2$ [1:3:4:6]. Got by saponification of its ether which is formed from sodium acetoacetic ether by the action, in presence of NaOEt, of chloroform, chloral, trichloro-acetic ether, or CCl_4 (Oppenheim a. Pfaff, *B.* 7, 929; 8, 884; 9, 321; Conrad a. Guthzeit, *A.* 222, 249). Needles, sl. sol. cold water, v. sol. alcohol and ether. $FeCl_3$ gives a reddish-violet colour. Softens at 290°, decomposing at the same time. Yields *m*-cresol on distillation with lime. PCl_5 forms a mixture of chlorides, whence water forms oxyuvitic acid and $C_{18}H_{14}O_9$ crystallising in needles.—K_2A'' aq.—BaA'' $1\frac{1}{2}$aq.—CaA'' $1\frac{1}{2}$aq.—CuA''.—Ag_2A''.

Methyl ether Me_2A''. [108°]. Plates.

α-OXY-VALERIC ACID $C_5H_{10}O_3$ *i.e.* $CH_3.CH_2.CH_2.CH(OH).CO_2H$. [31°]. Formed by the action of HClAq on its nitrile, which is the cyanhydrin of *n*-butyric aldehyde (Menozzi, *G.* 14, 46). Got also by boiling α-bromo-butyric ether with aqueous Na_2CO_3 (Juslin, *B.* 17, 2504). Silky hygroscopic laminæ, v. sol. water, alcohol and ether.—BaA'_2 $\frac{1}{2}$aq: plates.—CaA'_2. S. 3·6 at 100°.—ZnA'_2 2aq. S. 1·01 at 100°.—CdA'_2.—CuA'_2.—AgA': small scales, sl. sol. cold water.

Ethyl ether EtA'. (190°). Oil.

α-Oxy-isovaleric acid $(CH_3)_2CH.CH(OH).CO_2H$. [83°].

Formation.—1. By heating bromo-isovaleric acid with Ag_2O and water (Clark a. Fittig, *A.* 139, 199) or with KOHAq (Ley a. Popoff, *A.* 174, 61; Schmidt a. Sachtleben, *A.* 193, 87).—2. By digesting chloro-isovaleric acid with baryta-water (Schlebusch, *A.* 141, 322).—3. From its ether, which is a product of the action of zinc and isopropyl iodide on oxalic ether (Markownikoff, *Z.* 1870, 517).—4. From its nitrile, which is made by combination of HCy with isobutyric aldehyde (Lipp, *A.* 205, 24).

Properties.—Rectangular tables, v. sol. water, alcohol, and ether. Not deliquescent. Volatile with steam. Dilute H_2SO_4 at 140° splits it up into isobutyric aldehyde and formic acid.

Salts.—NaA'.—BaA'_2.—ZnA'_2.—CaA'_2 aq.—CaA'_2 $1\frac{1}{2}$aq.—CaA'_2 4aq.—MgA'_2 2aq.—CuA'_2aq.—AgA': feathery crystals (from hot water).

Ethyl ether EtA'. (175°). Oil.

Anhydride $C_5H_8O_2$. *Valerolactide.* [126°]. (220°–240°). Made by heating the acid in sealed tubes at 200°. Needles, v. sol. alcohol and ether. Not attacked by dilute alkaline solutions.

Amide $Pr.CH(OH).CONH_2$. [104°]. Got from the nitrile and HClAq. Crystals.

Nitrile Pr.CH(OH).CN. S.G. $\frac{0}{0}$ ·96. Oil, decomposed at 136° into isobutyric aldehyde and HCy.

α-Oxy-valeric acid $CMeEt(OH).CO_2H$. [68°] (M.); [66°] (B.).

Formation.—1. By saponification of its ether, which is made by the action of zinc on a mixture of MeI, EtI and oxalic ether (Frankland a. Duppa, *A.* 135, 37).—2. By boiling $CEtMeBr.CO_2H$ with baryta-water (Böcking, *A.* 204, 14).—3. From methyl ethyl ketone by combination with HCy and saponification of the resulting nitrile (B.).—4. By oxidation of $CMeEtH.CO_2H$ with dilute $KMnO_4$ (Miller, *A.* 200, 282).

Properties.—Needles (by sublimation), v. e. sol. water, alcohol, and ether. Oxidised to methyl ethyl ketone by chromic acid mixture. Reduced by HI to $CMeEtH.CO_2H$. Rotates on water.

Salts.—ZnA'_2.—AgA'. Nodules.

Ethyl ether EtA'. (165·5°). S.G. $\frac{13}{}$ ·977. V.D. 4·98 (calc. 5·04). Liquid, sol. water.

β-Oxy-isovaleric acid $(CH_3)_2C(OH).CH_2.CO_2H$.

Formation.—1. By oxidation of the alcohol $CMe_2(C_3H_5).OH$ with cold chromic acid mixture (Saytzeff, *A.* 185, 163; 197, 73), or with $KMnO_4$ at 0° (Schirokoff, *J. pr.* [2] 23, 206).—2. By the action of zinc on a mixture of acetone and chloro-acetic ether (Reformatsky, *B.* 20, 1210).—3. By oxidation of tri-oxy-hexane by $KMnO_4$ (Reformatsky, *J. pr.* [2] 40, 404).

Properties.—Syrup, v. sol. water, alcohol, and ether. Not volatile with steam. Reduced by HI to isovaleric acid.

Salts.—CaA'_2 12aq.—CuA'_2.—CuA'_2 2aq.—AgA': monoclinic crystals, sl. sol. water.

Ethyl ether EtA'. (180°).

β-Oxy-valeric acid $CH_3.CH(OH).CHMe.CO_2H$. Formed by reduction of methyl-acetoacetic ether with sodium-amalgam (Rohrbeck, *A.* 188, 229). Syrup, resolved by distillation into water and methyl-crotonic acid [62°].—NaA' (dried at 100°). [210°] (Miller, *A.*

200, 269). Crystalline powder.—BaA'_2aq.—AgA': laminæ, sl. sol. hot water.

(γ)-Oxy-valeric acid $CH_3.CH(OH).CH_2.CH_2.CO_2H$. The salts of this acid are made by dissolving the lactone in bases. The free acid quickly changes back to the lactone.

Salts.—The Ba and Ca salts are deliquescent amorphous masses.—AgA': triclinic needles.

Ethyl ether EtA'. Oil.

Lactone $CH_3.CH<\begin{matrix}CH_2.CH_2\\O-CO\end{matrix}$. (208° i.V.). S.G. $\frac{0}{}$ 1·072. Occurs in crude wood-vinegar (Grodski, *B.* 17, 1369). Prepared by boiling γ-bromo-valeric acid with water (Messerschmidt, *A.* 208, 96), and by reduction of acetyl-propionic (levulic) acid with sodium-amalgam (Wolff, *A.* 208, 104). Formed also by heating γ-oxy-propyl-malonic acid (Hjelt, *A.* 216, 56), and by the action of NaOHAq on nitroso-oxy-methyl-pyrrole dihydride (Tafel, *B.* 22, 1864). Liquid, miscible with water. Neutral to litmus. Separated from solution by K_2CO_3. Reduced by HI and P at 250° to *n*-valeric acid. Oxidised by HNO_3 to succinic acid. Boiling alcoholic NaOEt forms $C_{10}H_{14}O_3$ [c. 32°] (Fittig, *A.* 256, 126). Phenyl-hydrazine forms $C_{11}H_{16}N_2O_2$ [76°–79°], crystallising in needles, v. sol. water (W. Wislicenus, *B.* 20, 402).

Amide $CH_3.CH(OH).CH_2.CH_2.CONH_2$. [56°]. Formed by heating the lactone or the ether with NH_3Aq. Thin plates, v. e. sol. water and alcohol, sl. sol. ether. At 170° it is split up into NH_3 and the lactone (Neugebauer, *A.* 227, 97).

Di-oxy-valeric acid $CH_3.CH(OH).CMe(OH).CO_2H$. *Di-methyl-glyceric acid.* [107°]. Formed by the action of water at 99° on di-methyl-glycidic acid $O<\begin{matrix}CMe.CO_2H\\CHMe\end{matrix}$ [62°], which is formed from tiglic acid $CH_3.CH:CMe.CO_2H$ by successive treatment with HOCl and boiling KOHAq (Melikoff, *A.* 234, 228; *Bl.* [2] 47, 166).—KA'.—AgA'.

Tetra-oxy-valeric acid $C_5H_{10}O_6$ *i.e.* $CH_2(OH).CH(OH).CH(OH).CH(OH).CO_2H$. *Arabonic acid.* $[\alpha]_D = -67°$. Formed by allowing arabinose (10 g.), water (75 g.), and Br (20 g.) to stand for 36 hours (Bauer, *J. pr.* [2] 30, 379; 34, 46; Kiliani, *B.* 19, 3031; 20, 344). Hygroscopic crystalline mass.—$CaA'_2 5aq$.—$SrA'_2 5aq$: prisms.

References.—Bromo- and Chloro- oxy-valeric acid.

TETRA-OXY-VALERIC ALDEHYDE $CH_2(OH).CH(OH).CH(OH).CH(OH).CHO$. *Arabinose.* [160°]. Mol. w. 150, by Raoult's method (Brown a. Morris, *C. J.* 53, 619). H.C.p. 557,100. H.F. 259,400 (Berthelot, *C. R.* 111, 12). A product of the hydrolysis of Arabic acid (*q. v.*) (Scheibler, *B.* 1, 58, 108; 6, 612; 17, 1731; Kiliani, *B.* 13, 2304; 15, 37; 19, 3031; 20, 344; Claesson, *B.* 14, 1271; O'Sullivan, *C. J.* 45, 41). Trimetric prisms, v. sol. hot water, nearly insol. alcohol and ether. Dextrorotatory (*v.* vol. i. p. 297). Tastes sweet. Does not undergo alcoholic fermentation. Yields a phenyl-hydrazide [158°]. Arabinin $C_{10}H_{18}O_9$ is an anhydride of this aldehyde (O'Sullivan, *C. J.* 57, 59).

OXY-VALERO-CYAMINE *v.* α-Guanido-valeric acid.

OXY-VINYL-BENZOIC ACID. *Anhydride* *v.* Methylene-phthalide.

OXY-XANTHONE *v.* Oxy-diphenylene ketone oxide.

OXY-XYLENE *v.* Xylenol and Tolyl-carbinol.

Di-oxy-xylene. The (6,3,2,1)-, (5,2,3,1)-, and (5,2,4,1)- di-oxy-xylenes are described as Hydroxyloquinones. Oxy-tolyl-carbinol is an ω-*eso*-di-oxy-xylene. (5,3,4,1)-Di-oxy-xylene is described as Betorcin.

Di-oxy-*m*-xylene $C_6H_2Me_2(OH)_2$ [1:3:4:6]. *Xylorcin.* Mol. w. 138. [125°]. (278°). Formed from amido-*m*-xylenol [161°] by the diazo- reaction (Kostanecki, *B.* 19, 2324). White monoclinic plates (from chloroform), v. sol. water, alcohol, and ether. Not affected by air containing NH_3.

Di-acetyl derivative $C_8H_8(OAc)_2$. [45°]. (286°). Prisms, insol. cold water.

Di-oxy-xylene $C_6H_2Me_2(OH)_2$. [120°]. Got by potash-fusion from chloro-*m*-xylene sulphonic acid (Gundelach, *Bl.* [2] 28, 345). Gives a red colour with bleaching-powder solution.

Di-oxy-*m*-xylene $C_6H_2Me_2(OH)_2$[1:3:2:4]. [146°]. Formed from *m*-xylene by heating with H_2SO_4 at 150°, converting the resulting disulphonic acid into chloride and fusing the $C_6H_2Me_2(SO_2Cl)_2$ with potash (Wischin, *B.* 23, 3113). White needles (by sublimation), v. sol. water, alcohol, and ether. $FeCl_3$ colours its solution deep violet. Fusion with phthalic anhydride forms a fluoresceïn.

Di-ω-oxy-*o*-xylene $C_6H_4(CH_2.OH)_2$, *Phthal-alcohol. o-Tolylene alcohol. Xylylene alcohol. Di-methyl benzene glycol.* [64°]. S. (ether) 25 at 18°. Formed by the action of sodium amalgam upon a boiling solution of phthalyl chloride in HOAc (Hessert, *B.* 12, 646). Formed also by boiling di-ω-bromo-*o*-xylene with Na_2CO_3Aq (Baeyer a. Perkin, jun., *B.* 17, 124; *C. J.* 53, 6; Colson, *C. R.* 98, 1543; *Bl.* [2] 43, 6; 45, 6; *A. Ch.* [6] 6, 106). Tables (from ether), v. e. sol. water and alcohol. HBr forms $C_6H_4(CH_2Br)_2$ and HCl acts in like manner. $KMnO_4$ oxidises it to phthalic acid. Resinified by cold H_2SO_4. Hot H_2SO_4 forms amorphous insoluble $(C_8H_8O)_n$ and syrupy $C_{16}H_{18}O_3$ (Hjelt, *B.* 19, 1538). HNO_3 forms phthalide.

Di-acetyl derivative $C_{12}H_{14}O_4$. [37°].

Di-ethyl ether $C_8H_8(OEt)_2$. (248°) at 720 mm. Liquid (Leser, *B.* 17, 1825).

Di-ω-oxy-*m*-xylene $C_6H_4(CH_2OH)_2$. [47°]. S.G. (liquid) $\frac{18}{}$ 1·161; $\frac{53}{}$ 1·135. Formed by boiling $C_6H_4(CH_2Br)_2$ [77°] (1 mol.) with water containing K_2CO_3 (1 mol.) (Colson, *A. Ch.* [6] 6, 112; *C. R.* 99, 40). Got in like manner from $C_6H_4(CH_2Cl)_2$ (Colson a. Gautier, *Bl.* [2] 45, 6). Crystalline solid, with bitter taste, v. e. sol. water and alcohol, m. sol. ether. HBr regenerates di-ω-bromo-*m*-xylene. Gives isophthalic acid on oxidation.

Ethyl ether $C_6H_4(CH_2OEt)_2$. (248°) at 712 mm. Got by boiling $C_6H_4(CH_2Br)_2$ with alcoholic potash (Kipping, *B.* 21, 46; *C. J.* 53, 46). Oil. Yields isophthalic acid on oxidation.

Di-ω-oxy-*p*-xylene $C_6H_4(CH_2OH)_2$. *p-Xylenyl alcohol.* [113°]. Formed from $C_6H_4(CH_2Cl)_2$ (1 pt.) by heating with water (30 pts.) at 175° (Grimaux, *A.* 155, 342; Colson a. Gautier, *Bl.* [2] 45, 7). It is one of the products of the action of boiling NaOHAq upon terephthalic aldehyde (Löw, *A.* 231, 374). Needles, v. sol. water, al-

cohol, and ether. Yields terephthalic acid on oxidation.

Acetyl derivative $C_6H_4(CH_2.OAc)_2$. [47°]. Made from $C_6H_4(CH_2Cl)_2$ and KOAc in alcohol.

Benzoyl derivative $C_6H_4(CH_2OBz)_2$. Needles, v. sol. alcohol and ether (Grimaux).

Mono-ethyl ether $C_6H_4(CH_2OH)(CH_2OEt)$. (251°). Oil. Formed from di-ω-chloro-*p*-xylene and conc. alcoholic potash at 100° (G.). Successive treatment with PCl_5, and water converts it into terephthalic aldehyde (Colson, *C. R.* 99, 975).

Tri-oxy-xylene $C_6HMe_2(OH)_3$. [122°]. Formed by reducing oxy-isoxyloquinone with aqueous SO_2 (Fittig a. Siepermann, *A.* 180, 37). Crystallises from water in tables (containing aq). Melts at 90° when hydrated. Colours the skin brown. On spontaneous evaporation of the aqueous solution in air it forms a quinhydrone as dark lustrous needles [143°]. Yields *m*-xylene on distillation with zinc-dust.

Tri-acetyl derivative. [99°]. Prisms.

Reference.—TETRA-CHLORO-DI-OXY-XYLENE.

DI-OXY-XYLENE CARBOXYLIC ACID $C_6HMe_2(OH)_2.CO_2H$ [1:3:4:6:5]. *Xylorcin carboxylic acid.* [196°]. Got by heating *m*-xylorcin with $NaHCO_3$ and some water at 130° (Kostanecki, *B.* 19, 2323). Prisms from dilute alcohol), sl. sol. water. Gives off CO_2 on fusion. $FeCl_3$ gives a deep-blue colour.

Oxy-*m*-xyloquinone $C_6HMe_2(OH)O_2$. [103°]. Formed by distilling di-amido-mesitylene with chromic acid mixture and water, Me being displaced by OH (Fittig, *B.* 8, 16; *A.* 180, 27). Orange needles, smelling like quinone; m. sol. hot water, v. e. sol. alcohol and ether. Volatile with steam. Its alkaline solution is reddish violet. Reduced by SO_2 to tri-oxy-xylene. Acetyl chloride at 100° forms a crystalline body [124°], insol. water.—$C_8H_7O_2(OK)$. Small black needles, v. e. sol. Aq, m. sol. alcohol, insol. ether.—$(C_8H_7O_3)_2Ba$. Brownish-red pp.

α-OXY-XYLYL-ACETIC ACID [1:3:4] $C_6H_3Me_2.CH(OH).CO_2H$. [119°]. Got by reducing (1,3,4)-xylyl-glyoxylic acid (Claus, *J. pr.* [2] 43, 143). Rhombohedra (by sublimation), v. sl. sol. cold water, v. sol. alcohol and ether.

α-Oxy-xylyl-acetic acid [1:4:2]$C_6H_3Me_2.CH(OH).CO_2H$. [114°]. Got in like manner from [1:4:2] $C_6H_3Me_2.CO.CO_2H$ (Claus). Needles or prisms, v. sol. hot water.

DI-OXY-XYLYLENE-DI-METHYL-DI-PYRIMIDINE $C_6H_4(CH_2.C\left<\begin{matrix}N:C(OH)\\N.CMe\end{matrix}\right>CH)_2$. [above 250°]. Made from acetoacetic ether and *p*-phenylene-diacet-imido- ether (Glock, B. 21, 2661). Crystalline mass, insol. ordinary solvents.

OXY-XYLYL-METHYL-PYRAZOLE $C_6H_3Me_2.N\left<\begin{matrix}C(OH):CH\\N=\!=\!=CMe\end{matrix}\right.$. [159°]. Got from the product $C_{32}H_{34}N_4O_4$ of the action of (1,3,4)-xylyl-hydrazine on acetoacetic ether by heating with conc. HClAq at 150° (Klauber, *M.* 12, 215). Small white needles.—B'HCl. [185°].—$B'_2H_4FeCy_6$: white crystals.

Oxy-xylyl-di-methyl-pyrazole $C_6H_3Me_2.N\left<\begin{matrix}CO-CH\\NMe.CMe\end{matrix}\right.$. [113°]. Made by heating the compound $C_{32}H_{34}N_4O_4$ (*v. supra*) with MeI and MeOH at 130° (K.). Small white needles, v. sol. alcohol and ether, sol. cold water. Reduces Fehling's solution. $FeCl_3$ gives a violet-red colour.—B'HCl. [95°]. Small crystals.

DI-OXY-DI-XYLYL-PYRAZINE DIHYDRIDE $C_6H_3Me_2.N\left<\begin{matrix}CO.CH_2\\CH_2.CO\end{matrix}\right>N.C_6H_3Me_2$. [203°]. Formed by boiling bromo-acetyl-(1,4,2)-xylidine with alcoholic potash (Abenius, *J. pr.* [2] 40, 436). Flat needles, insol. water and ether.

OZOKERIT. A fossil resin, consisting chiefly of a hydrocarbon called lekene (*q. v.*). On chlorination in presence of $SbCl_5$ at 360° it yields CCl_4, C_2Cl_6, C_4Cl_6, and C_6Cl_6 (Hartmann, *B.* 24, 1019). (*V.* also PARAFFIN.)

OZONE. O_3. Mol. w. 47·91. A blue gas (Hautefeuille a. Chappuis, *C. R.* 91, 522); it usually occurs mixed with oxygen, and possesses a characteristic odour. (−106°) (Olszewski, *M.* 8, 69; *W.* 37, 337). V.D. 24. S. at 760 mm. ·366 at 18° (Schöne, *B.* 6, 1224); ·834 at 1° (Carius, *A.* 174, 30); and ·2745 at 14° (McLeod, *C. J.* 49, 607). Andrews states that it is insoluble in water.

Occurrence.—Ozone is believed to be a normal constituent of pure air. Hartley (*C. J.* 39, 111), Chappuis (*C. R.* 91, 985; 94, 858), and E. Schöne (*J. R.* 1884. 2, 250), who have examined the absorption-spectrum of ozone, have attributed the blueness of the sky to its presence. But the recent observations of Liveing a. Dewar (*P. M.* [5] 26, 286) show that the absorption-spectrum of compressed oxygen exhibits certain bands identical with those of the solar spectrum, which Ångstrom found to be equally strong whether the atmosphere was wet or dry, and that daylight when observed through a column of oxygen 18 m. in length and at 90 atmos. possesses a blue tint (*v.* also Olszewski, *W.* 42, 663). The proportion of ozone in the air varies very considerably, and is supposed by many observers to be greater at high than at low altitudes (*v.* also Thorpe, *C. J. Proc.* 72). Houzeau judges the maximum proportion at ordinary levels to be $\frac{1}{700,000}$ by volume (*C. R.* 74, 712). Andrews found that a temperature of 250° destroys the constituent of the air which exhibits the reactions of ozone, whereas air containing traces of chlorine, or of the higher oxides of nitrogen, is not so affected by heat (*Pr.* 16, 63). On the other hand, Ilosvay (*Bl.* [3] 2, 377) and Schöne (*B.* 13, 1503) conclude that the presence of ozone in the air is still unproved.

Formation. — 1. Ozone is formed in the electrolysis of *dilute sulphuric acid* (Schönbein, *P.* 50, 616; Marignac, *C. R.* 20, 808; Meidinger, *A.* 88, 57; *C. J.* 7, 251; Baumert, *P.* 89, 38; Andrews, *T.* 146, 1; Soret, *Arch. des Sciences*, 16, 218; *C. R.* 56 390; Berthelot, *C. R.* 86, 71; *A. Ch.* [5] 14, 345; Schöne, *B.* 6, 1224; Carius, *A.* 174, 1; Brodie, *C. J.* 17, 293; McLeod, *C. J.* 49, 591). Berthelot and Schönbein also obtained ozone by the electrolysis of other acid solutions. It has been supposed that the ozone formed in electrolysis is accompanied by H_2O_2, but Brodie (*C. J.* 17, 281), and, more recently, McLeod (*loc. cit.*), have shown that the oxidising body which remains in solution is probably S_2O_7. The proportion of ozone present in electrolytic oxygen appears to depend to a great extent on current-density. By using a positive electrode of very small area McLeod obtained O containing 17·4 per cent. of ozone; when electrodes of large

area are used the yield of ozone is sometimes very small.—2. When *air* or *oxygen* is exposed to the electric discharge, especially if it be the silent discharge, the O is partly converted into ozone. If air be used, oxides of N may be formed and mistaken for ozone. According to Berthelot (*C. R.* 92, 82) and Hautefeuille a. Chappuis (*C. R.* 92, 80, and 134), oxides of N may be formed to a slight extent even by the silent discharge, and H. and C. have obtained a new and unstable oxide of nitrogen in this way. Giannetti a. Volta (*G.* 5, 439) found that with the discharge from a Holtz machine the yield of ozone is increased by using a wire brush as negative electrode. Bichât a. Guntz (*C. R.* 107, 334; *A. Ch.* [6] 19, 131), who used an ozone generator consisting of a wire stretched along the axis of a metallic tube, found that the negative effluve produced by far the greatest yield of ozone. This they attribute to its higher temperature. It has been suggested that the production of ozone by the electric discharge is an effect of a condition of electro-static stress. But Thomson a. Threlfall (*Pr.* 40, 329) find that oxygen is only converted into ozone when there is an actual luminous discharge. This has been confirmed by Bichât a. Guntz; and some experiments by the writer seem to show that even when oxygen is illuminated by the ultra-violet rays ozone is only formed by actual luminous discharge. Dewar has obtained a body giving the reactions of ozone from air by passing a current of water through a glass tube, surrounded by a larger tube of platinum which was heated by the oxyhydrogen flame, the air from the annular space between the hot and cold tubes being sucked into the inner tube by the stream of water through a minute hole in the glass tube, and collected and examined. If the substance thus obtained was really ozone, this result seems to confirm the idea that the action of the electric discharge on oxygen is due to temperature (*v.* also Elster a. Geitel, *W.* 39, 321; and Ilosvay, *Bl.* [3] 2, 734).

The formation of ozone from O by electric discharge is greatest at low temperatures and under high pressure (von Babo, *A.* 1863. *Suppl.* ii.; Hautefeuille a. Chappuis, *C. R.* 91, 228). But the exact influence of temperature and pressure have probably not yet been made out. Hautefeuille a. Chappuis have noticed that at a pressure of about 50 mm. ozone is alternately produced and destroyed by the silent discharge (*C. R.* 94, 646). Von Babo a. Claus, and Hautefeuille a. Chappuis, consider that prolonged action of the discharge is favourable to ozonification. But Brodie, with the apparatus described below, found that the maximum effect was quickly reached. The writer's experience agrees with that of Brodie, and tends to show that observations to the contrary effect have been due to the irregular working of the machine employed.

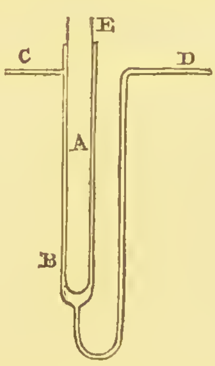
Bichât a. Guntz, using the apparatus described above, have failed to find any simple quantitative relation between the potential difference of the discharging surfaces and the yield of ozone, though they, and also Giannetti a. Volta (*G.* 5, 439) and Berthelot, find that an increase of potential produces an increased yield of ozone. (For details on various points *v.* Marignac a. De la Rive, *Arch. of Elect.* 5, 5; Fremy a. Becquerel, *A. Ch.* [3] 35, 62; Andrews, *T.* 146, 1; 150, 113; Brodie, *T.* 162, 435; Berthelot, *C. R.* 88, 50; *A. Ch.* [5] 12, 448; Hautefeuille a. Chappuis, *C. R.* 92, 80, 134; 94, 646; Shenstone a. Cundall, *C. J.* 51, 610.) Hautefeuille a. Chappuis (*C. R.* 91, 762) find that the production of ozone by the action of the electric effluve on oxygen is prevented by the presence of Cl, but that N, H, and SiF_4 are favourable to its production.

3. Brodie (*T.* 164, 83), by the action of the silent discharge on *carbon dioxide*, under the most favourable conditions, obtained as much as 85 p.c. of the liberated oxygen in the form of ozone.

4. Ozone has long been regarded as one of the products of various cases of *oxidation* such as the slow oxidation of P, Et_2O, and turpentine, the decay of organic matter, and the combustion of compounds containing H in the air; Thorpe a. Tutton observe that it is not formed in the oxidation of P_4O_6 (*C. J.* 57, 569). It is possible, however, that ozone is less frequently formed in such changes than has been supposed, and that the reactious attributed to ozone may often have been due to H_2O_2. The experiments of Kingzett (*C. J.* 37, 792) and McLeod (*C. J.* 37, 118), however, seem to make it certain that ozone is produced in the slow oxidation of P (*v.* also Ilosvay, *Bl.* [3] 2, 360; 4, 707; Leeds, *C. N.* 39, 157; 40, 70; 41, 164; 42, 17; Cundall, *C. J. Proc.* 78, 26; Loew, *B.* 22, 3325).

Heat of formation.—$3O_2 = 2O_3 = -59{,}200$ (Berthelot, *C. R.* 82, 1281); $-66{,}720$ (Mulder a. van der Meulen, *B.* 15, 511).

Preparation.—1. From oxygen. The following method, which was introduced by Siemens and Brodie, is perhaps the most couvenient. A tube, A, is sealed into a slightly larger tube B,

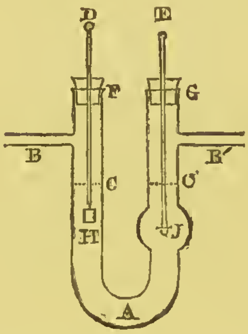


at E, before the blowpipe, or by means of solid paraffin. A and B should be of thin glass, and two narrow tubes, C and D, should be attached to B. A is filled with dilute H_2SO_4, and the apparatus is then immersed in dilute acid to the level C D; the electrodes of a Ruhmkorff coil, or of an electric machine, are respectively connected with the acid in A, and the contents of the cylinder, and a slow current of O is led through the apparatus from D to C while the discharge passes. The liquid in the cylinder should be cooled by ice, or it may be replaced by a freezing mixture, in which case a platinum wire should be wrapped round the outside of B. The gas which escapes at C is well charged with ozone. The ozonised oxygen may be collected over oil of vitriol. It must not be brought into contact with india-rubber; joints that will bear contact with ozone may be made by slipping a wider tube over the

ends of those that are to be connected, warming them, and running a little melted paraffin between the inner and outer tubes.

The character of the discharge in the ozone generator has been studied by Hautefeuille a. Chappuis (*C. R.* 91, 281), Thomson a. Threlfall (*Pr.* 40, 329), Shenstone a. Cundall (*C. J.* 51, 622), and by Bichât a. Guntz (*A. Ch.* [6] 19, 131).

2. By electrolysis. When dilute H_2SO_4 is electrolysed with electrodes of considerable area the proportion of ozone in the O is usually small. McLeod (*C. J.* 49, 591) recommends the following method. Place dilute H_2SO_4 (*S. G.* 1·1) in a U tube, A, attach delivery tubes to the



arms B B′. Let the negative electrode H be a sheet of Pt foil suspended by the glass D from a cork closing the mouth at F, and let the positive electrode J consist of two fine wires, sealed into a glass tube E, which is afterwards filled with mercury. On connecting D and E with a galvanic battery, O highly charged with ozone will escape at B′. It is best to immerse the U tube in ice-cold water. McLeod has obtained O containing as much as 17·3 p.c. of ozone by means of this apparatus.

3. To prepare ozone by the oxidation of phosphorus. Place clean sticks of P half submerged in water in a series of flasks, and conduct a rather slow stream of air through the flasks, and then through a little water. A temperature of 24°-25° gives the best results. H_2O_2 is also formed, but it remains dissolved in the water (Kingzett, *C. J.* 37, 792).

Properties and Reactions.—Ozone is more strongly magnetic than common oxygen (Becquerel, *C. R.* 92, 348). Its rate of diffusion is near to that required for the density 24 (Soret, *A. Ch.* [4] 13, 257). It is entirely destroyed at 270° (Andrews, *T.* 150, 113) by contact with platinum black at ordinary temperatures (Mulder a. van der Meulen, *B.* 1, 167), and on contact with pure Hg (Hg is not visibly oxidised if both be perfectly dry, Shenstone a. Cundall, *C. J.* 51, 619). Ozone is also decomposed by dry Ag, the silver being but slightly oxidised, and by contact with MnO_2 (Andrews). Volta (*G.* 9, 521) states that Au, Pt, Pd, and dry Ag are without action on ozone. Brodie came to a similar conclusion in regard to Au, Al, and Cu. Berthelot (*C. R.* 86, 76) and others have considered that dry ozone has no fixed pressure of dissociation. If suddenly compressed, or compressed without cooling, it explodes with a yellowish flame (Hautefeuille a. Chappuis, *C. R.* 91, 522). The action of ozone on salts has been studied by Maquenne (*C. R.* 94, 795), and by Mailfert (*C. R.* 94, 860). The latter has also studied its action on S, Se, Te, and several sulphides, and on CH_4, C_2H_4, C_2H_2, C_5H_{10}, C_6H_6, and C_7H_8 (*C. R.* 94, 1186). Ozone oxidises alcohols of small molecular weight more readily than the polyhydric alcohols (A. Renard, *A. Ch.* [5] 16, 289). Liquid ozone explodes violently on coming into contact with C_2H_4 (Olszewski, *A. Ch.* [2] 37, 337). It acts as a strong bleaching agent on vegetable colours, and quickly destroys india-rubber; its action on cork is much less rapid. It does not oxidise CO at 300° (Remsen, *Am.* 4, 50). It oxidises NH_3Aq, forming ammonium salts of nitrous and nitric acid (Carius, *A.* 174, 31), unless the solution is dilute (Hartley, *C. J.* 39, 123). It is believed to be completely absorbed by turpentine and oil of cinnamon (Soret, *A. Ch.* [4] 7, 113), peroxidised compounds being formed which react with water (Kingzett, *C. J.* 37, 800). When ozonised O acts on KIAq, I is set free and the ozone is destroyed, but the volume of the gas remains unaltered. With neutral solutions the initial action may correspond to the equation $2KIAq + O_3 = K_2OAq + O_2 + I_2$, but usually KIO_3 is a final product of the change. P glows freely in ozonised air (Thorpe a. Tutton, *C. J.* 57, 571). Ozone oxidises TlOH and As_2O_3; the latter action has been used in determining its heat of formation. It is destroyed by solutions of KHO, BaO, and CaO to a certain extent (Andrews). Hartley has observed the formation of peroxide of potassium by its action on solid KOH (*C. J.* 39, 124). But it is unaffected by solution of Na_2CO_3 (Brodie). It readily attacks I, forming periodic acid and lower oxides of I (Ozier, *C. R.* 86, 722). It converts ether into an ozonised substance which acts with water to form H_2O_2 (Kingzett, *C. N.* 34, 127; Berthelot, *C. R.* 86, 71; Dunstan a. Dymond, *C. J.* 57, 584). Several observers have concluded that it arrests putrefaction of animal matter, and have proposed its use as a preservative for meat. When present in the air in large quantities it frequently produces irritation of the mucous membrane.

Although its general action is that of a strong oxidiser, in certain cases ozone acts as a reducing agent. Thus when ozone acts with Na_2O_2 an expansion occurs which is due to the simultaneous decomposition of the two bodies in equivalent proportions (Brodie, *T.* 162, 454), probably according to the following equation:—$Na_2O_2 + O_3 = Na_2O + 2O_2$. Probably other unstable oxides, such as H_2O_2, react with it similarly under favourable conditions. Its action on blood has been said to resemble that of a reducing agent (Dogiel, *C. C.* 1875; Binz, *C. C.* 1882). It changes the red colour of the compound formed when sulphanilic acid is mixed with naphthylamine to orange-yellow (Ilosvay, *Bl.* [3] 2, 351).

Detection.—Paper impregnated with TlOH is turned brown by ozone even when dry (Schöne, *B.* 13, 1508). The similar change of colour produced by nitrous acid is destroyed by excess. The colour is also permanent when ozone is mixed with a relatively small proportion of nitrous acid (Ilosvay). The action of ozone on the red compound of naphthylamine and sulphanilic acid (*v. Properties*) also affords a test for ozone, even in the presence of traces of nitrous acid (Ilosvay, *Bl.* [3] 2, 360). Ozone may be distinguished from H_2O_2 by not yielding water when strongly heated, and by the absence

of any action with titanic acid or chromic acid, also by resisting the action of Na_2CO_3, which destroys H_2O_2. Papers saturated with solutions of KI and starch are often used for the detection of ozone, but are only trustworthy when the absence of Cl and of oxides of nitrogen can be assured. Houzeau employed test papers steeped in faintly-acid solution of litmus and then treated with KI. These he found to be insensitive to O, to traces of oxides of nitrogen, and to H_2O_2. When exposed to ozone, however, they are turned blue by the alkali that is set free.

Estimation.—1. Rough estimations of ozone are frequently made by comparing the tints produced by exposing some of the test papers mentioned above with a scale of tints. Such methods are not very satisfactory.—2. Thénard has estimated the proportion of ozone in the air volumetrically by means of a standard solution of As_2O_3 in HClAq of such strength that 1 c.c. is equivalent to 1 mgrm. of O. 10 or 20 c.c. of the solution are thoroughly agitated with the sample of gas, 30 c.c. of a 1 p.c. solution of H_2SO_4 are added, and it is then titrated in the usual manner with permanganate. For 8 grms. of O absorbed 24 grms. of O_3 are destroyed (Berthelot, *C. R.* 82, 1251). As oxides of nitrogen and H_2O_2, if present, tend to reduce the amount of ozone found, this method gives the minimum, and not the maximum, amount of ozone present.—3. If a solution of potassium arsenite containing ·73 grm. per litre, with an excess of pure KI, be agitated with air containing ozone, part of the arsenite is converted into arsenate by the ozone, and the amount of unaltered arsenite can be found by titrating with very dilute I solution after adding some ammonium carbonate and starch. This method is strongly recommended by Hartley (*C. J.* 39, 120). The solution of the arsenite should be acidified for keeping, and neutralised before use with $KHCO_3$.—4. The action of ozone on KIAq may also be employed to estimate ozone. The iodide must be perfectly free from iodate, and must be thoroughly brought into contact with the gas. When the action is complete, *and not before*, the product must be acidified with dilute HClAq or H_2SO_4Aq. The liberated I may then be titrated in the usual manner. The O equivalent to the I liberated, multiplied by three, gives the amount of ozone.—5. The amount of ozone produced in the electrification of oxygen may also be calculated from the contraction that occurs under the influence of the discharge (*v.* Babo, *A. Suppl.* 2; Andrews, *T.* 150). Shenstone a. Cundall (*C. J.* 51, 610) have devised an apparatus for this purpose. S. a. C. have shown that if the ozonised gas comes into contact with oil of vitriol in such a process, the acid should be previously thoroughly treated with ozone, otherwise the results are likely to be high.

History.—The earliest known record concerning ozone relates to an observation by van Marum, 1785, that air or O when submitted to the electric spark acquires a characteristic odour. About fifty years later, 1840, Schönbein, who published about sixty papers on this subject, published his first memoir on ozone in Poggendorff's *Annalen.* As the result of his numerous observations, Schönbein recognised ozone as a distinct form of matter, ascertained that it could be obtained by the electrolysis of dilute acid, by means of the electric discharge on O, and in the slow oxidation of P. And it is interesting to note that these still constitute the chief methods for the production of ozone. He also observed many of its chief properties. For several years after Schönbein's original discovery, comparatively little progress was made in ascertaining the nature of ozone till the experiments of Marignac and De la Rive, 1845 (*Arch. of Elect.*), and of Fremy and Becquerel, 1853 (*A. Ch.* [3] 35, 62), showed that the purest O then obtainable could be entirely converted into ozone, provided that the action of the spark took place in the presence of excess of KI, or of moist silver, which appeared to be capable of completely absorbing ozone. But it was not till a much later period that the researches of Andrews (*T.* 146, 1) and Soret (*C. R.* 56, 390) finally showed that ozone from all sources is identical. Although the researches of Marignac a. De la Rive, and of Fremy a. Becquerel, thus established the character of ozone and its production from oxygen, the exact relation of the two bodies was still imperfectly understood; and ozone seems to have been regarded as differing from oxygen either in regard to its electrification, or, by some, in being a compound of oxygen and water, until in 1860 Andrews and Tait (*loc. cit.*) examined the volumetric relations of ozone and oxygen, and by a masterly research showed that the ozonising of oxygen is accompanied by a contraction in the volume of the gas, and that, on the other hand, the reproduction of O from the ozone by heat causes the gas to recover its original volume. In this research A. and T. also showed that the iodine titre of a sample of ozonised oxygen corresponds in every case to the contraction that has occurred on ozonising it; a fact which, in the hands of Soret and Brodie, materially contributed to the further elucidation of the subject. Andrews and Tait also observed that when ozonised oxygen acts with KIAq, the gas remains unaltered in volume after the action is complete. The true bearing of these facts was not, however, perceived till Odling (*Manual of Chemistry*) pointed out, in 1861, that they were consistent with the adoption of O_3 as the simplest formula for ozone. This interpretation was afterwards supported by the experiments of Soret and Brodie. The former showed that when ozonised oxygen is allowed to act on turpentine, a contraction occurs that is equal to about twice the iodine titre of the gas, *i.e.* is about twice as great as the contraction which accompanies its formation, from which, if it be assumed that the ozone formed is wholly absorbed by the turpentine, it follows that two volumes of gaseous ozone contain three volumes of gaseous oxygen. Soret's experimental numbers did not agree very closely with this hypothesis. But the hypothesis was confirmed by subsequent experiments, in which he compared the rates of diffusion of ozone, Cl, and CO_2, and found that the rate of diffusion of ozone approximates to that of a gas having the S.G. 24 (*A. Ch.* [4] 13, 257). Finally, in 1872, Brodie (*T.* 162, 435), as one of the results of a beautiful series of experiments, found that, while in some cases, as in that of neutral KIAq, the oxidation caused by ozone is unaccompanied by any contraction in the volume of the gas, in other cases various degrees of con-

traction occur. Thus the oxidation of HIAq is attended by a diminution in the volume of the gas equal to half the volume that would be occupied by the weight of gas that is absorbed, and the action of the gas on turpentine and on $Na_2S_2O_3Aq$ is accompanied by a diminution of volume equal to two-thirds of the volume that the O absorbed would occupy in the free state. Intermediate contractions were observed, but in no case did the contraction seem to be greater than in the action of turpentine, a result which afforded strong confirmation of the views of Soret and Odling. An account of the early work on ozone exists in the *Handwörterbuch der Chemie*, 5, 835 (Braunschweig, 1853). (For later work *v.* Odling, *R. I.* 1872.)

Antozone. This name was formerly given to a substance whose action with ozone resulted in their mutual decomposition. Before the relations of ozone and oxygen were established, these bodies were by some supposed to consist of oxygen in opposite conditions of electrification. Antozone was probably hydrogen peroxide. W. A. S.

P

PACHYMOSE $C_{10}H_{24}O_{14}$. A substance, probably a glucoside, occurring in *Pachyma pinctorum*, a Chinese fungus (Champion, *J.* 1872, 789). Insol. water, sol. alkalis, forming a solution ppd. by Ca and Pb salts.

PACHYRHIZIDE. A substance, not containing nitrogen, extracted from the seeds of *Pachyrhizus angulatus* (Greshoff, *B.* 23, 3539). V. sol. alcohol, ether, and $CHCl_3$, v. sl. sol. water and KOHAq. Tastes bitter, and is extremely poisonous, especially to fishes. Begins to melt at 61°, and decomposes at 161°. Yields salicylic and protocatechuic acids on fusion with potash. The alcoholic solution is acid in reaction. Probably identical with a similar body in the root-bark of Derris (*Pongamia elliptica*).

PÆONOL $C_9H_{10}O_3$ *i.e.* $CH_3.CO.C_6H_3(OH)(OMe)$ [1:2:4]. [50°]. Got from the bark of *Pæonia montana* of Japan (Nagai, *B.* 24, 2847). White needles (from alcohol). Yields an acetyl derivative [46·5°], a phenyl-hydrazide [107°], and a crystalline oxim (Tiemann, *B.* 24, 2855). Potash forms resacetophenone $CH_3.CO.C_6H_3(OH)_2$. HIAq at 150° forms the same body.

PALISANDER RESIN $C_{21}H_{22}O_6$? [95°]. S.G. $\frac{15}{}$ 1·266. Extracted by alcohol from palisander wood, a red dye-wood from Madagascar (Terreil a. Wolff, *Bl.* [2] 33, 435; *cf.* Arnaudon, *Cimento*, 8, 278).

PALLADIUM. Pd. At. w. 106·3. Mol. w. unknown. Melts between 1360° and 1380° (Becquerel, *C. R.* 57, 855); at c. 1500° (Violle, *C. R.* 87, 981). S.G. 11·4 at 22·5° (Deville a. Debray, *P. M.* [4] 50, 651). For other numbers *v.* Clarke's *Table of Specific Gravities*, 2nd edit., 15. S.H. = ·0582 at 0°, = ·0582 + ·00002t at t° (Violle, *l.c.*). Heat of fusion = 363 cals. C.E. (linear) = ·00001176 at 40° (Fizeau, *C. R.* 68, 1125). E.C. 12·64 at 17·2° (Ag at 0° = 100) (Matthiessen, *P.* 103, 428). Volatilises in green vapour at c. 2000°. S.V.S. c. 9·3. For chief lines in emission-spectrum *v. B.A.* 1884. 434.

Occurrence.—In small quantities, about 2 p.c., as metal alloyed with Pt, Ir, Os, Ru, and Rh. Certain kinds of South American gold contain from 5 to 10 p.c. Pd. Occurs also, with gold and lead selenide, in the Harz (Zinken, *P.* 16, 491), and in small quantities in some specimens of silver (Rössler, *A.* 180, 240). In 1803 Wollaston (*T.* 1804. 428; 1805. 316) separated two new metals from Pt ore; to one of these metals he gave the name *palladium*, in allusion to the discovery, made about the same time, of the planet Pallas, and the other he called *rhodium*, because of the rose-coloured solutions of its salts (ῥόδον = a rose).

Formation.—1. By heating $PdCy_2$.—2. By heating $PdCl_4.2KCl$ and washing out the residual KCl.—3. By ppn. from solutions of its salts by means of Zn, Cu, or Fe.—4. By reducing $PdCl_2.2KClAq$ by oxalic or formic acid.

Preparation.—When Pt ore is heated in *aqua regia*, the Pd goes into solution, along with most of the Pt, as $PdCl_2$. From this solution Pd is obtained by various processes. 1. The solution is made as nearly as possible exactly neutral by Na_2CO_3, and $HgCy_2Aq$ is added; $PdCy_2$ is ppd., along with Cu_2Cy_2 if the ore contained Cu; the pp. is washed, dried, and strongly heated, whereby Pd is obtained, mixed with Cu; the metallic residue is dissolved in HNO_3Aq, the solution is neutralised by Na_2CO_3, and heated with HCO_2KAq and $H_4C_2O_2Aq$, whereby CO_2 is evolved plentifully, and Pd is deposited in lustrous plates, while Cu remains in solution (Dobereiner); or the metallic residue obtained by heating the cyanides may be dissolved in HNO_3Aq, the solution evaporated to dryness, and the residue strongly heated. By now treating with conc. HClAq, CuO is dissolved away, while Pd remains.—2. NH_4Cl is added to the solution in *aqua regia*, and the liquid is filtered from $PtCl_4.2KCl$; the filtrate may contain Ir, Rh, Ru, some Pt and Cu, besides Pd. These metals are ppd. by addition of Zn or Fe. The pp. is treated in various ways. Wilm (*B.* 15, 241; *v.* also *B.* 13, 1198; 14, 629) recommends to dissolve the ppd. metals in *aqua regia*, to boil the solution with excess of NaOHAq (von Schneider, *A. Suppl.* 5, 261), whereby the perchlorides of the metals, except that of Pt, are reduced to the lower chlorides, to acidify with HClAq, and add excess of NH_4Cl, in order to ppt. $PtCl_4.2KCl$. The filtrate from this pp. is boiled with excess of NH_3Aq, filtered, and excess of HClAq is added. After some time a yellow pp. forms, which is either almost pure $PdCl_2.2NH_4Cl$, or if somewhat dirty-yellow in colour, it may contain $Rh_2Cl_6.10NH_3$. This pp. is treated with cold NH_3Aq, in which the Rh salt is insoluble,

and pure $PdCl_2.2NH_4Cl$ is ppd. by adding HClAq to the solution. The pp. is collected, washed with absolute alcohol, dried, and heated strongly: a grey spongy mass of Pd is obtained.

This process may be used for purifying commercial Pd.

For other methods of preparing Pd *v.* Bunsen (*A.* 146, 265); Philipp (*D. P. J.* 220, 95); Guyard (*C. R.* 56, 1177); Rössler (*Z.* 1866. 175); Opificus (*D. P. J.* 224, 414).

Pd may be prepared from palladium containing gold by dissolving in *aqua regia*, ppg. with $HgCy_2Aq$, and proceeding as described under 1 above. Or the ore may be fused with an equal weight of Ag and some KNO_3, the regulus granulated, and treated with HNO_3Aq (Cock, *P. M.* [2] 23, 16), Ag ppd. by addition of NaCl, and Pd ppd. with other metals by Zn; the Pd may then be separated from this pp. as described under 2 above.

Properties. — As prepared by heating $PdCl_4.2KCl$ or $PdCy_2$, or by ppn. from solutions, Pd forms a grey metallic sponge which can be pressed together, more easily than Pt, to a compact mass. This compact form is also obtained by melting spongy Pd; Pd is a white metal, fairly malleable, ductile, and hard (somewhat softer than Pt). Compact Pd may be polished highly; it can be hammered into thin plates, and drawn into fine wire. In Brazilian gold ore Pd is found in regular octahedra, and in specimens of ore from the Harz it forms hexagonal plates. Joly (*N.* 43, 541) obtained it in cubic octahedra by dusting Pd ribbon with powdered topaz and heating to bright redness for some time by an electric current. Heated in the O-H flame to c. 2000°, Pd volatilises in greenish vapours, and condenses again to a brownish sublimate which is a mixture of metal and oxide. When the metal is melted in presence of O it absorbs O, which it gives up again on cooling (Deville a. Debray, *A. Ch.* [3] 56, 385). When strongly heated in air Pd is oxidised superficially, but the film of oxide is reduced at a higher temperature. Heated in an alcoholic flame, Pd black absorbs C and increases largely in volume. Pd absorbs H; it causes the combination of H and O when brought into electrolytic gas. Heated Pd foil brought into a mixture of NH_3 and O causes formation of NH_4NO_3 and NO_2. Pd is more easily acted on by acids than any other of the Pt metals; it is dissolved by cold HNO_3Aq.

The at. w. has been determined by analysing $PdCl_2.2KCl$ (Berzelius, *P.* 13, 455); and by estimating Pd in $PdN_2H_6Cl_2$, by reducing in H (Keiser, *Am.* 11, 398).

In its chemical relations Pd is closely allied to Ru and Rh, and less closely to Os, Ir, and Pt (*v.* Noble metals, this vol. p. 628).

On account of its silver-like appearance, and its resistance to the action of H_2S, Pd is used for making scales and division-marks on scientific instruments, and also for coating and preserving silvered metallic ware. Pd wire is used in dentistry; an alloy with steel is used in making parts of physical instruments; and an alloy with steel, Cu, and small quantities of Au, Ni, Pt, Rh, and Ag is used in watch-making, as it is non-oxidisable, hard, and non-magnetic. Finely-divided Pd is used in gas-analysis for absorbing H from mixtures, and for effecting the gradual combination of H or hydrocarbons with O (Hempel, *B.* 23, 636, 1006).

Reactions and Combinations.—1. When Pd is heated in *air* or *oxygen* Pd_2O is formed, but this oxide is reduced to Pd and O at a higher temperature.—2. Heated in *hydrogen* to c. 100° much H is absorbed, probably with formation of a hydride Pd_2H (*v.* Hydrogen, vol. ii. p. 720).—3. Brought into a mixture of *hydrogen and oxygen*, in the ratio 2H:O, Pd black causes formation of H_2O without explosion (Coquillon, *C. R.* 83, 709).—4. Heated with *sulphur* Pd_2S is formed.—5. PdSe is formed by heating Pd with *selenion*.—6. Digested with *bromine and water*, $PdBr_2$ is produced.—7. With *iodine tincture* PdI_2 is produced.—8. Glowing Pd wire causes the decomposition of many *hydrocarbons* into C and H (Coquillon, *C. R.* 84, 1503; Wilm, *B.* 14, 874).—9. In an *alcoholic flame* Pd becomes covered with C; spongy Pd increases largely in volume, probably with formation of a carbide (Wöhler, *A.* 184, 128).—10. Heated Pd foil brought into a mixture of *ammonia and oxygen* causes formation of NH_4NO_3 and NO_2 without explosion (Kraut, *B.* 20, 1113).—11. Pd is oxidised to $PdSO_4$ by fusion with *potassium-hydrogen sulphate*.—12. Pd dissolves in *acids* more easily than any other of the Pt metals: in *nitric acid*, even in the cold, it dissolves to $Pd(NO_3)_2$; in *hydrochloric acid*, especially when Cl is passed in, $PdCl_2$ is formed; in *hydriodic acid*, PdI_2 is produced; $PdBr_2$ is obtained by dissolving in *hydrobromic acid*, with a little HNO_3Aq; in *sulphuric acid*, with a little HNO_3Aq, $PdSO_4$ is produced; Pd dissolves in *aqua regia* to form $PdCl_2$, $PdCl_4$ being perhaps produced at first.

Qualitative discrimination between palladium and platinum. If a drop of an alcoholic solution of I is dropped on to Pd, a black stain of PdI_2 is formed, and this stain disappears on heating; as Pt is not acted on by I tincture, this reaction serves to distinguish between the two metals.

Palladium, alloys of. Alloys of Pd with several metals have been prepared. The alloy formed by heating equal weights of Pd and *lead*, and removing the excess of Pb, is a steel-grey powder, S.G. 11·255, agreeing in composition with the formula Pd_3Pb (Bauer, *B.* 4, 451). *Tin* forms an alloy which seems to be a compound Pd_3Sn_2 (Deville a. Debray, *A. Ch.* [3] 56, 385). Alloys with Sb, As, Ba, Bi, Cu, Au, Hg, Ni, Pt, and Ag have been described (*v.* Graham, *C. R.* 68, 1511; Mallet, *C. N.* 46, 216; Fischer, *S.* 51, 197).

Palladium, ammonio-salts of, or Pallad-ammonium salts. (*Palladamines. Ammoniacal palladium bases.*) When HClAq is added to $PdCl_2Aq$ containing an excess of NH_3, the salt $PdCl_2.2NH_3$ separates; by treatment with Ag_2O and H_2O, this salt gives the strongly alkaline base $Pd(OH)_2.2NH_3$, and by neutralising this base with acids various salts are obtained, *e.g.* $PdSO_4.2NH_3$, $PdCO_3.2NH_3$, &c. When a large excess of NH_3 is added to $PdCl_2Aq$ and the solution is evaporated, or when a solution of $PdCl_2.2NH_3$ in NH_3Aq is evaporated, the salt $PdCl_2.4NH_3$ separates. Similarly, when $PdSO_4$ is dissolved in a large excess of NH_3Aq, the salt $PdSO_4.4NH_3$ is obtained by evaporating this solution; decomposition of the sulphate with

BaOAq, and evaporation, gives the strongly alkaline base $Pd(OH)_2.4NH_3$, which yields salts by neutralisation with acids, *e.g.* $PdCO_3.4NH_3$, $PdSO_3.4NH_3$, &c. The compounds $Pd(OH)_2.2NH_3$ and $Pd(OH)_2.4NH_3$ represent the two series of palladium ammonio- salts. The reactions of these compounds and their derivatives lead to their representation as, in one case, compounds of the radicle PdN_2H_6—derived from N_2H_8 by replacing 2H by Pd—and, in the other case, compounds of the radicle PdN_4H_{12}—derived from PdN_2H_6 by replacing 2H by $2NH_4$. The two series of salts may be called *pallados-diammonium compounds*, $Pd(NH_3.NH_3)Cl_2$, &c.; and *ammonium pallados-diammonium compounds*, $Pd(NH_2NH_4.NH_2NH_4)Cl_2$, &c. The members of the first series are also sometimes called *palladosamine compounds*, and those of the second series *pallado-diamine compounds*. It is to be observed that both series are obtained from palladosochloride, $PdCl_2$ (*cf.* Iridium ammonio-salts, this vol. p. 47). The palladium ammonio- salts have been examined chiefly by Kane (*T.* 1842. 275); Fehling (*P.* 13, 466); Fischer (*P.* 71, 431); and Hugo Müller (*A.* 86, 341).

I. Pallados-diammonium compounds: $N_2H_6Pd.X^I_2$, or $(NH_3.NH_3)Pd.X^I_2$, or perhaps $NH_2(NH_4)Pd.X^I_2$.

Pallados-diammonium chloride, $N_2H_6Pd.Cl_2$ (simplest formula $PdCl_2.2NH_3$ = *di-ammonio-palladium dichloride*). This salt is known in two forms: 1. *Yellow crystals* are obtained by adding HClAq to $PdCl_2$ in excess of NH_3Aq; these crystals are scarcely sol. water, sol. with difficulty in cold acids, more sol. hot acids, easily sol. NH_3Aq, from which solution acids reppt. the salt unchanged. The salt dissolves in KOHAq, but no NH_3 is evolved even on heating; when the salt is suspended in water and Cl is passed in, solution is effected; addition of NH_3Aq now ppts. the red form of the salt, and boiling with KOHAq evolves NH_3 and leaves a liquid from which crystals of $PdCl_2.2NH_4Cl$ separate. The continued passage of Cl produces $PdCl_4.2NH_4Cl$, and finally $PdCl_4Aq$. 2. A *red salt* of the same composition is obtained by dissolving the yellow salt in conc. HClAq and adding NH_3Aq, also by adding a slight excess of NH_3Aq to a rather dilute cold solution of $PdCl_2Aq$. The yellow salt is produced by dissolving the red variety in NH_3Aq and adding excess of HClAq; also by heating the red salt to 200°. Jörgensen (*Gm.-K.* 3, 1242) regarded the red salt as polymeric with the yellow, and gave it the formula $Pd(NH_2.NH_4)_2Cl_2.Cl_2Pd$. The salts may be isomeric, one being $Pd.NH_3Cl.NH_3Cl$ and the other $Pd.NH_2Cl_2.NH_4$.

Pallados-diammonium hydroxide, $N_2H_6Pd.(OH)_2$ (simplest formula $Pd(OH)_2.2NH_3$ = *di-ammonio-palladium hydroxide*). This base is obtained by decomposing the corresponding chloride with moist Ag_2O in presence of water, or the sulphate with BaOAq; the solution thus obtained is yellowish, odourless, and has a strongly alkaline taste and reaction. The base is obtained as a curdy crystalline mass by evaporating at the ordinary temperature in absence of air. The solid rapidly absorbs CO_2 from the air, forming $N_2H_6Pd.CO_3$; it is decomposed by heating to somewhat above 100°. The base is sol. water; the solution decomposes NH_4 salts, and ppts. CuO_2H_2 and Ag_2O from solutions of salts of Cu and Ag. The solution may be boiled with very slight change; on boiling with alcohol, Pd is ppd. The other salts of this series which have been described are as follows: $M = PdN_2H_6$:—*bromide* MBr_2, *carbonate* MCO_3, *fluoride* MF_2(?), *iodide* MI_2, *nitrate* $M(NO_3)_2$, *nitrite* $M(NO_2)_2$, *sulphate* MSO_4, and *sulphite* MSO_3.

II. Ammonium pallados-diammonium compounds: $N_2H_4(NH_4)_2PdX^I_2$, or perhaps $(NH_3.NH_3)_2Pd.X^I_2$.

Ammonium pallados-diammonium chloride $Pd(NH_2.NH_4)_2Cl_2$; (or $Pd(NH_3.NH_3Cl)_2$ = *pallado-diamine chloride*; simplest formula $PdCl_2.4NH_3$ = *tetrammonio-palladium dichloride*). This salt is obtained in large, colourless, monoclinic prisms, with one molecule of water of crystallisation, by evaporating a solution of yellow $N_2H_6Pd.Cl_2$ with excess of NH_3, or a solution of $PdCl_2$ in considerable excess of NH_3Aq. Heating the salt to 120°, or adding acid to a solution of the salt, causes formation of yellow $N_2H_6Pd.Cl_2$. Addition of $PdCl_2$ to a solution of the salt causes ppn. of flesh-red $Pd(NH_2.NH_4)_2Cl_2.PdCl_2$ (Kane, Fehling). Treatment of $Pd(NH_2.NH_4)_2Cl_2$ with NH_4Cl and *aqua regia* is said to produce $Pd(NH_2.NH_4)_2Cl_2.PdCl_4$ (Croft, *C. N.* 16, 53).

Ammonium pallados-diammonium hydroxide $Pd(NH_2.NH_4)_2(OH)_2$; (or $Pd(NH_3.NH_3)_2(OH)_2$ = *pallado-diamine hydroxide*; simplest formula $Pd(OH)_2.4NH_3$ = *tetrammonio-palladium dichloride*). Obtained as a crystalline mass by decomposing a solution in water of the sulphate $Pd(NH_2NH_4)_2SO_4.H_2O$, produced by adding large excess of NH_3Aq to $PdSO_4Aq$ and evaporating with BaOAq, filtering and evaporating. The solution is odourless; it is strongly alkaline, and ppts. hydroxides from solutions of salts of Al, Co, Cu, Fe, and Ni, but not from salts of Ag; it sets NH_3 free from NH_4ClAq. The solution absorbs CO_2 from the air; it is decomposed by boiling with organic matter. If this base is neutralised exactly by acids, salts of the base are obtained, *e.g.* $Pd(NH_2.NH_4)_2CO_3$, $Pd(NH_2.NH_4)_2SO_3$, &c.; excess of acid, especially of a haloid acid, causes decomposition into a pallados-diammonium salt and a salt of NH_4, *e.g.* $Pd(NH_2.NH_4)_2(OH)_2 + 4HClAq = PdN_2H_6.Cl_2 + 2NH_4ClAq + 2H_2O$. The other salts of this series which have been described are as follows: $M = Pd(NH_2.NH_4)_2$:—*bromide* MBr_2, and the double compound $MBr_2.PdBr_2$, *carbonate* MCO_3, *fluoride* MF_2 (?), *iodide* MI_2, *nitrate* $M(NO_3)_2$, *double nitrite* $M(NO_2)_2.Pd(NO_2)_2$, *silicofluoride* $MSiF_6$ (?), *sulphate* $MSO_4.H_2O$, *sulphite* MSO_3.

The reactions of such *substituted ammonias* as NH_2Me, NH_2Et, and NH_2Ph on salts of Pd produce compounds analogous with the ammoniacal bases described above, *e.g.* *pallados-diethylammonium chloride* $N_2H_4Et_2Pd.Cl_2$, and *pallados-diphenylammonium chloride* $N_2H_4Ph_2Pd.Cl_2$, have been described (Müller, *A.* 86, 341).

The substitution of *tri-ethylarsine* and *tri-ethylphosphine* for ammonia, in the reactions with Pd salts, produces compounds similar to the N-containing bases; *e.g.* *pallados-ditriethylphosphonium chloride* $P_2Et_6Pd.Cl_2$

(Cahours a. Gal, *C. R.* 70, 897), and *pallados-di-triethylarsonium chloride* $As_2Et_6Pd.Cl_2$ (C. a. G., *C. R.* 71, 208).

Palladium, bromide of. Only one bromide of Pd is known, and that has not been prepared free from impurities.

PALLADIUM DIBROMIDE $PdBr_2$ (*Palladous* or *palladoso-bromide*). The brownish solid obtained by dissolving Pd in a mixture of HBrAq and HNO_3Aq, or digesting finely-divided Pd with BrAq, and evaporating, probably has the composition $PdBr_2$, but it has not been obtained pure. *Double compounds* of $PdBr_2$ with bromides of Ba, Mn, K, and Zn have been prepared, but not fully examined, by von Bonsdorff (*P.* 19, 347, 431); the K salt, K_2PdBr_4, crystallises in thick rhombic forms (Joannis, *C. R.* 95, 295).

Palladium, chlorides of. Two chlorides of Pd have been isolated, PdCl and $PdCl_2$; a third, $PdCl_4$, is known in combination. As none of these chlorides has been gasified, the formulæ are not necessarily molecular (*v.* PALLADIUM, HALOID COMPOUNDS OF; *post*). None of the chlorides has been formed by the direct union of Pd and Cl.

PALLADIUM DICHLORIDE $PdCl_2$ (*Palladous* or *palladoso-chloride*). By dissolving Pd in HClAq, Cl being passed into the liquid or a little HNO_3 being present, evaporating repeatedly with HClAq to remove HNO_3, and finally concentrating, red-brown prismatic needles of $PdCl_2.2H_2O$ are obtained; at a moderate temperature H_2O is given off, and $PdCl_2$ remains as a black-brown crystalline solid (Kane, *T.* 1842. 275; Böttger, *P.* 106, 495). $PdCl_2$ is also obtained, partly as a sublimate and partly as a garnet-red crystalline residue, by heating Pd_2S in a stream of Cl (Schneider, *P.* 141, 519). $PdCl_2$ dissolves in water to form a dark-red liquid, from which some oxychloride, $Pd_xO_yCl_z$, separates on evaporation. In water containing HCl, $PdCl_2$ dissolves very readily. The solution is dark brown, and on treatment with bases it gives salts of the form $M^I_2PdCl_4$—*chlorpalladites* (*v. infra*); this solution may be supposed to contain *pallados-chlorhydric acid* H_2PdCl_4.

Double salts; chlorpalladites $PdCl_2.2M^ICl$ or $M^I_2PdCl_4$. These salts are obtained by the reaction of various oxides with $PdCl_2$ in dilute HClAq, or by adding various chlorides to conc. $PdCl_2Aq$.

Ammonium-palladium dichloride or *Ammonium chlorpalladite* $PdCl_2.2NH_4Cl$ or $(NH_4)_2PdCl_4$. Olive-green needles with a bronze-coloured lustre; c. sol. water, insol. conc. alcohol. When strongly heated gives residue of finely-divided Pd. Obtained by adding NH_4Cl to $PdCl_2Aq$ containing HCl (Kane, *T.* 1842. 275: Wilm, *B.* 13, 1202).

Potassium-palladium dichloride, or *Potassium chlorpalladite* $PdCl_2.2KCl$ or K_2PdCl_4. Golden-yellow needles formed by adding KClAq to conc. $PdCl_2Aq$. The crystals are quadratic prisms (Joannis, *C.R.* 95, 295); they are fairly sol. in cold water, and much more sol. in hot water. Alcohol ppts. the salt from a hot conc. aqueous solution. An aqueous solution boiled with alcohol or SO_2 gives a pp. of Pd; the dry salt is very slowly decomposed by heat to KCl and Pd, the decomposition is slow even in presence of oxalic acid (Rössler, *Z.* 1866. 175), but rapid in a stream of H. The other chlorpalladites which have been described are: $PdCl_2.AlCl_3.10H_2O$ (Welkow, *B.* 7, 803); $BaPdCl_4$ (von Bonsdorff, *P.* 19, 347, 431); $BePdCl_4.6H_2O$ (W., *l.c.*); $CdPdCl_4$; $CaPdCl_4$; $MgPdCl_4$; $MnPdCl_4$; $NiPdCl_4$; $ZnPdCl_4$; $Co_2Cl_6.12NH_3.2PdCl_2$ (Gibbs, *Am. S.* [2] 37, 58); $Co_2Cl_6.10NH_3.2PdCl_2$ (Carstanjen, *Gm.-K.* 3, 1254); $PdCl_2.Hg_2Cl_2.5NH_4Cl$ (Wilm, *B.* 13, 1202).

PALLADIUM SUBCHLORIDE PdCl or Pd_2Cl_2. Small quantities of this chloride are said to be formed, as a dark reddish-brown crystalline solid, when $PdCl_2$ is heated to redness; the chloride deliquesces in air, and always contains $PdCl_2$ and Pd (Kane, *T.* 1842. 275).

PALLADIUM TETRACHLORIDE $PdCl_4$ (*Palladi-* or *palladic chloride*). This chloride probably exists in a solution of Pd in *aqua regia*, or of PdO_2 in conc. HClAq; the compound has not been isolated. As this solution yields salts of the form $M^I_2PdCl_6$ when treated with various metallic chlorides, it perhaps contains *palladichlorhydric acid* H_2PdCl_6.

Double salts; chlorpalladates $PdCl_4.2M^ICl$ or $M^I_2PdCl_6$. These salts are formed by adding metallic chlorides to a solution of Pd in *aqua regia*, or of PdO_2 in conc. HClAq, or to a solution of $PdCl_2$ in HClAq into which Cl has been passed; some of them are also produced by passing Cl into a solution of the corresponding chlorpalladite.

Ammonium-palladium tetrachloride or *Ammonium chlorpalladate* $PdCl_4.2NH_4Cl$ or $(NH_4)_2PdCl_6$. A bright-red pp. obtained by adding NH_4Cl to conc. $PdCl_2Aq$ saturated with Cl or treated with conc. HNO_3Aq. S.G. 2·418 (Topsoë, *J.* 1870. 393). Reduced with difficulty; treated with NH_3Aq, N is evolved and $PdCl_2.2NH_3$ is formed (H. Müller, *A.* 86, 341).

Potassium-palladium tetrachloride or *Potassium chlorpalladate* $PdCl_4.2KCl$ or K_2PdCl_6. A cinnabar-red powder, consisting of small regular octahedra, S.G. 2·738; obtained by mixing KClAq with $PdCl_2Aq$ saturated with Cl, or with Pd in *aqua regia*; also formed by treating K_2PdCl_4Aq with Cl (Topsoë, *J.* 1870. 393; Croft, *C. N.* 16, 53). When the aqueous solution is treated with NH_3Aq, N is evolved and K_2PdCl_4 is formed.

The other chlorpalladates which have been described are: $BePdCl_6.8H_2O$ (Welkow, *B.* 7, 38); $MgPdCl_6.6H_2O$ (Topsoë, *J.* 1870. 393); $NiPdCl_6.6H_2O$ (T., *l.c.*); $ZnPdCl_6.6H_2O$ (T., *l.c.*).

Palladium, cyanides of; and Double cyanides; *v.* vol. ii. p. 343.

Palladium, fluoride of, PdF_2. This compound is produced, according to Berzelius, by adding HFAq to conc. $Pd(NO_3)_2Aq$; it is described as a brown pp. scarcely sol. water or HFAq, and as forming double salts with alkali fluorides.

Palladium, haloid compounds of. The haloid compounds of Pd have not been at all fully investigated. The following table presents the compositions of those which have been isolated:—

PdX	PdX_2	PdX_4
PdCl	PdF_2	
	$PdCl_2$	$PdCl_4$
	$PdBr_2$	in solution and
	PdI_2	combination.

The compounds PdX_2 form double salts $PdX_2.2MX = M_2PdX_4$, and $PdCl_4$ forms $PdCl_4.2MCl = M_2PdCl_6$; the acids H_2PdCl_4 and

H_2PdCl_6 probably exist in solution. The chlorpalladates M_2PdCl_6 are not very easily reduced; the chlorpalladites M_2PdCl_4 are readily oxidised to chlorpalladates. None of the haloid compounds has been gasified; the formulæ are the simplest that express the composition, but they are not necessarily molecular. $PdBr_2$ is formed by digesting together finely-powdered Pd and Br in presence of water. $PdCl_2$ and $PdCl_4$ are easily soluble in water; PdF_2, $PdBr_2$, and PdI_2 are insoluble or but slightly soluble in water.

Palladium, hydride of. Pd absorbs H very freely. A piece of Pd foil which has been strongly heated *in vacuo* absorbs 643 times its volume of H at 90°–97°. When electrolytically ppd. Pd is used as the negative pole in the electrolysis of water, it absorbs 982 vols. H. The physical properties of Pd charged with H make it very probable that a definite compound is formed, and that this compound has the composition Pd_2H (for details *v.* HYDROGEN, vol. ii. p. 720).

Palladium, hydroxide of, *v. Palladium, oxides and hydrated oxides of.*

Palladium, iodide of, PdI_2. When KIAq is added to $PdCl_2Aq$ or $Pd(NO_3)_2Aq$, an almost black pp. of $PdI_2.H_2O$ is obtained, which loses H_2O *in vacuo* (Lassaigne, *J. Chim. méd.* 11, 57). PdI_2 is scarcely sol. water, alcohol, or ether, slightly sol. HIAq, easily sol. KIAq, from which solution dark-red deliquescent crystals of potassium iodpalladite, K_2PdI_4, separate on concentration. As PdI_2 is scarcely sol. water, the ppn. of this salt may be used in the quantitative estimation of I in presence of Cl and Br. PdI_2 is decomposed to Pd and I at somewhat above 350°; the last traces of I are not removed by heat alone, but by heating in H (Berzelius).

Palladium, oxides and hydrated oxides of. Three oxides have been isolated, Pd_2O, PdO, and PdO_2; another, Pd_5O_6, intermediate between PdO and PdO_2, seems to exist. PdO and PdO_2 seem to form hydrates, but the exact composition of these is not settled. These oxides all react with acids to form salts corresponding with PdO, Pd_2O at the same time forming Pd, and PdO_2 evolving O. It is, however, possible that some salts may be obtained corresponding with PdO_2. All the oxides are reduced to Pd when strongly heated. The examination of the oxides of Pd is very incomplete.

PALLADIUM SUBOXIDE Pd_2O. A black powder obtained by heating to low redness the pp. formed by adding Na_2CO_3 to solution of a salt of PdO (Kane, *T.* 1842. 276), or by heating Pd black in a stream of air (Wilm, *B.* 15, 2225). Decomposed to Pd and O by heating to full redness; reduced by H at ordinary temperatures; reacts with acids to form salts of PdO with separation of Pd.

PALLADIUM MONOXIDE PdO (*Palladous oxide*). A black powder, prepared by heating $Pd(NO_3)_2$, or by very gently heating a Pd salt with K_2CO_3 or Na_2CO_3, and washing the residue with water. Reduced very easily by H (Wöhler, *A.* 174, 160); gives Pd and O when heated to full redness. Soluble in acids with difficulty, forming salts PdX ($X = SO_4$, $2NO_3$, CO_3, &c.).

Hydrated palladium monoxide. The dark-brown pp. obtained by adding K_2CO_3 or Na_2CO_3 to solution of a salt of PdO was described by Berzelius as $PdO.H_2O$, but it may be a basic carbonate; heated to low redness this pp. gives Pd_2O.

PALLADIUM DIOXIDE PdO_2 (*Palladic oxide*). A black powder, obtained by ppg. $PdCl_4Aq$ or K_2PdCl_6Aq with excess of KOHAq, washing and boiling with water, and drying at 100°; also by the action of ozone on compounds of Pd, and by the decomposition of water using Pd as the positive pole (Wöhler, *A.* 146, 375; Mailfert, *C. R.* 94, 860, 1186). At low red heat gives PdO and O, and at a higher temperature all O is given off. Treated with dilute HClAq, gives $PdCl_2Aq$ and Cl, with conc. HClAq probably forms $PdCl_4$. No corresponding salts have been isolated with certainty.

Hydrated palladium dioxide. The pp. obtained by adding excess of KOHAq to $PdCl_4Aq$ or K_2PdCl_6Aq is probably $PdO_2.xH_2O$, but the exact composition of this pp. is not known.

PALLADO-PALLADIC OXIDE $Pd_5O_6 = 4PdO.PdO_2$. According to Schneider (*P.* 141, 519), an oxide of this composition is obtained by melting K_2PdS_3 or Na_2PdS_3 with KNO_3 and KOH, washing with water, and treating the residue with *aqua regia.* It is described as a dull-brown powder, which gives off all its O when heated to redness in air, and is reduced by H at the ordinary temperature.

Palladium, salts of. *Compounds obtained by replacing hydrogen of acids by Pd.* All the salts of Pd which have been isolated with certainty correspond with the oxide PdO; the salts of Pd are generally obtained by dissolving Pd in the various acids, with a little HNO_3Aq added, or in some cases by double decomposition from $PdCl_2Aq$ or $Pd(NO_3)_2Aq$. Only a very few salts have been examined; besides the salts of the haloid acids, the *carbonate, nitrate, nitrite, sulphate,* and *sulphite* have been isolated (*v.* CARBONATES &c.). $PdCl_4$, corresponding with PdO_2, probably exists in solution, and several compounds of this salt—the chlorpalladates—have been obtained (*v. Palladium tetrachloride,* p. 795).

Palladium, selenide of, PdSe. A grey infusible solid, resembling osm-iridium, with which it is perhaps isomorphous (Rössler, *A.* 180, 244); formed by heating together Pd and Se (Berzelius).

Palladium, sulphides of. Three sulphides are known, corresponding with the three oxides. The highest sulphide, PdS_2, reacts with sulphides of more positive elements as a sulphanhydride, forming *sulpho-palladates* M_2PdS_3.

PALLADIUM SUBSULPHIDE Pd_2S. A grey, hard solid; S.G. 7·303 at 15°. Prepared by fusing together, for 15–20 minutes over a blowpipe, 100 parts *yellow* $N_2H_6Pd.Cl_2$ (p. 794), or ·5 parts PdS, with 6 parts dry K_2CO_3 or Na_2CO_3, 6 parts S, and 3 parts NH_4Cl; the fused mass is treated with water, and the lustrous blue-violet crystals of $K_2Pd_3S_4$, which are mixed with the Pd_2S, are removed by agitating with water. Pd_2S is very stable; it is not acted on by acids, scarcely by *aqua regia,* melts at a red heat without change, loses S slowly when very strongly heated (Schneider, *P.* 141, 519).

PALLADIUM MONOSULPHIDE PdS (*Palladous sulphide*). Obtained by heating Pd, or certain

Pd salts, with S; also by ppg. a salt of PdO by H_2S. Prepared in the dry way, PdS forms a blue-white, lustrous, metal-like, very hard solid; prepared in the wet way, it is a black powder. Heated in air, slowly oxidises to a basic sulphate; heated in Cl forms $PdCl_2$ and S_2Cl_2 (Fellenberg, *P.* 50, 65). A colloidal soluble form of PdS was obtained by Winssinger (*Bl.* [2] 49, 452) by ppg. from an extremely dilute solution and dialysing.

PALLADIUM DISULPHIDE PdS_2 (*Palladic sulphide*). A dark-brown powder, scarcely acted on by HNO_3Aq: soluble *aqua regia* without separation of S (Schneider, *P.* 141, 519); heated in a stream of CO_2 forms PdS and then Pd_2S. Obtained by decomposing solution of a sulpho-palladate by dilute HClAq, and washing the pp.: *e.g.*

$Na_2PdS_3Aq + 2HClAq = 2NaClAq + PdS_2 + H_2S$.

This sulphide reacts as an acid anhydride with the sulphides of several of the more positive metals.

Sulphopalladates. These salts belong to two series, M_2PdS_3 and $M_2Pd_3S_4 = M_2PdS_3.Pd_2S$ (Schneider, *P.* 141, 519; 148, 625).

Sodium sulphopalladate Na_2PdS_3 (*Sodium-palladium sulphide*). This salt has not been obtained pure; as prepared by fusing 1 part $N_2H_6Pd.Cl_2$ (p. 794), or ·5 part PdS, with 6 parts dry Na_2CO_3, and 6 parts S, to full redness, and washing the residue with water, it forms reddish-brown needles, which dissolve in water to form a brown liquid decomposed by HClAq with ppn. of PdS_2.

Silver sulphopalladate Ag_2PdS_3. A black-brown powder obtained by adding the Na salt to an alcoholic solution of $AgNO_3$.

The members of the other series of sulpho-palladates, $M_2Pd_3S_4$, may be looked on as double compounds of M_2PdS_3 and Pd_2S, or as the salts of a hypothetical sulphopalladic acid $H_2Pd_3S_4$. These salts may perhaps be termed *meta-sulphopalladates.*

Potassium meta-sulphopalladate, $K_2Pd_3S_4$ or $K_2PdS_3.Pd_2S$. Formed by melting 2 parts $N_2H_6Pd.Cl_2$ (p. 794), or 1 part PdS, with 12 parts K_2CO_3 and 12 parts S, at a red heat, and washing the fused mass with water (Schneider, *P.* 141, 519). Six-sided, blue-violet, metal-like crystals; insol. water, treated with HClAq, K is removed but no H_2S is evolved, and the crystals become steel-grey; perhaps $H_2Pd_3S_4$ may be formed, but if so this soon decomposes, and a sulphide, said to be Pd_3S_4, remains (Schneider, *P.* 141, 625). Another compound, which may perhaps be K_4PdS_4 (corresponding with the hypothetical acid $Pd(SH)_4$) is formed, along with Pd, by heating in H.

Silver meta-sulphopalladate $Ag_2Pd_3S_4$ or $Ag_2PdS_3.Pd_2S$. A white-grey, lustrous, crystalline pp. obtained by treating the K salt with an alcoholic solution of $AgNO_3$.

Palladium, sulphocyanides of, *v.* vol. ii. p. 350.

Palladium, thio- salts of, *v. Sulphopalladates* under *Palladium, sulphides of, supra.*

M. M. P. M.

PALM OIL. Extracted from the fruit of *Elæis guineensis*. Soft orange mass containing palmitic and oleic acids and their glycerides (Pelouze a. Boudet, *A.* 29, 42; Guibourt, *J. Chim. Méd.* 1, 177; Henry, *J. Ph.* 51, 241). From palm kernels an oil is obtained containing the glycerides of oleic, stearic, palmitic, myristic, lauric, decoic, octoic, and hexoic acids (Oudemans, *J. pr.* [2] 2, 393).

PALMELLIN. A substance resembling hæmoglobin, which occurs in *Palmella cruenta*, a red fungus (Phipson, *C. R.* 89, 316, 1078; *C. N.* 41, 216).

PALMITIC ACID $C_{16}H_{32}O_2$. Mol. w. 256. [60·75°] (Reissert, *B.* 23, 2243). (271·5° i.V. at 100 mm.) (Krafft, *B.* 12, 1670; 16, 1721). (339°–356°) (Carnelley a. Williams, *B.* 12, 1360). S.G. (liquid) $\frac{62}{}$ ·853. S. (alcohol) 9·2 at 19·5° (C. a. S.). H.C. (solid) 2,371,788 (Louguinine, *A. Ch.* [6] 11, 223). Occurs as glyceride in a very large number of animal and vegetable fats and fixed oils (Chevreul, *Recherches sur les corps gras*; Fremy, *A.* 36, 44; Stenhouse, *A.* 36, 50; Sthamer a. Meyer, *A.* 43, 335; Schwarz, *A.* 60, 69; Heintz, *A.* 80, 299; 88, 298; 92, 291; von Böck, *J. pr.* 49, 295; Berthelot, *A. Ch.* [3] 41, 216, 432; 47, 297; Maskelyne, *C. J.* 8, 1). Its myricyl ether occurs in bees-wax (Brodie, *A.* 71, 150), and in human fat (Heintz), and its cetyl ether in spermaceti (L. Smith, *A.* 42, 241). Occasionally occurs in the free state, as in palm oil, and in *Lycopodium* spores (Langer, *Ar. Ph.* [3] 27, 625).

Formation.—1. By saponification of palmitin, spermaceti, and melissin.—2. By heating cetyl alcohol with potash-lime (Dumas a. Stas, *A. Ch.* [2] 73, 113).—3. Together with acetic acid by fusing oleic or elaïdic acid with potash (Varrentrapp, *A.* 35, 209).—4. By saponifying bird-lime with alcoholic potash (Divers a. Kawakita, *C. J.* 53, 271).—5. By saponifying the wax of *Myrica cerifera* (Chittenden a. Smith, *Am.* 6, 217).

Preparation.—1. Japanese wax (3 pts.) is saponified with KOH (1 pt.) and water (1 pt.), the solution ppd. by HClAq, and the acid rectified *in vacuo* (Krafft, *B.* 21, 2265).—2. The fatty acids obtained by saponifying fats are dissolved in alcohol, and fractionally ppd. with an alcoholic solution of lead acetate or a conc. aqueous solution of barium or magnesium acetate (*v.* vol. i. p. 56).

Properties.—Small hard crystals (from alcohol), insol. water, v. sol. boiling alcohol and ether. Slightly decomposed on distillation. Chlorination, in presence of $SbCl_5$, yields CCl_4, C_2Cl_6, and C_6Cl_6 [224°] (Hartmann, *B.* 24, 1018). Oxidation by alkaline $KMnO_4$ yields oxalic, succinic, adipic, acetic, butyric, hexoic, oxyvaleric, and dioxypalmitic acids (Gröger, *M.* 8, 486). Oxidation by nitric acid (S.G. 1·36) yields succinic and glutaric acids (Carette, *C. R.* 102, 692). The Ba salt distilled with NaOMe yields pentadecane (Mai, *B.* 22, 2133).

Salts.—$(NH_4)HA'_2$.—KA': pearly scales (from alcohol), insol. ether. Dissolves in a small quantity of water, but a larger quantity ppts. KHA'_2, which crystallises from alcohol in pearly scales [100°] (Schwarz).—NaA': laminæ.—$NaHA'_2$. Got by adding hot water (1500 pts.) to NaA'. Insol. water, v. sol. hot alcohol.—BaA'_2. S. (alcohol) ·0035 at 20°. Pearly crystalline powder. CaA'_2. S. (alcohol) ·0103 at 20°.—MgA'_2. [120°] (H.).—PbA'_2. [112°]. Powder.—CuA'_2: greenish-blue powder.—AgA': amorphous, sl. sol. water. Blackened by light.

Methyl ether MeA'. [28°] (Berthelot).

Ethyl ether EtA′. [24°] (Heintz).

Isoamyl ether $C_5H_{11}A'$. [9°] (Berthelot); [13·5°] (Duffy, *C. J.* 5, 314). Waxy.

Octyl ether $C_8H_{17}A'$. [8·5°]. Formed from the octyl alcohol of castor oil.

Dodecyl ether $C_{12}H_{25}A'$. [41°] (K.).

Tetradecyl ether $C_{14}H_{29}A'$. [48°].

Hexadecyl ether $C_{16}H_{31}A'$. [54°] (Krafft, *B.* 16, 3023). Probably identical with the *cetyl ether* $C_{16}H_{31}A'$ [49°], which is the chief component of spermaceti, from which it is prepared by crystallisation from boiling alcohol.

Octadecyl ether $C_{18}H_{37}A'$. [59°].

Ceryl ether $C_{27}H_{55}A'$. [79°]. The chief constituent of poppy wax (Hesse, *B.* 3, 639).

Myricyl ether $C_{30}H_{61}A'$. [72°]. The constituent of bees-wax that is insoluble in alcohol (Brodie, *A.* 71, 159).

Glyceryl derivatives or *Palmitins v.* vol. ii. p. 621.

Phenyl ether C_6H_5A'. [45°]. (250° at 15 mm.) (Krafft a. Burger, *B.* 17, 1379).

p-Tolyl ether C_7H_7A'. [47°]. (258° at 15 mm.).

Chloride $C_{16}H_{31}OCl$. [c. 12°]. (192·5° at 15 mm.) (Krafft a. Bürger).

Amide $C_{15}H_{31}.CONH_2$. [107°]. Formed by the action of NH_3 on the chloride or ether, and also by heating tetradecyl-malonic amide (Carlet, *Bl.* 1859, 175; Krafft a. Stauffer, *B.* 15, 1730; Hell a. Jordanoff, *B.* 24, 990).

Anilide $C_{15}H_{31}.CONHPh$. [90·5°]. (283° at 17 mm.). Made by boiling palmitic acid with excess of aniline (Hell a. Jordanoff, *B.* 24, 943). Silky needles (from alcohol), v. e. sol. ether.

Anhydride $(C_{16}H_{31}O)_2O$. [64°] (Villier, *B.* 9, 1932).

Nitrile $C_{15}H_{31}.CN$. [31°]. (252° at 100 mm.). S.G. $\frac{4°}{4}$ ·8186; $\frac{100}{4}$ ·776. Formed by distilling the amide with P_2O_5 (K. a. S.), and also by heating cyano-palmitic acid (H. a. J.). Six-sided tables. Reduced by alcohol and sodium to hexadecylamine (Krafft, *B.* 22, 811).

References. — Di-bromo-palmitic acid and Hexadecoic acid.

PALMITIC ALDEHYDE $C_{16}H_{32}O$. [58°]. (193° uncor. at 22 mm.). Prepared by distilling a mixture of calcium palmitate and calcium formate (Krafft, *B.* 13, 1416; 16, 1714). Plates, sl. sol. ether. Combines with $NaHSO_3$.

Palmitic aldehyde $C_{16}H_{32}O$. [47°]. S. (alcohol) ·64 at 16°; 12 at 78°. S. (ether) 16 at 16°. Got by oxidation of cetyl alcohol with chromic acid mixture (Fridau, *A.* 83, 23; Dollfus, *A.* 131, 287). Crystalline.

PALMITIN *v.* Glycerin.

PALMITOLIC ACID $C_{16}H_{28}O_2$. Mol. w. 252. [42°]. Formed by the action of alcoholic potash at 180° on di-bromo-palmitic acid (Schröder, *A.* 143, 22). Silky needles (from alcohol), insol. water, v. sol. ether. Br forms $C_{16}H_{28}Br_2O_2$ and $C_{16}H_{28}Br_4O_2$. Fuming nitric acid oxidises it to suberic acid and suberic aldehyde.—BaA'_2.—AgA′: amorphous powder blackened by light.

Reference.—Bromo-palmitolic acid.

PALMITONE $(C_{15}H_{31})_2CO$. *Di-pentadecyl ketone.* [83°]. S.G. $\frac{83}{4}$ ·799; $\frac{100}{4}$ ·794. Formed by distilling calcium or barium palmitate with lime (Piria, *C. R.* 34, 140; Maskelyne, *C. J.* 8, 1; Krafft, *B.* 15, 1714). Got also by heating palmitic acid with P_2O_5 at 210° (Kipping, *C. J.* 57, 986). Silvery plates, v. sol. alcohol and benzene. Does not unite with $NaHSO_3$ (Limpricht, *A.* 94, 246). Bromine forms $C_{31}H_{60}Br_2O$ [55°] (Herez, *A.* 186, 269).

Oxim $(C_{15}H_{31})_2C{:}NOH$. [59°]. Needles.

PALMITOXYLIC ACID $C_{16}H_{28}O_4$. [67°]. Formed, together with suberic acid and suberic aldehyde by the action of fuming HNO_3 on palmitolic acid (Schröder, *A.* 143, 35). Laminæ (from alcohol), insol. water, v. sol. ether.—AgA′: white pp., turned violet by light.

PANAQUILONE $C_{20}H_{42}O_{15}$. Occurs in the root of *Panax quinquefolius* (Garrigues, *A.* 90, 231). Amorphous powder, v. sol. water and alcohol, insol. ether. Has a bitter-sweet taste. Its solution is ppd. by tannin. H_2SO_4 forms a purple solution from which water ppts. panacone $C_{19}H_{30}O_7$ (?) a crystalline powder. HClAq also forms CO_2 and panacone on heating.

PANICOLE $C_{13}H_{20}O$ *i.e.* $C_{12}H_{17}.OMe$. [285°]. A crystalline substance in oil of millet (Kassner, *Ar. Ph.* [2] 25, 395; 26, 536). HClAq at 160° forms MeCl and $C_{12}H_{18}O$ [78°].

PAPAÏN *v.* Proteïds.

PAPAVERINE $C_{20}H_{21}NO_4$ *i.e.*

C(OMe):CH.C.CH:CH.N
C(OMe):CH.C————C.$CH_2.C_6H_3(OMe)_2$[1:3:4]

(Goldschmiedt, *M.* 9, 330, 349). [147°]. S. (ether) ·4 at 10°. Occurs in opium (Merck, *A.* 66, 125; 73, 50; Anderson, *T.E.* 21, Pt. 1; Hesse, *A.* 153, 75; *Suppl.* 8, 261; *Z.* [2] 7, 641).

Preparation.—1. The aqueous extract of opium is ppd. with Na_2CO_3, the pp. dissolved in ether and shaken with dilute HOAc. The acetic acid solution is ppd. by NaOH. The pp. digested with oxalic acid solution yields crystalline papaverine oxalate. It is better, however, to dissolve the pp. in acetic acid, remove thebaïne by tartaric acid, ppt. the mother-liquor with ammonia, wash the pp. with alcohol, and then treat with oxalic acid. The oxalate is recrystallised from hot water, ppd. by $CaCl_2$, the filtrate ppd. by NH_3 and the papaverine recrystallised from alcohol (Hesse).—2. A solution of the hydrochlorides of the opium bases is ppd. with conc. NaOAc. The pp., consisting of narcotine and papaverine, is dissolved in HClAq, and diluted till it contains only ·25 p.c. of narcotine. K_3FeCy_6 is then added and, after 24 hours, the pp. of papaverine ferricyanide is collected and decomposed by NaOHAq (Plugge, *Ar. Ph.* [3] 25, 343).

Properties.—Trimetric prisms (from ether-alcohol); $a{:}b{:}c = {\cdot}32{:}1{:}{\cdot}42$. Narcotic. Nearly insol. hot water, v. sol. hot alcohol and chloroform, m. sol. hot benzene. Cannot be sublimed. Inactive to light (Goldschmiedt, *M.* 9, 42). Conc. H_2SO_4 forms a colourless solution, becoming dark-violet on warming. On adding dilute H_2SO_4, HCl, or HNO_3 to a solution of papaverine in acetic acid, the sulphate, hydrochloride, or nitrate is ppd. A solution of papaverine in conc. H_2SO_4 gives a pp. of sulphate on adding water. Papaverine is a weak base; its solutions do not affect litmus. With ammonium selenite dissolved in conc. H_2SO_4 it gives a bluish colour changing to red (Ferreira da Silva, *Bl.* [3] 6, 87; *C. R.* 112, 126).

Reactions.—1. *Potash-fusion* yields methylamine, $C_6H_4Me(OMe)_2$[1:3:4], and protocatechuic acid (Goldschmiedt, *M.* 4, 704; 6, 969).—2. Yields

MeCl on heating with HClAq.—3. Aqueous $KMnO_4$ oxidises it to papaveric, veratric, *m*-hemipic, pyridine (α)-tri-carboxylic, dimethoxy-cinchonic, dimethoxy-phthalic, and oxalic acids, hemipic iso-imide NH_3, papaveraldine and CO_2. Papaveric acid (*v. infra*) is the main product (Goldschmiedt, *M.* 6, 372; 8, 510).

Salts.—B'HCl. [220°]. S. 2·7 at 18°. Large monoclinic crystals; $a:b:c = \cdot83:1:\cdot58$; $\beta = 92° 20'$ (Foullon, *M.* 6, 675).—$B'_2H_2PtCl_6$ 2aq. [198°].—$B'_2H_2ZnCl_4$: white dimetric crystals; $a:c = 1:\cdot84$.—$B'_2H_2Cl_2ZnI_2$: plates (from alcohol). —$B'_2H_2CdCl_4$. [176].—$B'_2H_2Cl_2CdBr_2$. [185°] (Jahoda, *M.* 7, 506).—$B'H_2Cl_2CdI_2$. [180°].—$B'_2H_2HgCl_4$: triclinic prisms.—B'HBr. [214°]. Monoclinic crystals; $a:b:c = \cdot83:1:\cdot58$; $\beta = 92° 60'$.—B'HI. [200°]. Monoclinic, sometimes isomorphous with the hydrochloride, but when crystallised from alcohol $a:b:c = 1\cdot3:1:2\cdot12$; $\beta = 91°$.—$B'HI_3$. Purple monoclinic prisms.—$B'HI_5$: thin reddish needles.—$B'_2H_2HgI_4$.—$B'HNO_3$: monoclinic tables; $a:b:c = \cdot82:1:\cdot55$; $\beta = 94° 9'$.—$B'H_2SO_4$: monoclinic prisms; $a:b:c = \cdot83:1:1\cdot38$; $\beta = 92° 29'$.—$B'H_2Cr_2O_7$. Flat orange needles.—$B'H_2C_2O_4$. S. ·26 at 10°. Prisms.—$B'C_6H_3N_3O_7$. [179°]. Golden tables (from alcohol). — Succinate $B'_2C_4H_6O_4$. [171°].—Benzoate $B'C_7H_6O_2$. [145°].—Salicylate $B'C_7H_6O_3$. [130°]. — Meconate $B'C_7H_4O_7$ aq: prisms, sl. sol. alcohol.—Ferrocyanide $B'_4H_4FeCy_6$ (Plugge, *Ar. Ph.* [3] 25, 793).

Methylo-iodide B'MeI 4aq. Melts at 195° when anhydrous: 55°–60° when hydrated. Insol. ether, sol. water and alcohol. Moist Ag_2O forms a caustic hydroxide, capable of giving a carbonate (Claus, *J. pr.* [2] 38, 496; Goldschmiedt, *M.* 10, 673). The following compounds have been prepared from the methylo-iodide (Stransky, *M.* 9, 751): B'MeOH *x*aq. Melting at 215° when anhydrous, B'MeCl [75°], $B'_2Me_2PtCl_6$ 3aq, $B'_2Me_2Cr_2O_7$ [85°], and the picrate $B'MeC_6H_2N_3O_7$. [205°].

Ethylo-bromide B'EtBr 4aq. [140°–145°] (Goldschmiedt, *M.* 6, 667) or B'EtBr aq. [111°] (Claus a. Hüetlin, *B.* 18, 1576). Trimetric needles; $a:b:c = \cdot70:1:\cdot64$. Boiling KOHAq forms the alkaline oxide $(B'Et)_2O$, sl. sol. cold water.

Ethylo-chloride B'EtCl 4aq: prisms. [80°]. Gives $B'_2Et_2PtCl_6$ $3\frac{1}{2}$aq [223°].

Ethylo-iodide B'EtI. [216°].

Ethylo-nitrate $B'EtNO_3$ 3aq. Prisms.

Ethylo-chromate $B'_2Et_2Cr_2O_7$. [78°].

Ethylo-picrate $B'EtC_6H_2N_3O_7$. [175°].

Benzylo-chloride $B'C_7H_7Cl$ 7aq. [165°]. $KMnO_4$ oxidises it to veratric acid, benzyl-papaveraldine, papaveraldine, and hemipic-iso-benzyl-imide. Aqueous (20 p.c.) KOH forms $(B'C_7H_7)_2O$ [165°].—$B'_2(C_7H_7)_2PtCl_6$: crystalline pp.—$B'C_7H_7C_6H_2N_3O_7$ [185°]. —$B'_2(C_7H_7)_2Cr_2O_7$. [85°].

o-*Nitro-benzylo-chloride* $B'C_7H_6(NO_2)Cl$. Crystallises with 4aq, 6aq, and 9aq (Scutter, *M.* 9, 859). $(B'C_7H_6(NO_2)Cl)_2PtCl_4$: crystalline pp.—$B'C_7H_6(NO_2)NO_3$ $1\frac{1}{2}$aq: prisms. — $(B'C_7H_6(NO_2))_2Cr_2O_7$: yellow prisms. — $B'C_7H_6(NO_2).C_6H_2N_3O_7$: yellow prisms (from alcohol).

Phenacylo-bromide $B'CH_2BzBr$ $2\frac{1}{2}$aq. Efflorescent pyramids (Scutter, *M.* 9, 1035). Forms the derivatives: $B'CH_2BzCl$ 6aq: yellow needles. — $(B'CH_2Bz)_2PtCl_6$. — $B'CH_2BzNO_3$ 2aq. —$(B'CH_2Bz)_2Cr_2O_7$ and $B'CH_2BzC_6H_2N_3O_7$ [182°]. An aqueous solution of the phenacylo-bromide gives with dilute NaOHAq a pp. $B'CH_2BzOH$, whence boiling alcohol produces $(B'CH_2Bz)_2O$ [186°], crystallising in colourless needles.

Tetrahydride $C_{20}H_{25}NO_4$. [201°]. Made by reducing papaverine with tin and HCl (Goldschmiedt, *M.* 7, 497). Small prisms (from dilute alcohol), m. sol. hot water, sl. sol. ether.—B'HCl 3aq [290°]. Monoclinic needles, with very bitter taste; causes albuminuria when injected internally. — Salts: $B'_2H_2PtCl_6$ 3aq.—$B'H_2SO_4$ 7aq. — $B'H_2C_2O_4$ 6aq. — $B'_2H_2Cr_2O_7$.—$B'C_6H_3N_3O_7$. [270°]. Yellow needles, v. sl. sol. alcohol.

Bromo-papaverine $C_{20}H_{20}BrNO_4$. [145°]. Got by adding bromine-water to a solution of papaverine hydrochloride. Monoclinic crystals, insol. water, v. sol. alcohol and ether.—B'HBr.

Nitro-papaverine $C_{20}H_{20}N_2O_6$ aq. [163°]. S. (ether) ·03 at 12°. Made by boiling papaverine with dilute nitric acid (S.G. 1·06) (Hesse, *A. Suppl.* 8, 292). Pale-yellow prisms (from dilute alcohol). Violently decomposes when quickly heated.—Salts: B'HCl $1\frac{1}{2}$aq. S. ·35 at 16°.—$B'_2H_2PtCl_6$.—B'HI: v. sl. sol. hot water.—$B'HNO_3$ aq.—$B'_2H_2SO_4$ 8aq.—$B'H_2C_2O_4$ 2aq: yellow prisms, v. sl. sol. water.

Papaveraldine $C_{20}H_{19}NO_5$ *i.e.* [4:3:1] $C_6H_3(OMe)_2.CO.C_9H_4(OMe)_2N$. [210°]. Made by oxidation of papaverine with $KMnO_4$ and dilute H_2SO_4 (Goldschmiedt, *M.* 6, 954; 7, 486). Yellowish crystalline powder (from alcohol), insol. water and alkalis, v. sol. hot HOAc. H_2SO_4 gives a red colour, changing to dark violet on warming. Potash-fusion splits it up into veratric acid and dimethoxyisoquinoline. Tin and HCl reduce it to papaverine tetrahydride. — $B'HNO_3$ 2aq: lemon-yellow needles.—B'HCl *x*aq: yellow crystals, decomposed by water.—$B'_2H_2PtCl_6$ aq: orange prisms. $B'H_2SO_4$.—$B'C_6H_3N_3O_7$. [209°].

Methylo-iodide B'MeI 3aq. [135°].

Ethylo-bromide B'EtBr 3aq [above 270°].

Benzylo-hydroxide $B'C_7H_7OH$ or its anhydride $(B'C_7H_7)_2O$ is a product of the oxidation of papaverine benzylo-chloride by dilute (2 p.c.) $KMnO_4$ at 45° (Goldschmiedt, *M.* 9, 327). It crystallises from boiling water or alcohol in slender colourless needles [154°], converted by boiling HClAq into papaveraldine.

Oxim $C_{20}H_{19}NO_4(NOH)$. [245°]. White needles, sol. hot benzene.

Phenyl-hydrazide $C_{20}H_{19}NO_4(N_2HPh)$. [81°]. Reddish-yellow nodules (from alcohol).

Papaveroline $C_{16}H_{13}NO_4$ *i.e.* [4:3:1] $C_6H_3(OH)_2.CH_2.C_9H_4(OH)_2N$. Formed by boiling papaverine (3 pts.) with HIAq (25 pts. of S.G. 1·96) and red P for 10 hours (G.; Krauss, *M.* 11, 351). White crystalline powder (containing 2 aq), insol. water, m. sol. alcohol, sl. sol. ether, v. sol. acids. Yields (α)-methyl-isoquinoline on distillation with zinc-dust.—Salts: B'HCl: white needles. — $B'_2H_2SO_4$ $8\frac{1}{2}$aq. — B'HI 2aq. — $B'_2H_2C_2O_4$ 3aq: needles, m. sol. hot water.

Papaveric acid $C_{16}H_{13}NO_7$ *i.e.* $C_6H_3(OMe)_2.CO.C_5H_2N(CO_2H)_2$. [233°]. Formed by oxidising papaverine with $KMnO_4$ (Goldschmiedt, *M.* 6, 380; 10, 158, 691). Minute

right-angled tables (containing aq), sl. sol. water, alcohol, and ether, m. sol. dilute alcohol. Its solutions are acid in reaction. Decomposes on fusion into CO_2 and pyropapaveric acid $C_{15}H_{13}NO_5$ [230°]. Potash-fusion forms protocatechuic acid.

S a l t s.—K_2A'' $2\frac{1}{2}$aq: white leaflets, v. e. sol. water. — KHA'' $x$aq: needles. — CaA'' $1\frac{1}{2}$aq. — BaA''. — $Cu_3A''_2(OH)_2$ 6aq. — Ag_2A'' $2\frac{1}{2}$aq. — $AgH_3A''_2$ aq.—$H_2A''HCl$ $2\frac{1}{2}$aq: yellow needles.

Anhydride. [170°]. Got by boiling papaveric acid with Ac_2O (Goldschmiedt, *M.* 10, 159).

Mono-ethyl ether $EtHA''$. [188°]. Got by boiling the anhydride with alcohol. Converted by NH_3Aq into the amic acid.

Oxim $C_{16}H_{13}NO_6(NOH)$. [c. 156°]. Small needles (from alcohol) (Goldschmiedt, *M.* 10, 692).

Phenyl-hydrazide $C_{16}H_{13}NO_6(N_2HPh)$. [190°]. Yellow needles (from dilute alcohol).

Nitro-papaveric acid $C_{16}H_{12}(NO_2)NO_7$. [215°]. Formed by dissolving papaveric acid in conc. HNO_3. Golden needles (containing aq).—Ag_2A''.

Pyropapaveric acid $C_{15}H_{13}NO_5$. [230°]. Formed by fusing papaveric acid. Minute white leaflets.—CaA'_2 4aq: groups of needles. — BaA'_2 4aq.—$HA'HCl$ aq: orange-red needles.— AgA': crystalline pp.

Oxim $C_{15}H_{14}N_2O_5$. [226°]. Needles (from alcohol).—$B'HCl$ aq: yellow needles.

Phenyl-hydrazide $C_{15}H_{13}NO_4(N_2HPh)$. [223°]. Yellow prisms.—$B'HCl$.

PAPAVEROSINE. An alkaloid in dried poppy heads of *Papaver somniferum* (Deschamps, *A. Ch.* [4] 1, 453). Nacreous needles (from alcohol). Coloured red by H_2SO_4.

PAPAYOTIN. An amorphous hygroscopic powder ppd. by adding alcohol to an aqueous extract of the juice of *Carica papaya* (Peckholt, *Ph.* [3] 10, 343). It has an astringent, slightly sweet taste.

PARABANIC ACID $C_3H_2N_2O_3$ *i.e.*

$\mathrm{CO}{<}\begin{smallmatrix}\mathrm{NH.CO}\\ \mathrm{NH.CO}\end{smallmatrix}$. *Oxalyl-urea.* Mol. w. 114. S. 4·7 at 8°. H.C. 212,700. H.F. 2,200 (Matignon, *C. R.* 113, 198).

Formation.—1. By dissolving uric acid (1 pt.) in nitric acid (7 pts. of S.G. 1·3) at 70° and evaporating to a syrup, when parabanic acid crystallises out on cooling (Liebig a. Wöhler, *A.* 26, 285; Menschutkin, *A.* 172, 74).—2. By oxidation of alloxan.—3. A product of the action of HOCl on guanine (Strecker, *A.* 118, 156).— 4. From uric acid by heating with MnO_2 and dilute H_2SO_4 (Wheeler, *Bl.* [2] 7, 521) or with KNO_2 and H_2SO_4 (Gibbs, *B.* 1, 341).—5. A product of the action of HCl and $KClO_3$ on uric acid (Laurent a. Gerhardt, *A. Ch.* [3] 24, 175).— 6. By the action of $POCl_3$ on oxaluric acid $NH_2.CO.NH.CO.CO_2H$ at 200° (Grimaux, *C. R.* 77, 1548).—7. By the action of PCl_3 on a mixture of oxalic acid and urea (Ponomareff, *Bl.* [2] 18, 97).—8. By heating nitro-pyruvic ureide with bromine and water (Grimaux, *C. R.* 79, 1478).— 9. By the action of Br and water on uric acid (Hardy, *Bl.* [2] 1, 445; Magnier, *Bl.* [2] 22, 56).

Properties.—Monoclinic laminæ (from water or alcohol); $a:b:c = 1:{\cdot}665:{\cdot}478$; $\beta = 81°\ 39'$. Decomposed above 200°, forming a white sublimate. Completely oxidised by $KMnO_4$ and H_2SO_4 to CO_2 and NH_3. Not attacked by HNO_3 in the cold. Its solution is not ppd. by Ca salts, but on boiling with alkalis it is split up into oxalic acid and ammonia. In the same way lead salts and a little NH_3 give a pp. of lead oxalate (Maly, *M.* 2, 284).

Reactions.—1. In aqueous solution the salts rapidly change to oxalurates.—2. *Zinc* and HCl reduce it to oxalantin.—3. Alcoholic NH_3 at 100° forms oxaluramide.—4. Alcoholic EtI at 100° forms $C_9H_{17}NO_5I_2$ crystallising from alcohol in green prisms, nearly insol. cold water (Hlasiwetz, *A.* 103, 200).—5. *Urea* (1 pt.) at 130° forms $C_4H_6N_4O_4$, a sparingly-soluble powder (Grimaux, *Bl.* [2] 32, 120).

S a l t s.—NH_4A'. Crystalline powder, got by adding alcoholic ammonia to a solution of parabanic acid in absolute alcohol. Gives off its NH_3 at 100°. Warm water converts it into ammonium oxalurate.—NaA'.—KA'. Got by using alcoholic KOEt.—AgA'. Crystalline pp., got by adding $AgNO_3$ to a solution of KA'.— $Ag_2C_3N_2O_3$ aq. Got by ppg. a solution of parabanic acid with $AgNO_3$. Insol. water, sol. HNO_3.—U r e a s a l t CON_2H_4HA'. Four-sided tables, sl. sol. cold water.—P h e n y l - h y d r a z i n e s a l t $(N_2H_3Ph)_2A'$ aq. [170°]. Insol. alcohol and ether. Boiling water converts it into $NH_2.CO.NH.CO.CO.N_2H_2Ph$ [215°] (Skinner a. Ruhemann, *C. J.* 53, 550).—A n i l i n e s a l t. [250°] (S. a. R.).

Hydrate $C_3H_2N_2O_3$ aq. S. 13·5 at 8°. Formed from uric acid (1 pt.) and nitric acid (3 pts. of S.G. 1·3) at 60°. The mixture is kept at 35°–55°, and finally heated to 70°, when the hydrate separates in large crystals (Tollens a. Wagner, *A.* 166, 321; 175, 227). Formed also by the action of $POCl_3$ on a mixture of urea and oxalic acid, heat not being applied (P.). At 150°–160° it loses water and changes to ordinary parabanic acid.

Methyl parabanic acid $\mathrm{CO}{<}\begin{smallmatrix}\mathrm{NMe.CO}\\ \mathrm{NH\ .CO}\end{smallmatrix}$.

Methyl-oxalyl-urea. Oxalyl-methyl-urea. [149°].

Formation.—1. By heating nitroso-creatinin with HCl at 100° (Dessaignes, *A.* 97, 342; Märcker, *A.* 133, 315).—2. From methyl-uric acid and HNO_3 (Hill, *B.* 9, 1093; 13, 739).— 3. By the action of $AgNO_3$ on methyl-thioparabanic acid (oxalyl-methyl-thio-urea) (Andreasch, *B.* 14, 1449; *M.* 2, 279).—4. By oxidation of theobromine or caffoline with chromic acid mixture (E. Fischer, *A.* 215, 297; Maly a. Hinteregger, *B.* 14, 727; *M.* 2, 94).

Properties.—Colourless trimetric prisms, sol. hot water. Acid in reaction. Not volatile with steam. Decomposed by alkalis, even in the cold, into methyl-urea and oxalic acid.

S a l t.—AgA'. Needles, sol. hot water.

Di-methyl-parabanic acid $\mathrm{CO}{<}\begin{smallmatrix}\mathrm{NMe.CO}\\ \mathrm{NMe.CO}\end{smallmatrix}$.

Cholestrophane. [146°]. (276°). S. 1·87 at 20°.

Formation.—1. The final product of the action of chlorine on caffeïne in water (Rochleder, *A.* 73, 123).—2. By boiling caffeïne with nitric acid (Stenhouse, *A.* 45, 371; 46, 229).— 3. By heating dry silver parabanate with MeI at 100° (Strecker, *A.* 118, 174).—4. By oxidation of caffeïne with chromic acid mixture (Maly a. Hinteregger, *B.* 14, 723).—5. By the action of $AgNO_3$ on $\mathrm{CS}{<}\begin{smallmatrix}\mathrm{NMe.CO}\\ \mathrm{NMe.CO}\end{smallmatrix}$ (Andreasch, *M.* 2, 283). 6. By the action of dilute HClAq on murexoïn

(Brunn, *B.* 21, 515).—7. By passing ozonised oxygen through water in which caffeïne is suspended (Leipen, *M.* 10, 184).

Properties.—Trimetric prisms (from alcohol). May be sublimed. Completely decomposed by alkalis. Gives no pp. with lead acetate until ammonia is added, when lead oxalate is ppd. Pure HNO_3 has no action (Franchimont, *R. T. C.* 6, 217).

Reactions. — 1. Alcoholic NH_3 forms di-methyl - oxaluramide [225°] on heating. — 2. HClAq at 200° splits it up into oxalic acid, CO_2, and methylamine (Calm, *B.* 12, 624).— 3. Cold alcoholic soda decomposes it into oxalic acid and di-methyl-urea (M.'a. H.).—4. *Zinc* and dilute H_2SO_4 reduce it to di-methyl-glyoxyl-urea $CO<\begin{matrix}NMe.CH.OH\\NMe.CO\end{matrix}$, a crystalline body, melting below 100°, decomposed by heating with baryta into glycollic acid, oxalic acid, methylamine, and CO_2 (Andreasch, *M.* 3, 436).—5. On warming with water containing $BaCO_3$ it yields di-methyl-oxamide (Maly a. Hinteregger, *M.* 2, 88, 132).

Phenyl-parabanic acid $CO<\begin{matrix}NH.CO\\NPh.CO\end{matrix}$. [208°]. Made from phenyl-urea and $ClCO.CO_2Et$ (Stojentin, *J. pr.* [2] 32, 11). Silky plates, v. sol. alcohol, ether, and hot water.

Di-phenyl-parabanic acid $CO<\begin{matrix}NPh.CO\\NPh.CO\end{matrix}$. [204°]. Formed by boiling an alcoholic solution of diphenyl-guanidine dicyanide (dicyanomel-aniline) $C_{15}H_{13}N_5$ or (α)-tri-phenyl-guanidine dicyanide with HClAq (Hofmann, *Pr.* 11, 275; *B.* 3, 764). Formed also by warming thiocarb-anilido-thio-oxanilide with alcoholic $AgNO_3$, and by the action of $ClCO.CO_2Et$ on di-phenyl-urea (Stojentin). Needles, insol. water, v. sol. alcohol and ether. Decomposed by boiling KOHAq into oxalic acid, aniline, and CO_2. Yields with fuming HNO_3 a di-nitro-di-phenyl-parabanic acid crystallising in needles.

PARACONIC ACID *v. Lactone of* Oxypyrotartaric acid.

PARAFFIN. Solid, wax-like, fatty mixture of hydrocarbons of the C_nH_{2n+2} series, very rich in carbon and characterised by a very marked indifference to most reagents.

Analysis.—

	1	2	3	4	5
C	85·15	84·9	85·31	84·86	85·5
H	14·85	14·31	14·44	15·02	14·9

1. Anderson, *J.* 1857, 480; 2, 3. Brodie, *P.M.* [3] 33, 178; 4. Pawlewski, *B.* 23, 327; 5. Gill a. Meusel, *C. S. J.* 6, 466. Beilstein states (*Bn.* 1, 139) that commercial paraffin usually contains 1 p.c. oxygen, which can be removed by heating with Na in a tube. Lippmann a. Hawliczek (*B.* 12, 69), from a sample of brown coal paraffin v. sl. sol. alcohol [37°] by heating with PCl_5, formed $C_{20}H_{40}Cl_2$; hence give formula $C_{20}H_{42}$. Bolley (*A.* 106, 230), by heating hot paraffin with Cl, formed $C_{25}H_{46}Cl_6$–$C_{25}H_{37}Cl_{15}$; hence gives formula $C_{25}H_{52}$. Gill a. Meusel (*Z.* 1869, 65) have formed from paraffin by oxidation with CrO_3, cerotic acid $C_{27}H_{54}O_2$, hence formula $C_{27}H_{56}$. Pawlewski, by Raoult's method, using glacial acetic acid, finds $C_{24}H_{50}$–$C_{27}H_{56}$, by dilute benzene and *p*-xylene $C_{48}H_{100}$–$C_{54}H_{112}$, and with saturated solutions in benzene and *p*-xylene $(C_{24}H_{50})_4$–$(C_{27}H_{56})_4$. It behaves as a colloid in most other solvents.

Melting-point [45°–65°]. By the action of solvents, small quantities of fractions [38°–45°] have also been obtained (Albrecht, *D. P. J.* 218, 280). Ozokerite paraffin [64°].

Boiling-point. Above 300°. In crude petroleum the portion (300°–400°) solidifies on cooling. On fractionating, Bolley and Tuchschmid found that the portion [53°] (300°) gave the following fractions (150°) [43°]; (200°) [44·5°] and residue [53·5°].

Specific gravity varies from 0·872–0·912 at 17° (Albrecht). Ozokerite paraffin [64°]. S.G. $\frac{20}{}$ 0·917. [38°]. S.G. $\frac{21}{}$ 0·874 (Beilby, *C. J.* 43, 388). Paraffins expand considerably on melting.

Occurrence.—Occurs native as fossil wax, hatchettine, and ozokerite. The latter is the most abundant, and is found in Galicia, Roumania, on the island of Tscheleken on the east coast of the Caspian Sea, and on the island of Swjatoi at Baku. When bleached it is called cerisine. According to Zawziecki, ozokerite contains a crystalline and amorphous paraffin. It is also found in Etna lava to the extent of 43 p.c. in certain geodes (Silvestri, *G.* 12, 9). It is obtained by the distillation of brown coal, turf, boghead coal, shales, schists, and natural bitumens, wood, wax, and wax and lime. It can also be obtained from brown coal tar. Details of various methods are given by von Boyen, *Z. f. Angew. Chem.* 1891. 261). Paraffin is also obtained in large quantities from American petroleum, being present in the high-boiling portions which form a residue after the lighting oils have been distilled off. Other mineral oils contain appreciable quantities of solid paraffin, *e.g.* Rangoon oil of Burma, 6 p.c. For the preparation of commercial paraffin from these bodies *v.* Thorpe's Dictionary of Applied Chemistry, and for a theory for its formation in nature by the decomposition of animal matter, *vide* Zawziecki, *D. P. J.* 280, 69, 85, and 133.

Properties.—Paraffin, when pure, is a solid, colourless, translucent substance, perfectly inodorous and tasteless, somewhat resembling spermaceti. It readily melts, forming a colourless oil; burns from a wick with a bright flame, but does not burn easily in the mass. It is insol. water, sol. hot alcohol, v. sol. ether and oils. The solubility of paraffin from ozokerite has been studied by Pawlewski a. Filipowicz (*B.* 21, 2973), who show that the liquid constituents are mostly sol. glacial acetic acid, whereas vaseline, cerisine, ozokerite and paraffin are almost insoluble. Pawlewski (*B.* 23, 327) also states that ozokerite paraffin is sol. formic acid, acetic acid, benzene, *p*-xylene, and chloroform. Thorpe a. Young (*A.* 165, 1), by heating paraffin in closed vessels at a high temperature, have resolved it into a little gas and hydrocarbons of the C_nH_{2n} series (C_5H_{10}–$C_{11}H_{22}$), and others of the C_nH_{2n+2} series (C_5H_{12}–$C_{11}H_{24}$). Higher solid and liquid hydrocarbons were also obtained. Long heating at 150° causes an increase of weight, attributed by Bolley and Tuchschmid to oxygen absorption (*Z.* 1868. 500; Jaznnowitch, *B.* 8, 768). Oxidised products can also be obtained by the action of oxidising agents. Champion (*C. R.* 75, 1576) has shown that nitrosulphuric acid slowly transforms it at

90° into a liquid oil of the composition $C_{13}H_{26}NO_5$ (called paraffinic acid), from which ethereal salts have been obtained, and at the same time yields a white solid $C_{11}H_{22}NO_6$ sol. Aq. Fuming nitric acid, according to Pouchet, also acts upon paraffin at 110°, forming a true paraffinic acid $C_{24}H_{48}O_2$ [46°] together with other fatty acids. The acid has a wax-like odour, is insol. water, but sol. alcohol, ether, and benzene, is easily decomposed by heat, and forms deliquescent salts of the alkaline metals, and yellow, cheesy plates with the earths and magnesia. It is carbonised by sulphuric acid (*Bl.* 23, 111; *C. R.* 79, 320) and nitric acid converts it into nitro-compounds and suberic acid. Champion has also shown that chlorine is absorbed by paraffin in sunlight, producing hydrochloric acid. According to Gill a. Meusel (*Z.* 1869. 65), CrO_3 and dilute HNO_3 oxidise paraffin to a mixture of cerotic $C_{27}H_{54}O_2$, succinic, and other fatty acids. According to Beilstein a. Wiegand (*B.* 16, 1548), ozokerite contains a solid hydrocarbon of the olefine series. It is formed by distilling the ozokerite *in vacuo*, and, after removing the first portions of oily distillate, crystallising the solid portion from a solution of alcoholic benzene. It is called *lekene* [79°] S.G. 0·9392, and is a very stable compound, being unacted upon by CrO_3, HNO_3, and $KMnO_4$. It is, however, completely oxidised by acid $KMnO_4$, and slowly forms a bromo- compound when heated with Br and H_2O in a sealed tube. For methods of analysis of paraffin scale, and determination of impurities therein, *vide* B. Redwood, *S. C. I.* 3, 430; *Journ. Soc. Arts*, 1886. 56; Sutherland, *S. C. I.* 6, 123, 271; and Stuart Thomson, *ibid.* 10, 342 *et seq.* S. R.

PARAFFIN HYDROCARBONS *v.* Hydrocarbons.

PARAFFIN OIL *v.* Petroleum.

PARAGLOBIN *v.* Proteids.

PARAHÆMOGLOBIN *v.* Hæmoglobin.

PARALBUMIN *v.* Proteïds, *Appendix C.*

PARALDEHYDE *v.* Aldehyde.

PARANILINE $C_{12}H_{14}N_2$. [192°]. A base found by Hofmann (*Pr.* 12, 314) in the preparation of crude aniline on a large scale. Long, silky needles (from dilute alcohol). EtI yields $C_{12}H_{13}EtN_2$ and $C_{12}H_{12}Et_2N_2$.—$B''_2H_2Cl_2$aq: six-sided plates (from conc. HClAq) converted by water into yellow needles of B″HCl aq, sl. sol. water.—$B''_2H_2PtCl_6$: yellow prisms.—$B''HNO_3$.—$B''H_2SO_4$.—$B''_2H_2SO_4$.

Benzoyl derivative $C_{12}H_{13}BzN_2$. Needles.

PARAPEPTONE *v.* Proteïds.

PARELLIC ACID $C_9H_6O_4$? An acid sometimes obtained in the preparation of lecanoric acid (Schunck, *A.* 54, 274). Needles (containing aq), v. sl. sol. cold water, sol. alcohol and ether. Tastes bitter. Reddens litmus.—PbA'_2?: white flocculent pp.

PARICINE *v.* Cinchona bases.

PARIDIN $C_{32}H_{56}O_{14}$. S. 1·5; S. (alcohol) 2. A neutral glucoside extracted by alcohol from the leaves of *Paris quadrifolia* (Walz, *Pharm. Cent.* 1841. 690; *N. Jahres. Pharm.* 13, 174; Delffs, *ibid.* 60, 25). Formed also, together with a sugar, by boiling paristyphnin with dilute H_2SO_4. Thin laminæ (containing 4aq) (from water) or tufts of needles (from alcohol). Conc. H_2SO_4 turns it red. Boiling HClAq decomposes it, in alcoholic solution, into a sugar and resinous paridol $C_{26}H_{46}O_9$.

PARILLIN $C_{48}H_{86}O_{18}$ or $C_{40}H_{70}O_{18}$. [210°]. S. ·008 in the cold; 5 at 100°. Ppd. by adding water to an alcoholic extract of sarsaparilla root (Flückiger, *Ph.* [3] 8, 488). Plates or prisms, sol. hot alcohol and chloroform. Conc. H_2SO_4 gives a yellow solution. Dilute HCl gives green fluorescence and splits it up into a sugar and parigenin $C_{28}H_{42}O_4$, which is insol. boiling water.

PARISTYPHNIN. An amorphous body which accompanies paridin, and may be ppd. by tannin. Boiling dilute acids split it up into a sugar and paridin.

PARPEVOLINE. Name given to the hexahydride of di-methyl-ethyl-pyridine, and to pyridine bases isomeric therewith.

PARSLEY. The volatile oil of parsley contains a terpene (162° i.V.), S.G. $\frac{12}{}$ ·865 (Gerichten, *B.* 9, 259; Sauer a. Grünling, *A.* 208, 75). The seeds contain apiol (*q. v.*). Water extracts Apiin (*q. v.*) from the plant.

PARSNEP. The volatile oil of parsnep seeds contains octyl *n*-butyrate (Renesse, *A.* 166, 80).

PARVOLINE $C_9H_{13}N$. (c. 200°). A product of the putrefaction of horse-flesh (Gautier, *Bl.* [2] 48, 11). Oil, smelling like hawthorn blossom, v. sol. alcohol and ether. Resinifies in air. Its platinochloride forms sparingly-soluble flesh-coloured crystals.

Parvoline $C_9H_{13}N$. (c. 220°). A product of the distillation of cinchonine with potash (Oechsner de Coninck, *C. R.* 91, 296).—$B'_2H_2PtCl_6$: brownish-yellow powder.

Parvoline $C_9H_{13}N$. (188°). A product of the dry distillation of the bituminous shale of Dorsetshire (Greville Williams, *C. J.* 7, 97).

Parvoline $C_9H_{13}N$. (188°). S.G. $\frac{22}{}$ ·986. Got by distillation of coal (Thenius, *J.* 1861. 502).

Parvolines of known constitution *v.* Di-ethyl-pyridine, Di-methyl-ethyl-pyridine, Tetra-methyl-pyridine, and Methyl-propyl-pyridine.

PASSIVE STATE OF METALS *v. Passivity of iron*, art. Iron, p. 52.

PATCHOULI. The volatile oil of patchouli, obtained from the leaves of *Pogostemon Patchouli*, contains a sesquiterpene (which yields $C_{15}H_{24}$2HCl [118°]), and a camphor $C_{15}H_{26}O$ [55°], (296°), S.G. $\frac{4·5}{}$ 1·051 (Gal, *C. R.* 68, 406; Montgolfier, *C. R.* 84, 88; *B.* 10, 234; Wallach, *A.* 238, 81). Patchouli camphor crystallises in hexagonal prisms, insol. water, v. sol. alcohol and ether. It is lævorotatory $[\alpha]_D = -118°$. On distillation with $ZnCl_2$, or on heating with HOAc and Ac_2O, it yields patchoulene $C_{15}H_{24}$ (254°), S.G. $\frac{0}{}$ ·946; $[\alpha]_D = -42°$.

PATELLARIC ACID $C_{17}H_{20}O_{10}$. [above 100°]. Occurs in the lichen *Patellaria* (or *Parmelia*) *scruposa*, from which it can be extracted by ether (Knop; Weigelt, *Z.* [2] 5, 298). Crystalline mass, insol. water, v. sol. alcohol and ether. Tastes bitter. Decomposed on fusion or on boiling with baryta, with formation of orcin and oxalic acid. $FeCl_3$ gives a purple colour. Cold baryta-water forms a salt with transient blue colour.

PAVIIN *v.* Fraxin.

PAYTINE $C_{21}H_{24}N_2O$. [156°]. $[\alpha]_D = -49{\cdot}5°$ in a ·45 p.c. alcoholic solution. An alkaloid extracted by alcohol from a white bark of an *Aspidosperma* from Payta in Peru (Hesse, *A.* 154, 287; 166, 259; 211, 280; Wulfsberg, *Ph.* [3] 11, 269; Arata, *G.* 11, 246; *C. J.* 40, 622). Prisms (containing aq) sl. sol. water, sol. ether, benzene, chloroform, and (unlike aspidospermne) ligroïn. Tastes bitter; is not poisonous. When heated with soda-lime it yields paytone, a non-nitrogenous substance. Conc. HNO_3 forms a colourless solution, changing through red to yellow. $FeCl_3$ and conc. H_2SO_4 give no colour. Chloride of gold gives a purple pp. $HgCl_2$ gives a yellow amorphous pp. Bleaching powder produces, in an acid solution, a red colour changing through blue to yellow.

Salts.—B'HCl. S. 6 at 15°. Prisms.—$B'_2H_2PtCl_6$: dark-yellow amorphous pp.; dissolves in hot HClAq, forming a red solution changing to blue and depositing a blue pp.

Paytamine $C_{21}H_{24}N_2O$. An amorphous alkaloid accompanying paytine. Unlike paytine, KI does not ppt. it from neutral solutions. Its salts are amorphous, and it does not yield paytone.

PECTOLACTIC ACID $C_8H_8O_6$. An acid got by boiling milk-sugar with NaOHAq and less CuO than is needful for complete oxidation (Boedeker, *A.* 100, 281). Brownish syrup, drying up to a varnish (containing $2\frac{1}{2}$aq). Miscible with water and alcohol, insol. ether. Reduces ammoniacal $AgNO_3$, forming a mirror.—BaA″$4\frac{1}{2}$aq: powder, insol. alcohol.

PECTOUS SUBSTANCES. Unripe fleshy fruits and fleshy roots (*e.g.* pears, carrots, and turnips) contain a substance (pectose) insoluble in water, alcohol, and ether, transformed under the influence of acids into pectin, which is soluble in water, and is ppd. as a jelly on adding alcohol or on boiling (Vauquelin, *A. Ch.* 5, 100; 6, 282; [2] 41, 46; Braconnot, *A. Ch.* [2] 28, 173; 30, 96; 47, 266; 72, 433; Guibourt, *J. Chim. Med.* 1, 27; Mulder, *J. pr.* 16, 277; 16, 246; Fremy, *A. Ch.* [3] 24, 9; Soubeiran, *J. Ph.* [3] 11, 417; Poumarède a. Figuier, *J. Ph.* [3] 11, 458; 12, 81; Chodeff, *A.* 51, 356; Scheibler, *Z.* [2] 4, 433; Reichardt, *Ar. Ph.* [3] 10, 116; Giraud, *C. R.* 80, 477; Stude, *A.* 131, 244; Rochleder, *Z.* [2] 4, 381).

Pectin, obtained from the juice of ripe pears and apples by removing albuminoids by tannin and calcium by oxalic acid, and then ppg. with alcohol, is, according to Bauer (*J. pr.* [2] 30, 370), a mixture of carbohydrates. Different analyses of pectin give C 39·5 to 46 p.c.; H 5·5 p.c.; O 48·5–55 p.c. Pectous substances differ from cellulose in being stained by methylene-blue, but, unlike lignin, the colour is destroyed by acids (Mangin, *C. R.* 109, 579). By boiling with water pectin is converted into 'parapectin,' a solution of which, unlike pectin, gives a pp. with lead acetate. Nitric acid yields mucic acid by oxidation. Boiling dilute acids convert pectin into 'metapectin,' which is acid in reaction and gives a pp. with $BaCl_2$ (unlike pectin and parapectin). Boiling alkalis convert pectin into pectic acid.

Pectic acid $C_{16}H_{22}O_{15}$? (Fremy). C 41·4 to 44·9 p.c.; H 4·71 to 5·4; O 49·7 to 53·8. Got by boiling an aqueous extract of carrots with Na_2CO_3 and ppg. with HCl. Produced also from pectin in fruit by the action of a ferment (pectase). Jelly, drying up to a horny mass. Acid in taste and reaction; insol. cold water, alcohol, and ether. Converted by boiling water, first into parapectic acid and then into metapectic acid. Boiling dilute acids yield arabic acid.

Salts.—$Na_2C_{14}H_{20}O_{14}$.—$PbC_{16}H_{20}O_{15}$.—$Ag_2C_{14}H_{20}O_{14}$ (Chodneff).—$Ag_2C_{16}H_{20}O_{15}$ (Fremy).

Arabic acid, when prepared by hydrolysis of pectic acid, is called metapectic acid, and the arabinose got by the action of HClAq upon it is called pectinose. Pectinose or arabinose is tetra-oxy-valeric aldehyde (*q. v.*).

References.—ARABIN and CELLULOSE.

PELARGONIC ACID *v.* ENNOIC ACID.

PELLETIERINE $C_8H_{15}NO$. (195°). S.G. $\frac{0}{}$ ·988. V.D. 4·88 (calc. 4·66). S. 5. Occurs, together with methyl-pelletierine, pseudo-pelletierine, and isopelletierine in the bark of the pomegranate (Tanret, *C. R.* 86, 1270; 87, 358; 88, 716; 90, 695; *J. Ph.* [4] 28, 168, 384). It may be extracted from the powdered bark by shaking with chloroform and milk of lime. If the chloroform is decanted and shaken with a dilute acid, the alkaloids will be taken up by the acid solution. The acid solution is mixed with NaOH and shaken with chloroform, which extracts pelletierine and pseudo-pelletierine, which may be separated by crystallisation of their sulphates; the pelletierine is finally distilled in a current of H.

Properties.—Colourless liquid, partially decomposed at 195°, but may be distilled *in vacuo*. M. sol. water, miscible with alcohol, ether, and $CHCl_3$. The sulphate is lævorotatory; $[\alpha]_D = -30°$. Resinified by absorption of oxygen. Fumes with HCl.

Methyl-pelletierine $C_9H_{17}NO$. (215°). S. 4 at 12°. Extracted from an acid solution of the mixed bases by adding $NaHCO_3$ and shaking with chloroform. Liquid, forming very deliquescent salts. V. sol. alcohol, ether, and chloroform. Its hydrochloride is dextrorotatory $[\alpha]_D = +22°$.

Pseudopelletierine $C_9H_{15}NO$. [46°] (when hydrated). (246°). S. 40 at 0°. S. (ether) 11 at 10°. Crystallises from water in prisms (containing 2 aq), v. e. sol. water, alcohol, and $CHCl_3$. Inactive as regards light. Powerful base, expelling NH_3 from its salts. Gives the alkaloidal reactions. Like pelletierine, it gives an intense green colour with H_2SO_4 and $K_2Cr_2O_7$.—B'HCl: rhombohedra. S. 100 at 10°.—$B'_2H_2PtCl_6$: needles.—$B'_2H_2SO_4$ 4aq: v. sol. water.

Isopelletierine $C_8H_{15}NO$. An inactive liquid, resembling pelletierine in other respects.

PELOSINE $C_{18}H_{21}NO_3 1\frac{1}{2}$aq. An alkaloid contained in the root of *Pareira brava* or *Cissampelos Pareira* (Wiggers, *A.* 27, 29; 33, 81; Bödeker, *A.* 69, 53; Flückiger, *N. J. P.* 31, 257). Extracted by dilute H_2SO_4, and ppd. by Na_2CO_3, and dissolved in ether or CS_2. Amorphous powder, almost insol. water. Strongly alkaline in reaction. Yields methylamine, dimethylamine, and a derivative of pyrrole on distilling with KOH (Williams, *Chem. Gaz.* 1858, 321).—B'HClaq: amorphous hygroscopic powder.—$B'_2H_2PtCl_6$: amorphous.—$B'H_2CrO_4$aq. According to Flückiger, pelosine is identical with buxine and bebeerine.

Pelluteïn $C_{18}H_{19}NO_3$? A yellow base, insol. ether, either formed from pelosine by atmospheric oxidation or occurring in *Pareira*.—$B'_2H_2PtCl_6$.

PENDECANAPHTHENE or Pentadecanaphthene $C_{15}H_{30}$. (247° cor.) S.G. $\frac{17}{}$ ·829. Occurs in Russian petroleum (Markownikoff, *J. R.* 15, 339). Liquid.

PENNYROYAL. The oil of pennyroyal from *Mentha pulegium* contains pulegone, which may be purified by fractional distillation *in vacuo* (Beckmann, *A.* 262, 3; *cf.* Kane, *A.* 32, 286).

Pulegone $C_{10}H_{16}O$. (131° at 60 mm.). S.G. $\frac{20}{}$ ·932. $[\alpha]_D = +22·9°$. Somewhat viscid oil, smelling like peppermint. Darkens in colour even in closed tubes. When reduced by Na it gives 40 p.c. of menthol.—$C_{10}H_{17}BrO$. [40·5°]. $[\alpha]_D = -33·8°$. Made by passing HBr into pulegone dissolved in ligroïn. Whetstone-shaped crystals, v. sol. alcohol and ether. This hydrobromide is converted by hydroxylamine into an oxim [38°] crystallising in four-sided plates, which on standing lose Br and then melt at 110°. This oxim also forms the hydrated oxim [157°] (*v. infra*) by taking up water. The hydrobromide is re-converted into pulegone by treatment with Ag_2O, while zinc-dust reduces it to pulegone hydride ($\alpha = -17·4°$), which yields an oxim [83°], and can be converted, by the action of Na on its ethereal solution, into lævorotatory menthol $[\alpha]_D = -21·3°$, giving a benzoyl derivative [54°].

Hydrated oxim $C_{10}H_{18}O(NOH)$. [157°]. $[\alpha]_D = -83·4°$ in alcoholic solution. Formed by the action of hydroxylamine on pulegone. Long matted needles, sl. sol. ether, cold alcohol, and benzene. Yields an acetyl derivative $C_{10}H_{18}AcNO_2$ [149°] and a benzoyl derivative [138°].—B'HCl. [118°]. $[\alpha]_D = -32·4°$. Trimetric crystals; $a:b:c = ·605:1:1·048$.—B'HBr. [111°].

Pulegonamine $C_{10}H_{19}NO$. Made by reducing the foregoing oxim with HI and P. Amber-coloured liquid, sl. sol. water, v. sol. alcohol and ether. Tastes bitter. Boiling MeI forms $C_{10}H_{18}MeNO$. Phenyl thiocarbimide forms $PhNH.CS.N(C_{10}H_{18}O)$ [198°]. Yields a benzoyl derivative $C_{10}H_{18}BzNO$ [101°].—$(C_{10}H_{19}NO)HCl$. [117°]. Long needles, v. sol. water.

PENTADECANE $C_{15}H_{32}$. [10°]. (270°). (136° at 10 mm.). S.G. $\frac{15}{4}$ ·772; $\frac{20}{4}$ ·769; $\frac{100}{4}$ ·713. Made by reduction of $C_{13}H_{27}.CCl_2.CH_3$ or of pentadecoic acid with HI and P (Krafft, *B.* 15, 1700). A pentadecane (114° at 15 mm.) is got by distilling barium palmitate with NaOMe (Mai, *B.* 22, 2134).

Pentadecane $C_{15}H_{32}$. (260°). S.G. $\frac{19}{}$ ·825. Occurs in American petroleum. It yields decane when passed through red-hot tubes (Pelouze a. Cahours; Vohl, *J.* 1865, 841).

PENTADECENOIC ACID $C_{15}H_{26}O_2$? *Di-amenylvaleric acid.* (300°–306°). A product of the action of CO at 160° on a mixture of sodium isovalerate and $NaOC_5H_{11}$ (Geuther a. Fröhlich, *A.* 202, 304). Liquid.

PENTADECENYL ALCOHOL? $C_{15}H_{30}O$? [73°]. The portion of the wax of *Ficus gummiflua* that is readily soluble in ether (Kessel, *B.* 11, 2114). Nodules (from ether).

PENTADECINENE $C_{15}H_{28}$. (230°–240°). Got by heating the acetyl derivative of di-oxy-pentadecane (triamylene acetate) with potash (Bauer, *A.* 137, 249). Thick liquid. Unites with bromine.

PENTADECOIC ACID $C_{15}H_{30}O_2$. [62°]. Formed by oxidation of cocceryl alcohol $C_{30}H_{60}(OH)_2$ or of cocceric acid $C_{31}H_{62}O_3$ with CrO_3 and acetic acid; the yield is about 40 p c. (Liebermann a. Bergham, *B.* 20, 964). Crystalline solid. V. sol. alcohol, ether, acetic acid, and benzene, less readily in ligroïn.—A'_2Ca and A'_2Ba: granular pps.

Methyl ether A'Me: [68°]; crystalline solid.

Pentadecoic acid $C_{15}H_{30}O_2$. [51°]. (257° at 100 mm.). Made by oxidation of methyl pentadecyl ketone with chromic acid mixture (Krafft, *B.* 12, 1671; 19, 2983). Pearly scales.—BaA'_2. —AgA'.

Pentadecoic acid $C_{15}H_{30}O_2$. [70°]. Occurs, together with mannite, in the fungus *Agaricus integer* (Thörner, *B.* 12, 1636). Small needles, v. e. sol. ether and boiling alcohol, insol. water.

Isomerides *v.* CETIC ACID and LACTARIC ACID.

PENTADECONENE $C_{15}H_{26}$. (220°). Made from $C_{15}H_{28}Br_2$ and alcoholic potash (Bauer, *A.* 147, 255).

Pentadeconene (235°–245°). Made from santonic acid and HI (Cannizzaro a. Amato, *B.* 7, 1104).

DI-PENTADECYL-CARBINOL $(C_{15}H_{31})_2CH(OH)$. [85°]. Made by reducing palmitone in boiling alcohol by adding sodium (Kipping, *C. J.* 57, 987). Silky needles or plates (from alcohol), sol. ether, insol. water. With boiling Ac_2O it yields $(C_{15}H_{31})_2CH.OAc$ [49°], a granular powder, v. sol. ether.

DI-PENTADECYL KETONE *v.* PALMITONE.

***n*-PENTANE** C_5H_{12} *i.e.* $CH_3.CH_2.CH_2.CH_2.CH_3$. Mol. w. 72. (37°). S.G. $\frac{13·7}{4}$ ·6282 (Schiff); $\frac{15}{15}$ ·6337; $\frac{25}{25}$ ·6250 (Perkin); μ_A 1·3607 at 6·5°; $\mu_D = 1·3649$; $\mu_H = 1·3769$ (Gladstone, *C. J.* 59, 290). M.M. 5·638 at 17·2°. Occurs in American and in Galician petroleum, in coal-tar oil, and in resin oil (Greville Williams, *C. J.* 15, 130; Schorlemmer, *C. J.* 25, 1085; *Pr.* 15, 131; Lachovitch, *A.* 220, 190; Renard, *A. Ch.* [6] 1, 225). Oil. Yields on chlorination two amyl chlorides (106°) and (104°), and finally $C_5H_8Cl_4$ (230°–240°) (Bauer, *C. R.* 51, 572; Schorlemmer; Lachovitch). CrO_2Cl, followed by water, yields $CH_2Cl.CO.C_3H_7$ (Etard). At a red heat it is decomposed with formation of ethylene, propylene, and butinene (Norton a. Andrews, *Am.* 8, 1).

Isopentane $(CH_3)_2CH.CH_2.CH_3$. *Tri-methyl-ethane.* V.D. 2·50 (calc. 2·48). (30°). S.G. $\frac{15}{15}$ ·6248; $\frac{25}{25}$ ·6159 (Perkin); $\frac{80·5}{4}$ ·6132 (Schiff, *A.* 220, 87); $\frac{13}{13}$ ·6375 (Just, *A.* 220, 153). S.V. 117·2 (Schiff). M.M. 5·750 at 16·4°. Occurs in American and in Galician petroleum (Warren, *Z.* 1865, 668; Lachovitch). Formed by the action of water on zinc isoamyl, or by heating isoamyl iodide with zinc and water at 140° (Frankland, *A.* 74, 47). It is also a product of the action of $ZnCl_2$ on hot isoamyl alcohol, and of zinc on dry isoamyl iodide.

The same pentane can be obtained from active amyl iodide by treatment, in alcoholic solution, with zinc and HCl in the cold (Just). Oil with characteristic odour, unlike 'benzoline.' Not attacked by Br or HNO_3. Chlorine yields

an amyl chloride (100°). Isopentane (1 c.c.) is oxidised by $K_2Cr_2O_7$ (4 g.) and CrO_3 (20 g.) in water (2000 c.c.) in five weeks at 15°–20° to iso-valeric acid (Berthelot, *C. R.* 79, 1435).

Pentane $C(CH_3)_4$. *Tetra-methyl-methane.* [c. −20°]. (9·5°). H.F.p. 47,850. H.F.v. 44,950 (Thomsen, *Th.*). Formed by the action of $ZnMe_2$ on *tert*-butyl iodide (Lwow, *Z.* [2] 6, 520; 7, 257; Naumann, *B.* 7, 173). Appears also to be formed from $CH_3.CCl_2.CH_3$ and $ZnMe_2$ (L.). Oil or gas.

References.—Di-bromo-, Di-chloro-, and Iodo-pentane.

PENTANE CARBOXYLIC ACID *v.* Hexoic acid.

Pentane dicarboxylic acid *v.* Butyl-malonic, Ethyl-glutaric, Di-ethyl-malonic, Di-methyl-glutaric, Pimelic, and Propyl-succinic acids.

***n*-Pentane tricarboxylic acid** $CPr(CO_2H)_2.CH_2.CO_2H$. [148°]. Got by saponifying its ether with alcoholic potash. Slender needles, v. sol. water, alcohol, and ether. Splits up at 175° into CO_2 and propyl-succinic acid.

Ethyl ether Et_3A'''. (280°). S.G. $\frac{13}{15}$ 1·052. Made from ethane tricarboxylic ether $CO_2Et.CH_2.CH(CO_2Et)_2$, NaOEt, and PrI (Waltz, *B.* 15, 608; *A.* 214, 58). Oil, miscible with alcohol and ether.

Mono-nitrile of the diethyl ether $CPr(CN)(CO_2Et).CH_2.CO_2Et$. (205° at 45 mm.). Formed from sodium cyano-succinic ether and *n*-propyl iodide (Barthe, *Bl.* [3] 1, 305; *C. R.* 108, 297). Oil.

Pentane tri-carboxylic acid. *Ethyl ether* $C_2H_5.CH(CO_2Et).CMe(CO_2Et)_2$. *Methylbutenyl tricarboxylic ether.* (281·5° cor.). S.G. $\frac{20}{4}$ 1·0575; μ_D 1·4347 at 20°. Formed by the action of Na on a mixture of α-bromo-butyric ether and sodium methyl-malonic ether (Bischoff, *B.* 22, 1817, 3180; 23, 647). Apparently the same acid ((281·8° cor.), S.G. $\frac{20}{4}$ 1·0523; $\mu_D = 1·4340$ at 20°) is got from sodium butane tricarboxylic ether and MeI. Both acids yield, on saponification by H_2SO_4, two methyl-ethyl-succinic acids [88°] and [168°].

Pentane tri-carboxylic acid. *Ethyl ether* $C_2H_5.C(CO_2Et)_2.CHMe.CO_2Et$. (272·8° cor.). S.G. $\frac{20}{4}$ 1·0609. μ_D 1·4374 at 20°. Formed by the action of Na on a mixture of α-bromo-propionic ether and sodium ethyl-malonic ether (Bischoff a. Mintz, *B.* 23, 648). The same, or an isomeric ether (282·8° cor.), S.G. $\frac{20}{4}$ 1·0607; $\mu_D = 1·4373$ at 20°) is got from sodium propane tricarboxylic ether and EtI. Both acids yield, on saponification with H_2SO_4, methyl-ethyl-succinic acid [168°]; the acid prepared by the second method yields also the isomeric acid [88°].

Pentane tri-carboxylic acid $CH_2(CO_2H).CH_2.CH(CO_2H).CH_2.CH_2.CO_2H$. [107°]. Formed from pentane tetra-carboxylic ether by saponifying with alcoholic potash, and boiling the product with conc. HClAq (Emery, *B.* 24, 284). Mass of needles.—Ag_3A''': white pp.

Pentane tri-carboxylic acid $C_2H_5.CH(CO_2H).CH(CO_2H).CH_2.CO_2H$. [148°]. Made by the action of fumaric ether on sodium ethyl-malonic ether, the product being saponified (Auwers, *B.* 24, 310). V. sol. water and alcohol.

Isopentane tri-carboxylic acid $(CH_3)_2CH.C(CO_2H)_2.CH_2.CO_2H$. [145°] (Hjelt, *B.* 16, 2622). Formed from its ether, which is made from ethane tricarboxylic ether, NaOEt and PrI (Waltz, *A.* 214, 60). Yields isopropyl succinic acid on fusion.

Ethyl ether Et_3A'''. (270°–290°).

Isopentane tri-carboxylic acid $(CH_3)_2CH.CH(CO_2H).CH(CO_2H)_2$. *Carbopimelic acid.* [160°]. Got from its ether by cold alcoholic potash. Monoclinic (?) crystals (from water), v. sol. water, alcohol, and ether. Decomposes on fusion into CO_2 and isopropyl-succinic (pimelic) acid.—$Ba_3A'''_2$: sticky pp.

Ethyl ether Et_3A'''. (277°). Made from α-bromo-isovaleric ether and sodium-malonic ether (W. Roser, *A.* 220, 274). Liquid, with bitter taste.

Isopentane tricarboxylic acid. *Ethyl ether* $CMe_2(CO_2Et).CMe(CO_2Et)_2$. (284·3° cor.). S.G. $\frac{20}{4}$ 1·0524. $\mu_D = 1·4333$ at 20°. Made from sodium methyl-malonic ether and α-bromo-iso-butyric ether (Bischoff a. Mintz, *B.* 23, 649). Yields, on saponification by H_2SO_4, tri-methyl-succinic acid [105°] and a small quantity of a substance melting between 108° and 122°. The same, or an isomeric ether ((277·8° cor.), S.G. $\frac{20}{4}$ 1·0575, $\mu_D = 1·4341$ at 20°) is got from sodium isobutane tricarboxylic ether and MeI. It yields, on saponification, tri-methyl-succinic acid [105°] and *u*-di-methyl-succinic acid [140°].

Pentane tetracarboxylic acid $(CO_2H)_2CH.CH_2.CH_2.CH_2.CH(CO_2H)_2$. Oil; split up by heat into CO_2 and *n*-pimelic acid $CO_2H.CH_2.CH_2.CH_2.CH_2.CH_2.CO_2H$.

Ethyl ether Et_4A^{iv}. (260° at 100 mm.). Got from sodium malonic ether and trimethylene bromide (Perkin, jun., *C. J.* 51, 241; *B.* 18, 3248). *Disodium salt* $CH_2(CH_2.CNa(CO_2Et)_2)_2$. Amorphous powder; converted by bromine into pentamethylene tetracarboxylic ether.

Pentane tetra-carboxylic acid $CH_2(CMe(CO_2H)_2)_2$. [164°]. Got by boiling its ether with alcoholic potash (Dressel, *A.* 256, 183). Crystalline mass, v. sol. water, m. sol. ether. Converted by heating, by itself or in aqueous solution, into $CH_2(CHMe.CO_2H)_2$ [90°].

Ethyl ether Et_4A^{iv}. (191° at 12 mm.). Made by the action of MeI on a solution of di-sodium propane tetra-carboxylic ether in alcohol. Oil.

Pentane tetra-carboxylic acid. *Ethyl ether* $C(CO_2Et)_2(CH_2.CH_2.CO_2Et)_2$. (215° at 13 mm.). S.G. $\frac{20}{4}$ 1·1084. A by-product in the action of NaOEt on a mixture of β-bromo-propionic ether with malonic ether (Emery, *B.* 24, 283). Colourless oil.

PENTANE PHOSPHONIC ACID *v.* Isoamyl phosphinic acid.

PENTANE SULPHONIC ACID $C_5H_{11}.SO_3H$. Formed by the action of nitric acid on isoamyl mercaptan, disulphide, or sulphocyanide (Gerathewohl, *J. pr.* 34, 447; Henry, jun., *A. Ch.* [3] 25, 246; Medlock, *A.* 69, 225). Deliquescent crystalline mass. Chlorine acting on it in sunlight forms $C_5H_{10}Cl.SO_3H$ (Spring a. Winssinger, *Bl.* [2] 41, 301). ICl_3 at 130° forms the same body, together with tri- and tetra- chloro-pentanes and $C_5H_9Cl_2(SO_3H)$.

Salts.—BaA'_2 (dried at 100°). Gyrates on water.—PbA'_2xaq: colourless laminæ.—CuA'_2.—AgA': plates. *Double salts with chloro-pentane sulphonates* $BaA'(C_5H_{10}ClSO_3)aq$.—$Ba_3A'_2(C_5H_{10}ClSO_3)_2Cl_2$ 2aq.

Chloride $C_5H_{11}SO_2Cl$. Liquid.

Pentane disulphonic acid $CEt_2(SO_3H)_2$. Formed from $CCl_3.SO_3H$ and $ZnEt_2$ in ether (Ilse, *A.* 147, 145). Syrup.—K_2A'' 2aq: needles (from alcohol).—BaA'' 2aq. S. 14 in the cold, c. 30 at 100°.—PbA''.—ZnA'' 4aq: plates.

PENTA-THIONIC ACIDS. *Thionic acids* under SULPHUR, OXYACIDS OF, vol. iv.

***n*-PENTATRIACONTANE** $C_{35}H_{72}$. [75°]. (331° at 15 mm.). S.G. $\frac{75}{4}$ ·7816; $\frac{80}{4}$ ·777; $\frac{100}{0}$ ·766. Formed by reduction of the dichloride of stearone with H and P (Krafft, *B.* 15, 1715).

PENTENE *v.* AMYLENE. The name pentene is also given sometimes to pentamethenyl trihydride.

Dipentene *v.* TERPENES.

PENTENOIC ACID $C_5H_8O_2$ *i.e.* $CHEt:CH.CO_2H$. *Propylidene-acetic acid.* (196°). S.G. $\frac{16}{4}$ ·988. Made by heating propionic aldehyde with malonic acid, and HOAc at 100° (Komnenos, *A.* 218, 166; Zincke a. Küster, *B.* 22, 494). Oil.—BaA'_2: plates [270°].—CaA'_2 aq: nodules, v. sol. water and alcohol.—CuA'_2: green pp. [91°]. Yields Cu_2O at 175°.—AgA': bulky pp. The same acid (S.G. $\frac{16}{4}$ ·983) appears to be got by adding sodium-amalgam to an alkaline solution of $CCl_2:CCl.CCl:CCl.CO_2H$ derived from pyrocatechin or o-amido-phenol. It combines with bromine.

Pentenoic acid $CMe_2:CH.CO_2H$. *Dimethyl-acrylic acid.* [70°]. (195).

Formation.—1. From $CH_2Pr.CO_2H$ by oxidising to $CMe_2(OH).CH_2.CO_2H$ and heating the product with dilute H_2SO_4 (Neubauer, *A.* 106, 62; W. von Miller, *A.* 200, 261).—2. From di-methyl-allyl-carbinol by oxidising to β-oxy-valeric acid and distilling this acid with dilute H_2SO_4 or treating its ether with PCl_3 (Semljanitzin a. Saytzeff, *A.* 197, 72; Ustinoff, *J. pr.* [2] 34, 478; *Bl.* [2] 45, 255).—3. A product of the action of alcoholic NaOEt on α-bromo-isovaleric ether (Duvillier, *C. R.* 88, 913, 1209; 112, 1012; *A. Ch.* [5] 19, 428).—4. The chief product of the action of iodoform on sodium isobutylate (Gorboff, *J. pr.* [2] 41, 228).

Properties.—Monoclinic prisms; $a:b:c = 1·53:1:·71$; $\beta = 74°\ 13'$. Sl. sol. water, v. sol. alcohol and ether. Bromine combines, forming $C_5H_8Br_2O_2$ [108°]. Converted into isobutylene and CO_2 by heating for 30 hours at 220°.

S a l t s.—NaA'.—BaA'_2 2aq: groups of needles.—CaA'_2.—CaA'_2 4aq.—ZnA'_2 4aq.—CuA'_2 2aq.—PbA'_2 aq.—AgA'.

Isomerides.—ALLYL-ACETIC, ANGELIC, TETRA-METHYLENE CARBOXYLIC, and TIGLIC ACID.

PENTENYL ALCOHOL $C_5H_{10}O$ *i.e.* $CH_2:CH.CHEt.OH$. *Vinyl-ethyl-carbinol.* (114°). S.G. $\frac{0}{0}$ ·856; $\frac{19·5}{0}$ ·840. Formed from acroleïn by successive treatment with $ZnEt_2$ and water (Wagner, *J. R.* 16, 319; *B.* 21, 3349; *Bl.* [2] 42, 330). Pungent liquid. Yields on oxidation by $KMnO_4$ propionic and formic acids, CO_2, and tri-oxy-pentane.

Acetyl derivative $C_5H_9.OAc$. (132°) at 748 mm. S.G. $\frac{0}{0}$ ·913; $\frac{21·5}{0}$ ·893. Liquid.

Pentenyl alcohol $CH_2:CH.CH_2.CHMe.OH$. *Methyl-allyl-carbinol.* (116°). Formed by the action of zinc on a mixture of allyl iodide and acetic aldehyde (Wagner, *B.* 21, 3350). Yields on oxidation a tri-oxy-pentane, formic and acetic acids, and acetic aldehyde.

Pentenyl alcohol $C_5H_{10}O$. *Valerylene hydrate.* (115°–120°). Got by treating its acetyl derivative with solid KOH.

Acetyl derivative C_5H_9OAc. (135°). A product of the action of AgOAc on $C_5H_{10}Cl_2$ obtained by combination of valerylene with HCl (Reboul, *Z.* 1867, 174).

Pentenyl alcohol $CH_3.CH:CH.CMeH.OH$. *Methyl-propenyl-carbinol.* (118°). Formed by the action of water on the corresponding pentenyl chloride, which is a product of chlorination of $CHMe:CHEt$ (Kondakoff, *B.* 24, 931).

Pentenyl alcohol $CH_2:CH.CMe_2.OH$. *Di-methyl-vinyl-carbinol. Isoprenic alcohol.* (99°). Formed from C_5H_9Cl, which is obtained from isoprene and HCl (Gradziatzky, *Bl.* [2] 47, 168). Smells like camphor. Dilute H_2SO_4 at 100° forms a hydrocarbon.

Acetyl derivative C_5H_9OAc. (121°).

A pentenyl alcohol (125°–135°) is a product of reduction of tiglic aldehyde (Lieben a. Zeisel, *M.* 7, 57).

References.—BROMO- and CHLORO-PENTENYL ALCOHOL.

PENTENYL-AMIDO-PHENYL MERCAPTAN $C_6H_4{<}{}^{N}_{S}{>}C.CH_2Pr$. Liquid, formed from o-amido-phenyl mercaptan and isovaleryl chloride (Hofmann, *B.* 13, 8, 1223).—$B'_2H_2PtCl_6$: needles.

PENTENYLAMINE $C_5H_{11}N$ *i.e.* $CH_2:CH.CH_2.CHMe.NH_2$. (85°). Got by reducing nitro-amylene with zinc and HCl (Gal, *J.* 1873, 333).

Pentenylamine $C_5H_9NH_2$. *Valerylamine.* A product of the action of NH_3 on chloro-amyl alcohol (amylene chlorhydrin) at 100° (Wurtz, *A. Suppl.* 7, 89).—$B'_2H_2PtCl_6$: orange crystals.

PENTENYL-BENZENE $C_6H_5.C_5H_9$. (173°–177°). S.G. ·84. Formed, together with a polymeride $C_{22}H_{28}$ (c. 210°), S.G. $\frac{23}{}$ ·96, by boiling bromo-amyl-benzene $C_6H_5.CHEt.CHBr.CH_3$, with water (Dafert, *M.* 4, 153, 616). Yields benzoic and acetic acids on oxidation.

PENTENYL BROMIDE *v.* BROMO-AMYLENE.

PENTENYL THIOCARBIMIDE C_5H_9NCS. (190°). Formed from isoamylene bromide by successive treatment with alcoholic NH_3 and CS_2 (Hofmann, *B.* 12, 990). Liquid.

PENTENYL-THIO-UREA $C_5H_9NH.CS.NH_2$. [103°]. Formed from pentenyl thiocarbimide and alcoholic NH_3 at 100° (Hofmann, *B.* 12, 991).

PENTHIOPHENE. The homologue of thiophene $CH_2{<}{}^{CH:CH}_{CH:CH}{>}S$, known in some of its derivatives (Krekeler, *B.* 19, 3270).

PENTIC ACID $C_6H_8O_3$ *i.e.* $\begin{matrix}CHEt.CO\\CO—CH_2\end{matrix}{>}O$? [128°]. A product of the action of alcoholic potash on bromo-ethyl-acetoacetic ether (Demarçay, *Bl.* [2] 27, 483; *C. R.* 88, 126). Got also by heating bromo-ethyl-acetoacetic ether at 100° (Wedel, *A.* 219, 104). Trimetric crystals, v. sol. hot $CHCl_3$.

S a l t s.—NaA' aq.—KA' $\frac{1}{2}$aq: v. e. sol. water. MgA'_2 5aq.—CaA'_2 aq.—BaA'_2 2aq.—ZnA'_2 5aq.—MnA'_2 4aq.

Ethyl ether $\begin{matrix}CEt—CO\\C(OEt).CH_2\end{matrix}{>}O$. Mol. w. 153 (obs. by Raoult's method); (calc. 156) (Moscheles a. Cornelius, *B.* 21, 2607; 22, 244). Liquid.

Phenyl-hydrazide $C_6H_8O_2(N_2HPh)$. Crystals (from alcohol).

PENTINENES C_5H_8. *Pentylenes. Pentines.* Mol. w. 68. Of the eight possible isomerides, three are derived from acetylene and precipitate ammoniacal silver and cuprous solutions; the remaining five, so far as they are known, give no metallic derivatives. The following are known:

1. **Propyl-acetylene** $CH_3.CH_2.CH_2.C:CH$. (48°–49°). Methyl-propyl-ketone by action of PCl_5 gives a dichloride, from which alcoholic potash withdraws 2HCl (Friedel, *Z.* 1869, 124). Forms liquid dibromide (190°) and tetrabromide (275°) (Bruylants, *B.* 8, 411).

2. **Isopropylacetylene** $(CH_3)_2CH.C:CH$. (28°–29°). The chloride from isovaleric aldehyde (Bruylants, *B.* 8, 413) or isopropyl-ethylene bromide, is decomposed by alcoholic potash (Eltekow, Flawitzky, Krylow, *B.* 10, 707 and 1102). Oxidised by chromic liquor into acetone, acetic, and isobutyric acids. Bromides liquid, $C_5H_8Br_2$ (175°), $C_5H_8Br_4$ (275°) (Bruylants, *B.* 8, 407). The silver compound C_5H_7Ag is white, dissolves slightly in ammoniacal silver nitrate solution, and crystallises therefrom in small prisms. Converted by a solution of iodine in KI into the compound C_5H_7I (140°).

3. Eltekow (*B.* 10, 1904), by treating commercial amylene with sulphuric acid (dil. with ½ vol. H_2O) at 0°, obtained an insoluble amylene, the bromide of which, by the action of KHO, yielded a mixture of two hydrocarbons, of which one, the smaller amount (35°), gave a pp. with ammoniacal silver solution. This he believed to be isopropylacetylene, though differing from the compound described above in b.p.

4. **Valerylene.** This name was given to the liquid (44°–46°) obtained by Reboul (*A.* 131, 238) from the dibromide prepared from commercial amylene. This substance is a mixture from which Eltekow obtained the hydrocarbon described under 3, and a larger quantity of another (51°–52°), which is stated (*B.* 10, 2057) to yield acetic and propionic acids by treatment with chromic acid. Hence Eltekow ascribes to it the formula, $C_2H_5.C:C.CH_3$, although it does not yield metallic derivatives. Reboul's valerylene, heated to 250°–260°, yields a terpene $C_{10}H_{16}$ (180°) (Bouchardat, *Bl.* [2] 33, 24). Strong sulphuric acid converts it into a hydrate $C_{10}H_{16}H_2O$ and polymerides $C_{15}H_{24}$, &c. (Reboul, *A.* 143, 372). Yields a dibromide, which on treatment with alcoholic potash gives C_5H_7Br, C_5H_6 (valylene), and valerylene (Reboul, *A.* 135, 372). Valerylene tetrabromide $C_5H_8Br_4$ is liquid.

5. **Piperylene** (42°) (Hofmann, *B.* 14, 665). Distinguished by the production of a crystalline tetrabromide, fusible [114·5°] and volatile without decomposition. Gives no pp. with solutions of silver or copper, and probably has the constitution $(CH_3)_2C:C:CH_2$, or β-dimethylallene.

6. **Isoprene** (about 37°). Originally obtained (*v.* Gr. Williams, *Tr.* 1860, 241), along with caoutchene and heveene, by destructive distillation of caoutchouc (*q.v.*). Formed also in notable quantity by the action of very low red heat upon turpentine oil and its isomerides (Tilden, *C. J.* 45, 410). A colourless, limpid liquid, S.G. ·6823 at 20°. Oxidises rapidly on exposure to air, forming a syrupy compound which, on being quickly heated, often explodes. Contact with strong acids in the cold converts it into a substance apparently identical with caoutchouc. Combines violently with bromine, forming a tetrabromide which remains liquid at −20° and is decomposed by distillation. Absorbs hydrochloric acid, forming a mixture of mono- and di-hydrochlorides: $C_5H_8 2HCl$ (145°–150°), unstable liquid. Oxidised by chromic acid to carbonic, formic, and acetic acids; by nitric acid to oxalic and a small quantity of undetermined acid.

Heated to 280° isoprene is converted into dipentene $C_{10}H_{16}$, identical with the product from turpentine (*v.* TERPENES) (Bouchardat, *C. R.* 87, 654 a. 89, pp. 361, 1117). W. A. T.

PENTINENE CARBOXYLIC ACID *v.* HEXINOIC ACID.

Pentinene tricarboxylic acid $C_8H_{10}O_6$ *i.e.* $C_3H_5.C(CO_2H)_2.CH_2.CO_2H$.

Allyl-ethane tricarboxylic acid. [151°]. Got from its ether, which is made from sodium ethane tricarboxylic ether and allyl bromide (Hjelt, *B.* 16, 333). At 160° it splits up into allyl-succinic acid and CO_2.

Ethyl ether Et_3A''' (c. 282°).

PENTINOIC ACID $C_5H_6O_2$. [206°]. A product of the oxidation of oil of turpentine by HNO_3 (Roser, *B.* 15, 293). Tables (from water); sl. sol. water.

PENTINYL ETHYL OXIDE $C_7H_{12}O$, *i.e.* $C_5H_7.O.C_2H_5$. (125°–130°). Formed from $C_5H_8Br.OEt$ and alcoholic potash at 155° (Reboul, *A.* 133, 86). Light oil. Combines with bromine.

PENTOIC ACID *v.* VALERIC ACID.

PENTONENE C_5H_6. (42·5°). S.G. ·803. V.D. 2·45. Occurs in oil deposited by compressed gas derived from bituminous shale (Etard a. Lambert, *C. R.* 112, 945). Oil polymerises in the cold, becoming $C_{10}H_{12}$, which forms crystalline $C_{10}H_{12}2H_2SO_4$.

PENTONYL ETHYL OXIDE $C_7H_{10}O$ *i.e.* $CH:C.CH_2.C(OEt):CH_2$. (155°). V.D. 3·87. Got by heating di-chloro-pentinene $CH_2(CCl:CH_2)_2$ with alcoholic potash (Combes, *A. Ch.* [6] 12, 223). Colourless liquid, with unpleasant smell.

PENTOSE. Name given to compounds resembling glucose but having only 5 atoms of carbon in the molecule; *e.g.* tetra-oxy-valeric aldehyde.

PENTYL. Another name for the radicle AMYL.

PENTYLENE *v.* AMYLENE and PENTINENE.

PENTYLENE-GLYCOL *v.* DI-OXY-PENTANE.

PENTYLIC ACID is VALERIC ACID.

PENTYLIDENE *v.* AMYLIDENE.

PENTYLIDENE-ACETONAMINE *v.* ACETONAMINE.

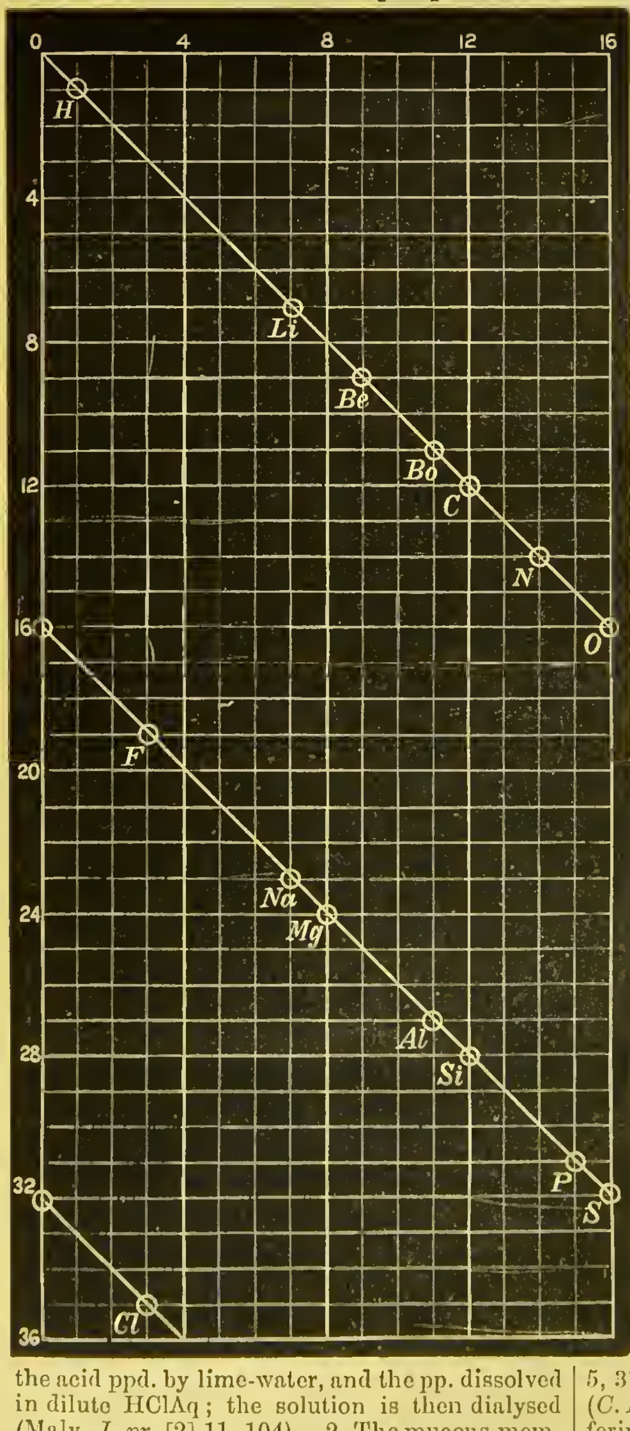
PEPPER OIL. S.G. $\frac{15}{}$ ·875. The oil of black pepper is lævorotatory ($\alpha = -3{\cdot}2°$) and contains a terpene (165°) which is lævorotatory ($\alpha = -7{\cdot}8°$) and gives a crystalline tetrabromide (Eberhardt, *Ar. Ph.* [3] 25, 515; *cf.* Dumas, *A.* 15, 159; Soubeiran, *A.* 34, 327).

PEPPERMINT OIL. The essential oil from *Mentha piperita* contains menthol, $C_{10}H_{20}O$, and a liquid terpene. The oil obtained by distilling *M. arvensis* deposits crystals of menthol, and appears also to contain $C_{10}H_{18}O$, an inactive product

of oxidation of menthol (Moriya, *C. J.* 39, 82). The oil from *M. viridis* contains a terpene and $C_{10}H_{14}O$ [225°] (Gladstone, *C. J.* 17, 1).

PEPSIN. The digestive ferment of the stomach (Schwann; Brücke, *Sitz. W.* 43, 601; Schmidt, *A.* 61, 311). It also occurs sometimes in the urine (Stadelmann, *Zeit. Biol.* 25, 208).

Preparation.—1. The glandular layer of the stomach is extracted with dilute phosphoric acid,



the acid ppd. by lime-water, and the pp. dissolved in dilute HClAq; the solution is then dialysed (Maly, *J. pr.* [2] 11, 104).—2. The mucous membrane of pigs' stomachs is macerated with water containing HClAq and the pepsin separated from the filtrate by adding NaCl (Scheffer, *Ph.* [3] 2, 761, 783, 843).—3. The mucous membranes are kept 24 hours after death, and then extracted with glycerin. The extract is ppd. with alcohol (Wittich, *J.* 1870, 894; Podwyssozky, *Pf.* 39, 62).

Properties.—Amorphous. Does not give the xanthoproteic reaction, and is not coloured by H_2SO_4 and sugar. It renders insoluble proteïds soluble, converting them into peptones; this action is greatly enhanced by the presence of ·05 p.c. HCl. Digestion is more rapid at 37° than at 24°. Dry pepsin does not lose its power by heating to 100° (Huppe, *C. J.* 44, 101). According to Gautier (*C. R.* 94, 1192), pepsin contains some insoluble amorphous granules which also possess digestive power in presence of HClAq (*cf.* Béchamp, *C. R.* 94, 970).

PEPTONES *v.* Proteïds.

PER. *Use of this prefix applied to inorganic compounds*; for *per- compounds* and *per- salts v.* the element the per- compound of which is sought for, or the salts to the name of which *per-* is prefixed. Thus *peroxides* are dealt with under Oxides; *peroxide of nitrogen* under Nitrogen, oxides of; *perchloric acid* under Chlorine, oxyacids of; *permanganates* under Manganese, oxyacids of.

PEREIRINE $C_{19}H_{24}N_2O$. [124°]. An alkaloid, occurring with geissospermine in the bark of *Pao Pereiro* (*Geissospermum Vellosii*, Peckolt). It is separated from geissospermine by ether (Hesse, *A.* 202, 147). Amorphous powder, nearly insol. water, v. sol. alcohol and ether. Conc. H_2SO_4 gives a violet-red and HNO_3 a purple red colour. — $B'_2H_2PtCl_6$ 4aq: yellowish amorphous pp.

PERIODIC LAW. In the history of modern chemistry we find several attempts to trace connections between the properties of the elements and their atomic weights. Döbereiner (*G. A.* 26, 331) was the first to show that a simple relation exists between the atomic weights of closely related elements. Ca, Sr, and Ba are very closely related elements, and the atomic weight of Sr is the mean of those of Ca and Ba. Again, Se has an atomic weight equal to the mean of the atomic weights of the closely related elements S and Te. This doctrine of triad groups was further extended by Dumas (*J.* 1851. 291), Kremers (*P.* 85, 56), and Lenssen (*A.* 103, 121). Lenssen endeavoured to embrace all the elements in a classificatory system composed of 20 triads. Pettenkofer (*A.* 105, 188) pointed out that the atomic weights of analogous elements, *e.g.* the alkali metals, form simple arithmetical series, and he emphasised the analogy between such natural families of the elements and the homologous series of organic compounds. Kremers (*P.* 83, 56), Gladstone (*P. M.* [4] 5, 313), Cooke (*Am. S.* (2) 17, 387), and Dumas (*C. R.* 45, 709) followed with generalisations differing only in detail from that of Pettenkofer.

These discoveries did not, however, herald any immediate great advance. It was, of course, interesting to find that elements showing gradational similarity of properties possess atomic weights, which are also, so to speak, numerically similar; but the newly discovered relationships

did not result in immediate practical applications, and did little more than emphasise pre-existing natural classifications. The investigations altogether failed to afford a generalisation capable of embracing the groups of related elements in a complete classificatory system. Instead of furnishing one inclusive scheme dealing with all the elements, they rather favoured a classification consisting of a number of isolated and partial systems, each system comprising only very closely allied elements, a classification similar in its imperfections to that which would have resulted in organic chemistry had chemists been content to differentiate empirically alcohols, aldehydes, and acids, without any knowledge of the relationships existing between these distinct, but closely connected, classes of bodies.

The idea of arranging all the elements in the order of their atomic weights with a view to a more comprehensive classification based on the relations of these magnitudes and the salient properties of the elements, both chemical and physical, seems first to have suggested itself to M. A. E. Béguyer de Chancourtois in the year 1862. His method of exhibiting the relationship was a geometrical one. On a right cylinder with circular base he traced his 'telluric helix' at a constant angle of 45° to the axis. On this curve lengths corresponding to the 'characteristic numbers' (atomic weights) were measured in terms of a unit equal to one-sixteenth of the turn of the helix. The extremities of these lengths were the 'characteristic points' for the elements. De Chancourtois enunciated the principle that the relations between the properties of different bodies are manifested by simple geometrical relations between the positions of their characteristic points. For instance, elements with analogous properties fall together on vertical lines parallel to the generatrix. This relation becomes apparent when the cylinder is plane developed as in fig. on p. 808. It follows from this that the atomic weights of any natural group of elements are expressible in terms of the general algebraic formula $(n + 16m)$, where m is an integer; in other words, that the differences between the atomic weights of allied bodies are, in general, multiples of 16.

O	S	Se	Te
16 ;	$16+16=32$;	$16+(4\times16)=80$;	$16+(7\times16)=128$

Other similar relations were developed by means of secondary helices.

De Chancourtois, evidently absorbed in the numerical relations exhibited by members of the individual groups, omitted to consider sufficiently the relations of the various groups, and so he failed to give clear expression to the periodicity of properties which his telluric helix implies. A mathematician and geologist, de Chancourtois expressed himself in terms not at all calculated to attract the attention of the chemical world at large; consequently his work fell into an oblivion from which it has but lately been withdrawn to the light of day (*v. N.* Dec. 26, 1889; *C. N.* 63, 51).

Newlands was the first to look beyond the relations of analogous bodies merely, and to insist on a relationship of a higher order, connecting the properties and atomic weights of all the elements taken collectively.

This relationship, first roughly indicated by Newlands in 1864 (*C. N.* 10, 94), was further developed in 1865 under the title of the *law of octaves* as follows :—

'If the elements are arranged in order of their equivalents, with a few slight transpositions, as in the accompanying table, it will be observed that elements belonging to the same group usually appear on the same horizontal line :—

H	1	F	8	Cl	15	Co and Ni	22	Br	29	Pd	36	I	42	Pt and Ir	50
Li	2	Na	9	K	16	Cu	23	Rb	30	Ag	37	Cs	44	Tl	53
Be	3	Mg	10	Ca	17	Zn	25	Sr	31	Cd	38	Ba and V	45	Pb	54
B	4	Al	11	Cr	19	Y	24	Ce and La	33	U	40	Ta	46	Th	56
C	5	Si	12	Ti	18	In	26	Zr	32	Sn	39	W	47	Hg	52
N	6	P	13	Mn	20	As	27	Di and Mo	34	Sb	41	Nb	48	Bi	55
O	7	S	14	Fe	21	Se	28	Rh and Ru	35	Te	43	Au	49	Os	51

It will also be seen that the numbers of analogous elements generally differ by 7 or some multiple of 7 ; in other words, members of the same group stand to each other in the same relation as extremities of one or more octaves in music (*C. N.* 12, 83).'

As will be seen, Newlands' law was retrospective rather than prophetic;[1] it recapitulated and co-ordinated old facts, but did not suggest new ones. Though Newlands admitted the probability of the discovery of new elements, his rigid disposition into 8 octaves of the 62 elements then known neither admitted of interpolations nor suggested additions. In his development of the conception of chemical octaves there was a too evident subordination of fact; and chemists gave but little heed to a classificatory scheme which formed octaves at the cost of grouping together elements chemically dissimilar, and then only succeeded in producing octaves varying in range from 8 to 10 constituent elements.

In March 1869 Mendeléeff read a paper on the periodic law before the Russian Chemical Society. This periodic law was nothing else than a generalised and developed form of the law of octaves, the conceptions underlying both laws being practically identical. Yet Mendeléeff's law was the law of octaves so elaborated and expanded that it at once attracted general attention. Operative not only in the realm of the known, but boldly presuming to deal with the unknown, this periodic law clearly indicates methods of testing its own validity. The law states that *the properties of the elements, as well as those of their compounds, are periodic functions of the atomic weights of the elements.* That is to say, if in a co-ordinate system atomic weights be measured along one axis, and any measurable property along the other, a line joining the *loci* of the intersections of corresponding abscissæ and ordinates will form a sinuous curve showing maxima and minima. As the atomic weight increases the property considered will not increase or diminish indefinitely, but will exhibit periodical waxing and waning in intensity.

[1] The predictions to which Newlands lays claim in the preface to his pamphlet 'The Periodic Law' are founded on theoretical considerations at which he arrived independently of, and prior to, his law of octaves, and which, therefore, do not involve any idea of periodicity.

Contemporaneously with the enunciation of the periodic law by Mendeléeff, but quite independently, L. Meyer (*A. Suppl.* 7, 354) showed that such a periodic curve results when the relatively measurable property considered is atomic volume (at. wt. ÷ S.G. in solid state). In fact, nearly every measurable property—physical and chemico-physical—has been investigated, and in every case the law has been substantiated.[1] On examination of the characteristic ultra-violet spectra of the elements, Hartley (*C. J.* 41, 84) found these to vary periodically in such a way that elements belonging to the same group have analogously disposed spectra; in fact, Hartley made use of this generalisation in assigning Be (*vide infra*) a place in the periodic system (*C. J.* 43, 316; see also Lecocq de Boisbaudran, *C. N.* 1886 (2) 4). Laurie (*P. M.* [5] 15, 42) obtained periodic curves when he plotted out the values of the heats of formation of haloid compounds of the elements in diagrams in which atomic weight was taken as the other variable. In this connection also Carnelley investigated the melting-points, boiling-points, and heats of formation, of the halogen compounds of the elements (*P. M.* [5] 8, 1); the colours of corresponding compounds of the elements (*P. M.* [5] 18, 130); the occurrence of the elements in nature (*P. M.* [5] 18, 194); the salient physical properties of the compounds of the elements with alkyl radicles (*P. M.* [5] 20, 259); and finally the magnetic properties of the elements (*B.* 12, 1958). Carnelley and Walker have examined the relation of the phenomenon of the complete dehydration of hydrated oxides to the periodic law (*C. J.* 53, 59). Prud'homme (*C. R.* 112, 236) found that the shades produced by using different metallic oxides to fix one and the same colouring matter varied periodically with the atomic weights of the metals. Brauner and Watts found confirmation of the law in studying the molecular volumes of the oxides (*B.* 14, 48). Roberts-Austen experimented with a like result on the tenacity of gold when alloyed with about ·2 per cent. of other metals (*Pr.* 43, 425). Recently, Sutherland (*P. M.* [5] 30, 318) has asserted a periodicity of the vibration-periods of the atoms of elements at their melting-points.

For a fairly complete summary of such investigations showing that the atomic weights of the elements are the true variables which determine the properties of matter *v.* Meyer's *Modern Theories of Chemistry*, pp. 119-154.

At first sight it might seem that the best method of giving detailed expression to this periodic law would be the geometrical one of tracing periodic curves as above indicated; but in the present state of science this is impossible, for we have yet to learn methods of measuring chemical properties. Further, the periodicity which Mendeléeff asserts is peculiar in its discontinuity, and contrasts strongly with the continuous periodic curves of the geometer, such, for instance, as the curve of sines. Conclusions respecting *any* point on such a curve as the curve of sines, where the periodicity may be called continuous, are warranted; but unless geometrical analysis be modified in a special manner the connecting by a continuous curve of the *loci* of intersection of ordinates and abscissæ in a coordinate system, of which properties and atomic weights are the variables, amounts to a virtual negation of the indivisibility of atoms, and to an assertion that the number of elements is infinite. No elements intermediate between, *e.g.*, silver and cadmium, and with atomic weights between 107·6 and 112, are known. Even if they existed, we could not for a moment suppose that they would form oxides with formulæ containing a fractional number of oxygen atoms. Yet, as will be seen later on, if the periodic law were represented and interpreted geometrically it would certainly involve not only the existence of such intermediate elements, but also the existence of oxides and other compounds incompatible with the fundamental conception of modern chemistry —the conception of the atom.

For these and similar reasons it is not only desirable but imperative that the periodic law should have a non-geometrical representation at present. Let the elements (hydrogen excepted) be arranged in order of their atomic weights. It will then be found that the properties vary gradually as the value of the atomic weight increases; that when the eighth element is reached we have reproduced in varying intensity many of the properties characterising the first. The same is true of the fifteenth element. Similarly, in the ninth and sixteenth elements we have the recurrence of the properties of the second in the series, and so on.

If now, instead of this linear disposition, we arrange the elements in two dimensions, placing elements with analogous properties in the same vertical lines, and if we suppose that certain elements exist which have not yet been isolated, we obtain the table on the following page (taken from Brauner (*C. J.* 41, 68), and differing in slight details from the one first proposed by Mendeléeff), consisting of twelve horizontal rows and eight vertical columns.

The horizontal rows are called 'series,' and consist of elements whose properties vary gradually from one member to the next. It will be seen that hydrogen, on account of the anomalous relations between the value of its atomic weight and those of succeeding elements, is regarded as constituting a series in itself. The vertical columns are called 'groups,' and comprise elements with similar properties, *i.e.* elements which would occur at comparable points on periodic curves, could such be traced as already indicated. The similarity in properties shown by members of a group is a regularly gradationed one, and while in a series the properties of the elements vary in kind, in a group the variation is, speaking widely, one of degree only.

It will be noticed that the perfect symmetry of the table and the analogy which for the first few series it shows with the notes of the diatonic scale disappear when the end of the fourth series is reached. The three elements Fe, Ni, and Co, following upon Mn, and showing no analogies with the elements of Groups I., II., and III. respectively (where, guided solely by considerations of symmetry, we should be inclined to locate them), inaugurate the eighth group of Mendeléeff's table; a group containing many of the more important industrial metals, all very

[1] It should be noted, however, that the specific heats of the elements in the solid state do *not* vary periodically with the atomic weights.

Series	GROUPS I.	II.	III.	IV.	V.	VI.	VII.	VIII.
	R_2O	R_2O_2	R_2O_3	R_2O_4	R_2O_5	R_2O_6	R_2O_7	R_2O_8
1	H=1	—	—	—	—	—	—	—
2	Li=7	Be=9	B=11	O=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27	Si=28	P=31	S=32	Cl=35·5	
4	K=39	Ca=40	Sc=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56 Ni=58·6 Co=59 (Cu=63)
5	Cu=63	Zn=65	Ga=70	Ge=72	As=75	Se=79	Br=80	
6	Rb=85	Sr=87	Y=89	Zr=90	Nb=94	Mo=96	? 100	Ru=101 Rh=103 Pd=106 (Ag=108)
7	Ag=108	Cd=112	In=114	Sn=118	Sb=120	Te=125	I=127	
8	Cs=133	Ba=137	La=139	Ce=140	Di=143	? 149	Sm=150 ?	?152—156 4 Elements ?
9	← ? 4 Elements 156 to 162 ? →				Er=166	? 167	? 169	
10	? 170	? 172	Yb=173	? 178	Ta=182	W=184	? 190	Os=190 Ir=192·5 Pt=194 (Au=197)
11	Au=197	Hg=200	Tl=204	Pb=207	Bi=208	← ? 2 Elements 212 to 220 ? →		
12	← ? 3 Elements 220 to 230 ? →			Th=232	? 237	U=240	? 245	

(In this Table the atomic weights are only approximate.)

closely allied from a chemical point of view. (*A. Suppl.* 8, 147), and a group anomalous in that even series only are represented, three elements occurring in each series. According to Mendeléeff, the metals Cu, Ag, and Au, similar in many respects to the elements of Group I., nevertheless show, in their higher oxidation forms and physical properties, such analogies with the members of Group VIII. as to warrant their double representation in the table (*A. l.c.* p. 152). It should also be noticed that the table is so constructed as to indicate a subdivision of each of the groups I.–VII. into two sub-groups or 'families,' one family in each case being constituted of members of even series only, the other of members of odd series only. This subdivision is more apparent in the following tabular ar-

Sub-groups	SERIES 1	2	4	6	8	10	12
Ia.		Li= 7·02	K=39·11	Rb= 85·5	Cs=132·9	—	—
IIa.		Be= 9	Ca=40	Sr= 87·6	Ba=137	—	—
IIIa.		B=11	Sc=44	Yt= 89·1	La=138·2	Yb=173	—
IVa.		C=12	Ti=48	Zr= 90·6	Ce=140·2	—	Th=232·6
Va.		N=14·03	V=51·4	Nb= 94	Di=142·3	Ta=182·6	—
VIa.		O=16	Cr=52·1	Mo= 96	—	W=184	U=239·6
VIIa.		F=19	Mn=55	—	—	—	—
VIII.			Fe=56 Ni=58·7 Co=59 Cu=63·4	Ru=101·6 Rh=103·5 Pd=106·6 Ag=107·92	— — — —	Os=190·8 Ir=193·1 Pt=195 Au=197·3	— — — —
Ib.	H=1·007	Na=23·05	Cu=63·4	Ag=107·92	—	Au=197·3	—
IIb.		Mg=24·3	Zn=65·3	Cd=112	—	Hg=200	—
IIIb.		Al=27	Ga=69	In=113·7	—	Tl=204·18	—
IVb.		Si=28·4	Ge=72·3	Sn=119	—	Pb=206·95	—
Vb		P=31	As=75	Sb=120	Er=166·3	Bi=208·9	—
VIb.		S=32·06	Se=79	Te=125	—	—	—
VIIb.		Cl=35·5	Br=79·95	I=126·85	—	—	—
SERIES	1	3	5	7	9	11	13

(In this Table O=16 is the starting-point of atomic weights. See F. W. Clarke, *C. N.* 63, 76.)

rangement of the elements which Mendeléeff suggests as a truer representation than the foregoing table of the peculiarly compounded periodicity which obtains.

The reason for this subdivision—which may not inaptly be compared with the subdivision of the hydroxyl derivatives of the paraffins into the minor classes of primary, secondary, and tertiary alcohols—is that, although there is a general similarity between all the members of a group, yet there is a more pronounced similarity between the members of odd series and the members of even series respectively; in other words, alternate members of a group are in general more closely related than successive members.

Nevertheless the advisability of a rigid subdivision of all the groups as indicated is open to question. In the case of Group II. this division is undoubtedly warranted. Mg, Ca, Zn, Sr, Cd, Ba, Hg have all certain properties in common. But the family Ca, Sr, Ba, on the one hand, and the family Mg, Zn, Cd, Hg, on the other, have respectively so many similarities that we are justified in making the subdivision in this case (*v.* CLASSIFICATION, vol. ii. p. 204).

But in the case of Group V. the 'family characteristics' do not so predominate over those of the group. N, P, V, As, Sb, &c., are all so much alike in properties that here a resolution

into families is by some regarded as superfluous; this group, it is said, is more conveniently studied as a whole, for now the 'group characteristics' predominate over those of the families (*v.* vol. ii. p. 210).

The elements constituting the eighth group have so many characteristic properties in common that subdivision of the group in any way would be artificial and unnecessary.

There have been various other methods (di- and tri-dimensional) suggested for representing the periodicity in properties of the elements, but none of them perhaps sums up the facts known more simply and clearly than Mendeléeff's table (*v.* Meyer's *Modern Theories*, p. 120; Reynolds, *N.* 34, 423; Crookes, *C. J.* 53, 503; Bayley, *P. M.* [5] 13, 26; Kremers, *Physikalisch-chemische Untersuchungen*, Wiesbaden, 1869–70; Baumhauer, *Die Beziehungen zwischen den Atomgewichte und der Natur. der Elemente*, Braunschweig, 1879).

On inspecting his table in the light of known facts, Mendeléeff was led to make the following generalisations:—

(i.) Excluding Series 2, the most markedly non-metallic elements occur in odd series.[1]

(ii.) Omitting Series 2, only members of odd series form compounds with organic radicles (the organo-metallic compounds).[2] Just as the hydrides of Pd, Cu, and Nb contrast strongly with the hydrides of elements belonging to odd series, so organic compounds of members of even series (should such be hereafter discovered) will possess properties very different from those of similar compounds with which we are at present acquainted.

Mendeléeff expressly omits Series 2 in making these generalisations. If, excluding the very incomplete Series 10 and 12, we tabulate the differences between the atomic weights of corresponding elements of Series 2 and 4, 4 and 6, 6 and 8, we find that, whereas the mean difference of corresponding elements of consecutive series is about 42, the mean difference for Series 2 and 4 is only 34·5. Since properties and atomic weights are dependent, we should expect from the above relations that the properties of the elements of Series 2 would contrast with the general properties exhibited by the other members of the families which they head. Such is actually the case to a greater or less extent with all the members of Series 2; *e.g.* Li differs from the other alkali metals, and approaches the alkaline earths in its insoluble phosphate, its easily soluble bicarbonate, its difficultly soluble carbonate, and in the formation of diglycollic acid by the interaction of LiOH and monochloracetic acid. N is more closely related to P than to V; O to S than to Cr. Again F and Mn contrast very strongly. On this account Mendeléeff has styled the elements composing Series 1 and 2 *Typical Elements*. Though the differences (averaging about forty) between the atomic weights of Na and Mg (Series 3) and those of the corresponding elements Cu and Zn (Series 5) are greater than those derived from a consideration of Series 2 and 4, yet the properties of Na and Cu on the one hand, and of Mg and Zn on the other, contrast so strongly, in Mendeléeff's opinion, as to induce him to enrol Na and Mg also among the typical elements. It is open to question whether the differences between Mg and Zn are sufficient to justify the classification of the former as a typical element; most chemists would probably find in Na the limit of the typical elements. Meyer, however, insists that the differences between Mg, Al, Si, and the other members of the corresponding groups is such as to justify the enrolment of these three substances among the typical elements, as follows:—

	Types		Li	Be	B	C	N	O	F	—	—	—	Na	Mg	Al	Si
P	S	Cl	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	—
As	Se &c.															

Yet the typical elements after nitrogen exhibit so little analogy with the groups placed below them in the above scheme that Meyer proposes the following as perhaps a more scientific disposition of the typical elements:—

			Li	Be	B	C										
N	O	F	Na	Mg	Al	Si										
P	S	Cl	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	—
As	Se	Br &c.														

Some go still further than Meyer, and regard H to Cl inclusive as typical elements; but such extreme views can scarcely be regarded otherwise than as unwarranted subordination of fact to considerations of symmetry suggested by Mendeléeff's table.

Mendeléeff compares his so-called typical elements to the lower members of homologous series in organic chemistry, which, as is well known, possess many properties peculiar to themselves and unrepresented in the higher members. In this connection contrast H_2O and CH_4O with the higher alcohols of the $C_nH_{2n+2}O$ series.

While some disapprove of the title 'typical elements,' maintaining that this nomenclature connotes exactly the opposite of what it should, seeing that the typical elements are by no means types (as this word is generally understood) of the groups or even of the families which they head, others attempt to justify Mendeléeff's nomenclature. The former would rechristen the typical elements as anomalous elements; the latter would either find in the typical element of the group a combination of individual characteristics of each of the constituents of the sub-groups (*vide* vol. ii. p. 207), or in the typical elements as a class a representation of the gamut of variations of chemical properties.

(iii.) The passage from even to odd series is

[1] To render these generalisations unconditional Walker (*C. N.* 63, 251) has proposed that H to F be regarded as constituting Series 1, Series 2 being regarded as wanting. If this proposal is adopted, it becomes hardly necessary to differentiate typical elements (*v. infra*).

[2] Recently it has been shown by Winkler (*B.* 24, 873, 1906) that the same generalisation can scarcely be applied to the hydrides also.

accompanied by a more gradual change in the properties of the elements than is the passage from an odd to an even series. This fact is in a manner emphasised in Mendeléeff's second table.

(iv.) As the at. wt. increases in each group :—

(α) The elements become more electropositive, and their oxides become more basic. This is well exemplified by the oxides of the types R_2O_3 and R_2O_5 formed by the elements of Gr. V.

(β) Corresponding compounds of the elements become more easily reduced. This is well instanced in the triplets S, Se, Te, and Cu, Ag, Au.

(γ) There is a tendency to form stable oxides (and the salts corresponding to these) containing less O than the maximum salt-forming oxide characteristic of the group (*vide infra*). Thus, the characteristic oxide of Gr. V. is of the type R_2O_5, and the haloid and oxyhaloid salts of the lower members of the group P, V, Nb, belong to this form, *e.g.* PF_5, $VOCl_3$, $NbCl_5$; but Bi, which is the highest known member of Gr. V., forms salts corresponding to the oxide R_2O_3. Again in Gr. IV. no oxide of Si having the formula SiO is known ; SnO is known but is unstable ; while PbO figures as the stable oxide of lead.

(v.) Periodicity of valency and limiting forms. It has long been admitted that the atoms of those elements which form hydrides are limited with respect to the maximum number of H atoms which they can hold in combination, but it was only with the introduction of the periodic law that it was noticed that this limited power of combining with H atoms varies in a regularly periodic manner with the atomic weights. Little is as yet known of metallic hydrides, so that we have to look to Groups IV.–VII., consisting of what may broadly be called the non-metals, for a confirmation of this periodicity.

For instance :—

Gr. IV. furnishes us with CH_4, SiH_4 ;
Gr. V. ,, ,, NH_3, PH_3, AsH_3, SbH_3;
Gr. VI. ,, ,, OH_2, SH_2, SeH_2, TeH_2;
Gr. VII. ,, ,, FH, ClH, BrH, and IH.

In the same way, but more perfectly, the law teaches us that the maximum number of oxygen atoms with which the elementary atoms can severally combine to form definite salt-forming oxides—either acidic or basic, as the case may be—also varies periodically with the atomic weights of the elements. The oxides characteristic of Gr. IV. are of the type R_2O_4 (or RO_2), those of Gr. V. of the type R_2O_5, and so on regularly till we come to the eighth group, which has maximum salt-forming oxides of the type R_2O_8 (or RO_4). In carrying back this regularity to the groups I.–IV., consisting for the greater part of metals, we find that it assigns to each of these groups exactly that type of oxide which we know to be characteristic of the individual members of the group. Hence we are justified in broadly asserting that the types of the hydrides (so far as they are already known), as well as those of definite salt-forming oxides, are periodic functions of the atomic weights of the elements. At the present time they are merely considerations of a regular periodicity, and not facts actually known, that lead us to assign R_2O_7 to Group VII. as its characteristic oxide. Fluorine, so far as we know, forms no oxides at all ; and the highest halogen oxide is of the type R_2O_5. In fact, Mn is the only member of the group that has an oxide conforming to the type R_2O_7. Yet, having regard to the successes (to be detailed later) attendant on other predictions of the law, founded only on considerations of symmetry and general plan, all this is simply tantamount to admitting that the conditions of the existence of such oxides as Cl_2O_7, I_2O_7, &c., are legitimate subjects for research. Again, in Gr. VIII. the only oxides of the form RO_4 yet isolated are RuO_4 and OsO_4;[1] but chemistry is by no means a completely worked-out science wanting nothing, and the periodic law would be at fault did it fail to mirror forth such shortcomings and imperfections as still exist. The forms of complex oxyacids are determined by the forms of the maximum oxides, and may be derived from these by replacing O by its equivalent $(OH)_2$ or H_2. Thus from SO_3 we can derive the chief oxyacids of S: $SO_2(OH)_2$, $SO_2H(OH)$, and SO_2H_2.

The highest compounds of the elements with halogens also correspond in type to the maximum oxide forms, and therefore exhibit a regular periodicity. In many cases, however, *e.g.* $TeCl_4$, ICl_5, $AsCl_3$, only haloids lower in type than the maximum oxides are known ; but in no case is a simple haloid known of higher type than the maximum oxide of the element considered.

Against the doctrine of a maximum oxide-form peculiar to all the members of each group, and of the types assigned (Table, top p. 811), the existence of such oxides as K_2O_2, BaO_2, &c., has been adduced. In reply it has been pointed out that these oxides belong to the class of peroxides,[2] all of which are distinguished by their instability in the presence of the so-called 'contact agents,' as well as by their inability to form corresponding salts with a given basic or acidic oxide, as the case may be ; and that a generalisation explicitly extending only to salt-forming oxides, strictly so called, cannot be impugned by considerations originating in the study of a class of bodies lying wholly without the pale of its jurisdiction.

Yet this reply is scarcely satisfactory ; for in certain cases we are bound, in order to justify the principle advanced, to recognise such bodies as PbO_2 and Bi_2O_5—oxides currently regarded as peroxides. But PbO_2 is undoubtedly an acidic oxide, forming with basic oxides the corresponding plumbates, and Bi_2O_5 would also seem to have the power of forming with strong basic oxides unstable bismuthates—so unstable, in fact, that their true composition is still very doubtful. Hence Mendeléeff (*B.* 15, 242) asserts that the oxides in question are *not* peroxides ; for, according to him, true peroxides such as BaO_2, Cr_2O_7, TiO_3, H_2O_2, cannot form corresponding salts,[3] and must of necessity contain relatively

[1] Some of the recently isolated carbonyl compounds of the elements of Group VIII. conform to type MO_4 (*C. J.* 57, 749 ; 59, 1090 ; *C. R.* 112, 1481).

[2] It seems more than probable that a wider study of the higher forms of oxidation will result not only in the discovery of several new peroxides, but also of a distinct periodicity of type amongst this class of bodies also.

[3] The recent isolation of persulphates, $M'SO_4$, by Berthelot (*C. R.* 112, 1481) and Marshall (*C. J.* 59, 771) does not harmonise with Mendeléeff's views. Nor does Péchard's work (*C. R.* 112, 720, 1060) on higher oxidised compounds of Mo and W.

more O than do the maximum salt-forming oxides (acidic or basic) as defined by the periodic law (*v.* also Piccini, *B.* 18, *Ref.* 255). Still the case of CuO (which cannot be regarded as a peroxide) presents a difficulty, if Cu is rightly placed in Gr. I.; for, in accordance with this position of Cu among the elements, the principle under discussion would lead us to expect a maximum salt-forming oxide of the formula Cu_2O.

In conclusion it may be said that although there undoubtedly is some connection between the at. wts. of the elements and the types of oxides they form, yet with the imperfect methods which we have of representing the periodic law, and in the absence of any firmly grounded and generally recognised classification of oxides, it is impossible to give a hard-and-fast enunciation of this connection.

We may assert that, so far as we are aware, a single atom of an element combines with at most four atoms of O or four atoms of H. The periodic law teaches us that the hydrogen-holding power of the non-metals decreases regularly with increasing at. wt., while the oxygen-holding power, as measured by the group-oxides, increases regularly in such a way that the sum of the number of equivalents of both is equal to eight. For instance, S combines with two equivalents of H to form H_2S; it cannot, therefore, form a higher salt-forming oxide than SO_3, which contains six equivalents of O.

Some chemists have proposed to extend this principle to the metals, *i.e.* to Groups I., II., and III. Since Na combines with one equivalent of O to give a salt-forming oxide, it must, they argue, combine with not more than seven equivalents of H or its equivalent. Similarly Ba combining with two equivalents of O must combine with six equivalents of H; and so on. But Brauner (*Sitz. W.*, 'Math.-naturwiss. Classe,' 84, 1165) would go still further. Let X denote a single equivalent of any element or radicle ($X = H, \frac{O}{2}, \frac{S}{2}, \frac{N}{3}$, OH, &c.); then he asserts that the whole of the compounds of Na will be constituted on the types NaX or NaX_7, or on types intermediate between these two; that all the compounds of Ba will be constituted on some of the types included in the scheme $BaX_2 \ldots BaX_6$, and so on. In short he would make out that there are certain limiting forms defining the complexities not only of the binary, but of all the compounds formed by each element, and that the range of these limits varies regularly and periodically with the atomic weights. In order to substantiate this view, recourse has been had to formulæ not yet authorised by Avogadro's law, and sweeping assumptions are made as to the dispositions of the constituent atoms or atomic groups in the molecules or reacting masses of the bodies taken to exemplify this doctrine of limiting forms. Thus, out of all the numerous compounds of the alkali metals, the only one that can be found conforming to the type RX_7 is the substance $NaOH.3H_2O$, and then only provided we manipulate the constituent atoms as follows: $Na(OH)(OH)_3H_3$. Si belongs to Group IV.; therefore, according to Brauner, all its compounds ought to be of the type RX_4. Its oxide SiO_2 certainly conforms to the rule, but the highly characteristic body SiH_2F_6 does not. Again, can such compounds of Pt as $PtCl_4 8H_2O$, $PtCl_4 2HCl 6H_2O$, &c., be regarded as belonging to the type RX_8? These are one or two examples, out of very many, of the kind of difficulties that stand in the way of a full recognition of Brauner's extension of Mendeléeff's views (*v.* CLASSIFICATION, vol. ii. pp. 210–13).

The idea that the valencies of the atoms vary regularly and periodically with their weights is one which has often been mooted, but in the absence of any recognised definition of valency it is an idea difficult to criticise.

If, as was originally done, the valency of an element be referred back to some constant objective attribute of the atom, and measured by the number of H atoms with which the given atom can combine, a partial periodicity involving only groups IV.–VII. is undoubtedly apparent.

Group	IV.	V.	VI.	VII.
	CH_4 SiH_4	NH_3 PH_3 AsH_3	OH_2 SH_2 SeH_2	FH ClH BrH
Valency	IV.	III.	II.	I.

This conception of constant valency not only lacks in generality (since out of the 70 or so elements only some 17 combine with H), but for the establishment of its validity demands a division of compounds into the two classes of atomic and molecular—a division altogether too artificial to be admitted. If we forgo the idea of constant valency, and merely attempt to define the valency of an element as a number expressing the maximum number of monovalent atoms (H, F, Cl, Br, I) with which a single atom of the element in question combines to form true gaseous molecules, *i.e.* if we give a mere name to the maximum number of 'equivalents' represented in an atom, the alleged periodicity is still far from being perfect, as the table on the following page, embracing the latest results, shows.

Regarding this question of valency in the light of what has been said of limiting hydride and oxide forms, it is at least apparent that our crude conceptions of valency do not admit of a satisfactory quantitative interpretation. The sulphur atom fixes 2 equivalents of H and 6 of O; the arsenic atom fixes 3 equivalents of H and 5 of O. Why, we may ask, should we decide to overlook these essential relations exhibited by the oxides, to say nothing of the peroxides, and regard the valencies as deduced from the hydrides and haloids merely as fundamental properties of the atoms?

Mendeléeff himself regards the theory of valency as extreme and not very valuable. Originating in the study of carbon compounds, valency finds in the domain of organic chemistry its only legitimate application; for the carbon atom, in accordance with its position in the periodic scheme, combines with *equal* numbers of equivalents of H and O, and, further, carbon compounds do not form so-called molecular compounds. He maintains that the forms of chemical compounds (including here isomerism, and therefore structural formulæ) are fully explained, without the spurious aid of a statical

Series	GROUPS I.	II.	III.	IV.	V.	VI.	VII.	VIII.
1	H^{i}							
2	Li	Be^{ii}	B^{iii}	C^{iv}	N^{iii}	O^{ii}	F^{i}	
3	Na	Mg	Al^{iii}	Si^{iv}	P^{v}	S^{ii}	Cl^{i}	
4	K^{i}	Ca	Sc	Ti^{iv}	V^{iv}	Cr^{iii}	Mn^{ii}	Fe^{iii} Ni Co
5	Cu	Zn^{ii}	Ga^{iii}	Ge^{iv}	As^{iii}	Se^{ii}	Br^{i}	
6	Rb^{i}	Sr	Y	Zr^{iv}	Nb^{v}	Mo^{v}		Ru Rh Pd
7	Ag^{i}	Cd^{ii}	In^{iii}	Sn^{iv}	Sb^{v}	Te^{iv}	I^{i}	
8	Cs^{i}	Ba	La	Ce	Di			
9					Er			
10			Yb		Ta^{v}	W^{vi}		Os Ir Pt
11	Au	Hg^{ii}	Tl^{i}	Pb^{iv}	Bi^{iii}			
12				Th^{iv}		U^{iv}		

(The index numbers express valencies.)

theory of valency, in terms of the periodic principle together with more generalised views on substitution involving the recognition of Newton's third law, which states that action and reaction are equal (*v. A. Suppl.* 8, 211; *N.* 40, 354).

Uses of the Periodic Law.—An induction of any value should be suggestive of deductions admitting in their turn of experimental confirmation. Judged from this standpoint, the periodic law is well worthy the exalted position accorded it among the principles of chemistry; for it has opened up immense fields of research which deduction has already, to a small extent, successfully explored.

In order to maintain a general identity of properties in the vertical columns or groups of Mendeléeff's table, it was found necessary to make gaps here and there; to leave certain series unrepresented in the various groups. It was asserted that these empty places in the scheme were the positions of undiscovered elements for which Mendeléeff proposed a provisional and temporary nomenclature. Thus, in the year 1869, the element next to $Ca = 40$ with a higher atomic weight was $Ti = 48$; but Ti could not find a place in Group III. Series 4, as its properties resemble those characterising Group IV. and show no analogies with those of the other members of Group III. Ti was accordingly placed in Group IV. Series 4, and the vacancy in Group III. Series 4 was assigned to a then unknown element provisionally styled *ekaboron*. The principles of this nomenclature are very simple. The predicted element takes its temporary name from the one immediately above it in the group-family, the Sanskrit prefixes *eka-*, *dvi-*, *tri-*, &c. being prefixed according as the unknown element is one, two, &c., removes lower down in the family than the name-determining element.

Those elements of a family which stand immediately above and below a gap, together with those which immediately precede and succeed it in the series, are called the *atom-analogues* of the element to which the gap corresponds. Thus B, Yt, Ca, and Ti are the atom-analogues of ekaboron. Now it follows from the very nature of the law that the properties of any given element must be determinable from those of its atom-analogues; that the properties of ekaboron, for instance, must be similar to, but intermediate in intensity between, those of B and Yt, and at the same time while dissimilar from those of Ca and Ti, they must show an intermediacy in their dissimilarity. Hence it becomes possible to predict the properties of still undiscovered elements; the mean of means of the properties of the atom-analogues forming the basis of the prophecy. How closely the properties of ekaboron thus predicted by Mendeléeff tallied with the properties of Sc experimentally investigated ten years later by Nilson is shown in the article ATOMIC AND MOLECULAR WEIGHTS (vol. i.). Even were this case of ekaboron an isolated one, the wonderfully exact concordance between prediction on the one hand and experimental realisation on the other would go far to establish the periodic law as a generalisation of the highest order. But ekaboron is not an isolated example of the prophetic infallibility of the law which has as strikingly asserted itself in connection with the two recently discovered elements Ga and Ge (*q. v.* vol. ii. 597, 610).[1] The periodic law is and will be to the science of chemistry what Newton's law of gravitation was and is to the science of astronomy. Neptune had its place assigned in the worlds around us before it was seen; before they were discovered Sc, Ga, and Ge had their properties detailed and their places assigned them among the elements, which by means of the periodic law have been raised from the level of 'mere fragmentary and incidental facts in nature.'

The validity of Mendeléeff's generalisation has also been confirmed in connection with the question of atomic weights. Before the enun-

[1] It yet remains to be seen whether the new element, austriacum, separated by Brauner from tellurium ores, will identify itself with dvi-tellurium, whose properties have recently been specified by Mendeléeff.

ciation of the periodic law the values for the atomic weights formed a series of isolated and purely empirical numbers; the atomic weight of an element once ascertained, there was nothing in the actual numerical value itself, even when considered along with the properties, either to confirm or cast doubt on it as the true atomic weight. But the periodic law teaches that the atomic weights are by no means disconnected quantities, but that, taken in connection with the properties of the elements, their values constitute a series of mutually corrective numbers; in short, the law gives significance to the expression 'the probability of an atomic weight.'

In dealing with this aspect of the law it will be well to distinguish two sets of cases:—

α. Those in which the law has actually fixed certain atomic weights indeterminable at the time by other means.

β. Those in which the law has merely served to correct the values of atomic weights inaccurately determined by the usual methods.

As illustrative of *α* we may consider the case of Be.[1] The equivalent of Be having by accurate experiment been fixed at 4·51, it follows that the atomic weight must be numerically equal to $n \times 4{\cdot}51$, where n is an integer. At first chemists were led to assign the formula Be_2O_3 to the oxide of Be on account of its isomorphism and many points of similarity with Al_2O_3. This taken in conjunction with the analysis of the oxide makes $n = 3$, and consequently fixes the atomic weight as 13·5. But Brauner repeatedly emphasised the view that the oxide of Be has the formula BeO, and that Be has therefore the atomic weight 9. The keynote of the many arguments advanced by Brauner in favour of his views was the incompatibility of the existence of an element with an atomic weight of 13·5, and having the properties of Be, with the system of the elements as arranged and classified by the periodic law.

In this system he argued that, not only was there no room for an element at. wt. 13·5, but that the proved existence of such an element would be totally subversive of the law. On the other hand, he pointed out that a vacancy existed in Series 2, Group II., for an element with an atomic weight equal to 9; and a careful examination of the relations of the members of Series 2 as a whole to those of other series, taken along with the known relations of beryllium to the magnesium group, absolutely demanded in his opinion the filling up of this vacancy with the element beryllium. Brauner's views were fully confirmed by Nilson and Pettersson, who succeeded in taking the vapour density of beryllium chloride; the application of Avogadro's law to their results gave the atomic weight of Be equal to 9 and the formula of the oxide BeO.

We are inclined to wonder that the question of the atomic weight of so rare and comparatively unimportant an element as Be has originated such a large amount of work and stimulated such lively discussion, unless we remember that a question of much greater import than the atomic weight of Be was at issue; the validity of the periodic law itself was at stake. And it is of interest to note that Mendeléeff regards the substantiation of Brauner's views on Be as a confirmation of his law of the same order as the discovery by Nilson of Sc, the ekaboron of prophecy. In a similar way the suggestions thrown out by the periodic law anent the atomic weights of U, Ce, and In have all met with corroboration. Up to the date of the periodic law, Péligot's value 120 (= three times the equivalent 40) was received as the atomic weight of U; but Mendeléeff (*l.c.* 178) suggested six times the equivalent, or 240, as the correct atomic weight, thus conferring on U the distinction, which it is now universally admitted to hold, of being the element with the highest known atomic weight.

[1] In what immediately follows the values given for atomic weights and equivalents are only approximate.

In 1870 the recognised atomic weight of Ce was 92 (2×46). Mendeléeff (*l.c.* 186), however, showed that no place existed in the system for an element with this atomic weight, and showing the properties of Ce, but that a suitable vacancy existed in Group IV. Series 8, if Ce was regarded as having an atomic weight one and a half times the then accepted value. Mendeléeff's proposal has been fully justified by later work on the cerite metals (*C. J.* 41, 68).

The equivalent of In is 37·8, and formerly its atomic weight was taken equal to twice this, or 75·6. But Mendeléeff (*l.c.* 174) showed the necessity of trebling the equivalent, thus assigning the value 113·4, which is now accepted, to the atomic weight of this metal. Similarly Mendeléeff suggested, what has not yet been very satisfactorily settled, that the atomic weight of yttrium is three times its equivalent number, 29·87 (*v.* EARTHS).

The investigations on tellurium are fairly illustrative of the cases summed under the heading *β*. The adoption of the value 128 for the atomic weight of Te as determined by Berzelius would necessitate iodine (at. w. 126·5) taking precedence of Te in Series 7 of the periodic scheme; iodine being thus separated from the rest of the halogens and falling into Group VI. with such elements as S and Se, with which it shows no analogies, and Te falling into Group VII. with such elements as Cl, Br, and Mn, with which it in turn shows no kinship. This violation of the principle of identity of chemical behaviour in the groups suggested some grave error in the accepted atomic weight of Te; an error causing this element to succeed iodine in the series instead of preceding it, as the general plan of the law requires. The subject has recently been investigated by Brauner (*C. J.* 55, 382), who for a second time has vindicated the law in a most striking manner by showing that the *ci-devant* tellurium is probably not elemental, and that the atomic weight of unalloyed tellurium is considerably lower than that of iodine, being equal to about 125.

In much the same way the law has led to the correction of the previously accepted atomic weights of osmium, platinum, and gold.

Formerly the accepted atomic weights of Os, Ir, Pt, and Au were in accordance with the scheme

$$Os > Ir > Pt > Au.$$

But from the analogies existing between Os, Ru, and Fe, and the disposition of the first two series represented in Group VIII. Mendeléeff (*A. l.c.*) predicted alterations of the atomic weights in accordance with the scheme

$$Os < Ir < Pt < Au.$$

This prediction has been fully confirmed by recent researches; it has not, however, yet been found possible to verify and substantiate the results now accepted for the last three metals by the application of Avogadro's law.

As will be seen from the case of tellurium, the periodic law in its relation to atomic-weight determinations is broadly suggestive rather than accurately definitive. It may be that ere long the discovery of the exact character of the periodicity, which at present we comprehend only vaguely, will raise Mendeléeff's law to the rank of an instrument for the absolute evaluation of atomic weights.

Mendeléeff has repeatedly emphasised the great advantage accruing to students and chemists generally from an adoption of the periodic classification as a working basis—the advantage lying in the great mnemonic power of the law, which, introduced into the disheartening chaos of accumulated chemical fact, at once resolved the complexities of the apparent and rearranged them so as to exhibit the simplicities of the real. With one mental effort we commit to memory a large mass of facts which previously demanded so many independent but severally no less taxing mental exertions. No longer is phosphorus studied as an element apart from arsenic, but the general scheme of properties of the whole fifth group is learnt, and the facts about P, As, V, &c., are easily mastered by remembering their small individual deviations from this general scheme.

The law is also useful in that it points out the directions which should be taken by future research on the as yet unknown compounds of well-known elements. It is well called 'the finger-post of modern chemistry.' Examples of its utility in this respect have been indicated when treating of the law in its relation to limiting forms and to atomic-weight determinations.[1] In fact, every generalisation made in connection with the law suggests new work; organo-metallic compounds of In and Tl, and of the form MR_3 (where R = organic radicle) must be forthcoming (*v. supra*, ii.); a suboxide of Cd having the formula Cd_2O is looked for (*v.* iii.γ), while various new peroxides of Mo and W, also a true peroxide of lead (Pb_2O_5) are very probable realisations of the future (*v.* v.).

Theories having their origin in the Periodic Law.—Although, according to Mendeléeff (*C. J.* 55, 634), the periodic law, solely founded as it is on the solid rock of well-ascertained chemical fact, in no way indicates the nature of the elements nor predicates the existence of a unique matter, yet many have made it a peg whereon to hang theories respecting either the compound nature of our elements or the existence of a primordial matter.

The simple relations holding between the atomic weights of elements constituting some of the natural families, and the analogy between the relations so obtained and those found between the molecular weights of members of homologous series, led Dumas (*C. R.* 45, 46, 47) and Gladstone (*P. M.* [4] 5, 313) to suggest that the so-called elements are not primary, but are composed of two or more simpler elements.

Pelopidas (*B.* 16, 1868) called attention to the fact that the residues of hydrocarbons and nitrogenous organic bodies can be arranged in a periodic system, exhibiting in the number of members constituting the period, as well as in the gradual passage in each period from basic to acidic characters, a close analogy to Mendeléeff's periodic arrangement of the elements. The following are examples of the periods arranged by Pelopidas:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII
a	C_6H_{13} C_6H_5	C_6H_{12}	C_6H_{11}	C_6H_{10}	C_6H_9	C_6H_8	C_6H_7	C_6H_6
b	NH_6C or $NH_3(CH_3)$	NH_5C	NH_4C	NH_3C	NH_2C	NHC	NC	

The monovalent radicles $NH_3(CH_3)$ and C_6H_{13} undoubtedly show many analogies with the alkali metals; and CN has always been compared with the halogens of Group VII. Sulphur, Group VI., forms the acid $SO_2(OH)_2$; so the radicle C_6H_8 forms the acid $C_6H_8O_2(OH)_2$, and so on.

Carnelley (*C. N.* Nos. 1375 and 1378), from a consideration of the fact that the salient physical properties of the normal halogen and alkyl compounds of hydrocarbon radicles exhibit relationships similar to those of corresponding compounds of the elements, develops the view that elements are analogous to the hydrocarbon radicles both in form and function. On the supposition that C and H are true elements, he then attempts to draw up a scheme of compounds of two primary elements, A and B, corresponding to Mendeléeff's scheme of the alleged elements, the compounds possessing the same 'atomic weights' and showing the same periodicity as the accepted elements. In this scheme the elements appear as bodies of the type $A_nB_{2n+(2-x)}$, where x is the group and n the homologous series to which the element belongs; A is a tetrad element identical with carbon, and B, 'probably the ethereal fluid of space,' is a monad element with atomic weight = −2! These views of Carnelley are as much in advance of the earlier ones of Dumas and Gladstone as is the periodic law in advance of their disconnected schemes of classification; but they cannot be regarded otherwise than as ingenious and bold speculations indicating the directions in which investigations on the *rationale* of the periodic law, and on the nature of the elements, will probably be prosecuted before we arrive at anything approaching the truth, either concerning the law on the one hand or the elements on the other.

The attempt to discover some kind of unity in the sea of apparent diversities by which we are surrounded, or, rather, the natural inclination to assume such a unity, is as old as philosophy itself. Prout merely gave scientific definiteness to the views of the early Grecian philosophers when he suggested that the atomic

[1] The existence of Curtius' azoimide N_3H was foreseen by Mendeléeff (*B.* 23, 3464).

weights of all the elements were whole multiples of that of hydrogen, which he identified with the primary matter; and in later years many have in turn thought to find in the periodic law a warranty for resuscitating the principle underlying Prout's law, at the same time either shifting the primary matter lower down in the scale, so that hydrogen itself appears as a highly condensed form of matter, or not attempting in any way to particularise concerning the primary matter.

The application of recent developments in spectroscopy, combined with improved methods of fractionation, has resulted in the view that many of our so-called rare elements at least are not strictly elemental (*v.* METALS, RARE, and ELEMENTS). At first sight the large increase in the number of recognised elements which this recent work involves would seem to militate against the indications of the periodic law. But Crookes (*C. J.* 53, 487) has attempted to show that the new views may be brought into complete harmony with the periodic law if we will but admit into chemistry the principle of evolution. Granted that the different forms of matter have been cyclically evolved from a primitive formless fluid (protyle), and that the units of Mendeléeff's generalisation are rather 'elementary groups' than true elements, then the periodic law with its limited accommodation necessarily follows (*v.* also Mills, *infra*).

Some attempts have recently been made to express the atomic weights of the elements by means of general algebraic formulæ. While it must be allowed that we are more likely to arrive at clear views regarding the periodicity of the elements through methods founded on the theory of numbers than through methods of a purely geometrical nature, yet many of the researches so far undertaken in this direction do not even promise to help towards the final solution of the periodic law. In a few cases expressions have been obtained which, as they involve constants numerically equal to some of the important constants occurring in the principles of chemistry, may on a more detailed study culminate in a clearer understanding of the nature of the elements and the *rationale* of the law. Mills (*P. M.* [5] 18, 393; 21, 151) arranges all the elements according to their atomic weights, and then subdivides this arrangement into sixteen groups. He then finds that all atomic weights are involved in the logarithmic expression $15.p - 15\ (\cdot9375)^x$, in which x is an integer and p is the group-number of the element considered.[1] This expression arrived at empirically is, according to Mills, such as we should expect if we regard the elements as stable, but more or less incomplete, stages in the polymerisation of the primary matter as it cooled. It is also noteworthy that the above expression, in that it points to the existence of an upper limit to our existing system of atomic weights, confirms views originally expressed by Mendeléeff.

Carnelley's attempt (*P. M.* [5] 29, 97) to give a general expression to the atomic weights of the elements is of more interest in that it is founded, not on a conveniently assumed and artificial periodicity, but on the natural periodicity as this finds expression in Mendeléeff's schemes.

Carnelley's equation is $A = c\ (m + \sqrt{v})$, where A = approximate atomic weight; m = a member of an arithmetical progression depending on the series to which the element belongs; v = number of the group of which the element is a member; and c is a constant.

Excluding the elements of the first three series (typical elements), the expression for the atomic weights of all the other elements may be thrown into the more convenient form

$$A = c\ (3\tfrac{1}{2}\ a - 9 + \sqrt{v}),$$

where a is the number of the series to which the element belongs. In his paper, Carnelley notes the following points of interest: the mean value of $c = 6{\cdot}64$ is nearly identical with the mean value of the atomic heats of the elements. Assume that c in the above formula actually represents atomic heat, then it follows that the specific heats of the elements should be given by the expression $\dfrac{1}{m + \sqrt{v}}$; and this is found actually to be the case. It should be noted, however, that these coincidences may be purely accidental and meaningless, being simply the result of the particular units adopted. D. C.

[1] G. J. Stoney has also arrived at a logarithmic expression for the atomic weights (*C. J. Proc.* 1888. 65).

PERSEITE $C_7H_{16}O_7$. [188°]. S. 5 at 18°. Mol. w. (by Raoult's method) 179 (calc. 212). A body resembling mannite, occurring in the fruit and leaves of *Laurus persea* growing in the tropics (Müntz a. Marcano, *C. R.* 99, 38; *A. Ch.* [6] 3, 279; Maquenne, *A. Ch.* [6] 19, 5; *C. R.* 106, 1235; 107, 583, 658; Dehérain, *C. R.* 108, 101; *cf.* Avequin a. Melsens, *A. Ch.* [2] 72, 109). Extracted by water at 60°, the extract treated with lead acetate, filtered, freed from lead by H_2S, concentrated, and mixed with MeOH. Formed by reduction of mannoheptose by sodium-amalgam (E. Fischer a. Passmore, *B.* 23, 2228). Small needles (from alcohol), sl. sol. cold, v. sol. hot water and alcohol. Its solution becomes dextrorotatory when borax is added. Does not reduce Fehling's solution or undergo alcoholic fermentation. On oxidation by nitric acid it yields mannoheptose $C_7H_{14}O_7$ and finally oxalic acid. Boiling HI and P give C_7H_{12} (c. 104°) and $C_7H_{15}I$ (190°-200°). HCl yields C_7H_{14} (92°). An alcoholic solution treated with HCl and benzoic aldehyde yields $C_7H_{12}(CHPh)_2O_7$ [c. 219°].

Acetyl derivative $C_7H_9(OAc)_7$. [119°]. Crystalline powder, insol. water, sol. alcohol.

Butyryl derivative $C_7H_9(O.C_4H_7O)_7$. (c. 300° *in vacuo*). Syrup.

Nitrate $C_7H_9(NO_3)_7$. [138°]. Made from perseite (1 pt.), fuming HNO_3 (5 pts.), and conc. H_2SO_4. White needles, insol. water, sol. hot alcohol. Explodes when struck.

PETROCENE. The highest boiling portion of American petroleum contains, according to Hemilian (*B.* 9, 1604), a hydrocarbon $C_{32}H_{22}$ [above 300°] crystallising from benzene in yellow laminæ. Prunier (*A. Ch.* [5] 17, 28) found carbopetrocene $C_{24}H_8$ [268°] which yielded $C_{24}H_8C_6H_3N_3O_7$ [185°] and $C_{24}H_82C_6H_3N_3O_7$ [135°]. Prunier also found, in petroleum, petrocin $C_{12}H_8$? [102°] yielding $C_{12}H_8C_6H_3N_3O_7$ [98°] and a hydrocarbon C_7H_4? [119°]. *V.* also PETROLEUM.

PETROLEUM. *Earth-oil, Rock-oil, Naphtha, Mineral oil, Erdöl, Steinöl, Petrole, Huile de*

pierre, Bitume liquide. Petroleum is the general name given to the natural oily liquids occurring in the earth at different depths and in many localities. The natural oil is a mixture of several hydrocarbons, has a strong bituminous smell, but differs very considerably in its physical properties and chemical composition. It is found in large quantities in the United States, in the Caucasus, and in the country situated at the mouth of the Danube, in considerable quantities in Burmah and in Galicia, and has been found in Persia, the West Indian islands, Italy, parts of Germany, Switzerland, China, India, France, and England. Its specific gravity ranges from ·77 to 1·1, and its colour from pale yellow to brown, dark green, and black. The colour of crude petroleum not only varies with the locality, but varies from time to time in the same district. B. Redwood has recorded the colours of various kinds of crude petroleum (*Journ. Soc. Arts*, 34, 823, 878), and Lovibond's tintometer is used for determining the colour of commercial samples. Crude petroleum varies considerably in its composition, that from North America consisting chiefly of hydrocarbons of the C_nH_{2n+2} series, while that from Baku (Caucasus) contains in addition the hydrogenised aromatic hydrocarbons of the general formula C_nH_{2n} (Beilstein a. Kurbatow, *B.* 13, 1818, 2028) and small quantities of other hydrocarbons (Markownikow a. Oglobine, *J. R.* 15, 237, 307). Galician petroleum contains hydrocarbons of the series C_nH_{2n+2} and C_nH_{2n-6} (Freund, *A.* 115, 19), and also the hydrogenised aromatic hydrocarbons of the formula C_nH_{2n} (Lachowicz, *A.* 220, 168). Crude petroleum also contains small quantities of compounds containing sulphur, nitrogen, and oxygen. 0·23 per cent. of nitrogen has been found in petroleum from Ohio, and 1·11 per cent. in that obtained from California. Beilby has also found ·05 per cent. of nitrogen in Baku oil and 0·188 per cent. in Galician ozokerite. Crude American petroleum contains at least 0·008 per cent. of nitrogen (*S. C. I.* 10, 120). Sulphur amounts to 1·87 per cent. in certain Russian petroleums, and is present in that obtained from California, Lima, Ohio, and Canada, but is absent from Pennsylvanian and West Virginian oils (Vohl, *D. P. J.* 216, 47; Woodmau, *A. C. J.* [1891] 13, 179). From the variable composition of crude petroleum it follows that its volatility will be very different, the several constituents of crude petroleum extending from the gaseous members of the marsh-gas series to solids which boil at 400°. As a rule, the petroleum with lowest specific gravity is the most volatile and inflammable. Crude petroleum also may contain water and sediment, and is tested commercially for its specific gravity, odour, colour, its feel when rubbed between the fingers, and the percentage of naphtha (or portion volatile below 150°) yielded on fractional distillation (Allen, 'Commercial Organic Analysis,' 11, 369; Nawratic, *D. P. J.* 246, 328, 423). The flashing-point and burning-point of petroleum are also important factors for ascertaining its commercial value, but these tests are usually applied only to the refined petroleum or kerosene, which consists of the more volatile portions of the crude oil which can be burned with a wick (*Petroleum Act*, 1871, 34 and 35 Vict. cap. 105; *Petroleum Amendment Act*, 1879; and for variation of flashing-point with climate *S. C. I.* 1, 471; *C. N.* 40, 305; 49, 196). For calorific values of petroleum, see Deville, *C. R.* 72, 195, and 68, 348. Co-efficient of absorption of oxygen is higher for petroleum than for water (*Zeit. Phys. Chem.* 1, 70). When crude petroleum is distilled, the various fractions are separately collected and used for a variety of commercial purposes. In America the distillation is conducted in large stills, and the first fractions, known as 'cymogene' and 'rhigolene,' are condensed by artificial cold and pressure. The fraction which next comes over, having a density increasing from ·636 to ·725 or ·750, is separately collected, and when re-distilled is termed 'gasoline,' 'naphtha,' and 'benzine.' The next fraction consists of oils of S.G. ·75 to ·84, and is known as 'kerosene' or 'photogene'; while the residue is distilled in other retorts for lubricating oils, S.G. ·84–·9, and solid paraffin, until coke is left as a residue combustible with difficulty. Petroleum ether is the fraction containing hydrocarbons of S.G. ·625–·665, and consists of 'rhigolene' and 'gasolene,' while petroleum spirit or benzoline consists of the 'naphtha' and 'benzine' fractions, S.G. ·68–·745.

In Russia the petroleum is distilled in a series of stills in a continuous process, and yields three fractions: light benzine, S.G. ·754; 'gasolene' or heavy benzine, S.G. ·787; and kerosene, S.G. ·825. The residue on further distillation yields (1) lubricating oils, (2) solar oil, and (3) 'astatki,' which last is either used as fuel or distilled at a red heat, yielding benzenes and anthracene. Baku petroleum contains only traces of solid hydrocarbons, while that from the Caucasus yields about 6 per cent. of paraffin (B. Redwood, *S. C. I.* 4, 74).

In Germany the crude naphtha is refined into four distinct products:

Petroleum ether (40°–70°). S.G. 0·640–0·650.
Benzine (70°–120°). S.G. 0·700.
Ligroin (120°–135°). S.G. 0·730.
Cleaning oil (130°–160°). S.G. 0·745–0·750

(Schenkel, *Chem. Ind.* 13, 512).

Further details on the petroleum industry, and the properties and uses of these commercial products, will be found in Thorpe's DICTIONARY OF APPLIED CHEMISTRY.

Early Literature.—Before 1864 very little accurate knowledge of the chemical constitution of the various petroleum oils was known, the earlier investigations chiefly recording the localities in which the oil had been found, its physical properties, and its behaviour on distillation.

On the next page is a list of the more important of these examinations.

AMERICAN PETROLEUM. Pelouze a. Cahours (*C. R.* 54, 124; 56, 505; 57, 62) made a systematic investigation of the Pennsylvanian oil in 1864, and showed that it contained hydrocarbons of the formula C_nH_{2n+2}, including representatives of every member of the series from C_5H_{12} to $C_{15}H_{32}$. Ronalds added C_2H_6, C_3H_8, and nC_4H_{10} to this list (*C. J.* 18, 529). Above 280°, the boiling-point of the highest of these hydrocarbons, the oil yielded fusible paraffins [45°–65°], and they when distilled in closed vessels were resolved into other C_nH_{2n+2} and C_nH_{2n} hydro-

Date	Description	Author	Reference
1788	Black Hungary	Wintere	*Crell's Chem. Annal.* 1, 493
1791	Galicia	Martinovich	,, ,, 1, 72
1817	Naphtha of Miano, Parma	Saussure	*Bibl. Univ.* 1832, 160
1829	Persia	Unverdorben	*S.* 57, 243
1831	Rangoon	Christison a. Gregory	*T. E.* 13, 118, 124
1833	Persia	Blanchet a. Sell	*A.* 6, 309
1836	Bavaria	Kobell	*J. pr.* 8, 305
—	Galicia	Torosiwiecz	*R. P.* 55, 15; 61, 398
—	Baku	Hess	*P.* 34, 417
1840	Miano	Pelletier a. Walter	*J. Ph.* 26, 549
1848 } 1849 }	Derbyshire	Ure a. Mansfield	*C. J.* 1, 249 *Ph.* 7, 485
1857	Rangoon	De la Rue a. Müller	*Pr.* 8, 221
1858	Hanover	Eisenstück	*A.* 113, 151
—	,,	Uelsman	*A.* 114, 279
—	Galicia	Freund a. Pebal	*A.* 115, 19

carbons. Schorlemmer found small quantities of benzene and its homologues, and Beilstein a. Kurbatoff a hydrogenised aromatic hydrocarbon of the C_nH_{2n} series, which they isolated and determined to be hexahydro-metaxylene.

The paraffin hydrocarbons above alluded to have also been examined in detail, and in many cases their constitution determined.

In the neighbourhood of the North American oil wells methane is evolved, and is associated with ethane in the gases which issue from the De la Mater well at Pittsburg (Sadtler, *Am. Ch.* 1876, 98; Fouqué, *C. R.* 67, 1015). Ethane, propane, and *n*-butane exist dissolved in the petroleum. Of the higher paraffins the following have been isolated:

C_5H_{12}, *n*-pentane, dimethyl-propane;
C_6H_{14}, *n*-hexane, ethyl-iso-butane;
C_7H_{16}, *n*-heptane and an isomeride; either dimethyl-diethyl-methane or methyl-ethyl-isopropyl-methane (Schorlemmer, *C. J.* 26, 319);
C_8H_{18}, *n*-octane and an isomeride;
C_9H_{20}, two isomerides exist (Lemoine, *Bl.* [2] 41, 164):

α (136°) S.G. $\frac{12}{4}$ 0·742
β (130°) S.G. $\frac{12}{}$ 0·734.

$C_{10}H_{22}$, constitution not known (160°). Pelouze a. Cahours; (156°) Wurtz, *Bl.* 1863, 300; (160°) S.G. $\frac{16}{}$ 0·753 Lemoine. The solid paraffins $C_{25}H_{52}$, $C_{27}H_{56}$, and $C_{30}H_{62}$ have also been separated. (*V.* also Greville Williams, *Tr.* 1857, 737; *C. J.* 15, 130; Pelouze a. Cahours, *A. Ch.* [4] 1, 5; *J.* 1862, 410; Warren, *Z.* 1865, 668; *J.* 1868, 330; Warren a. Storer, *Z.* 1868, 228; Lefebvre, *Z.* 1869, 185; Schorlemmer, *Tr.* 162, 111; Ronalds, *Z.* 1865, 523; *C. J.* 18, 54; *J. pr.* 95, 421; Wurtz, *A.* 96, 372; and for the occurrence of the same hydrocarbons in boghead coal and cannel oil, Schorlemmer, *A.* 125, 109; Williams, *A.* 125, 107; and for a comparative table showing the C_nH_{2n+2} hydrocarbons found in petroleum, or by distilling paraffin and reducing the fatty acids, Beilstein, vol. i. 136.) Warren also obtained the olefines $C_{10}H_{20}$, $C_{11}H_{22}$, and $C_{12}H_{24}$ from American petroleum, and traces of volatile benzene hydrocarbons and the hydro-benzene compounds present in Caucasian oil have also been detected in this oil. Canadian petroleum contains a somewhat greater percentage of aromatic hydrocarbons, and is further characterised by its large amount of sulphur derivatives.

The action of heat on American petroleum products has been studied by many observers. When the crude oil is heated alone the lower members of the C_nH_{2n+2} series of hydrocarbons are evolved as gas. As the temperature increases the higher paraffin hydrocarbons distil over; but at the same time vapours are evolved which are absorbable by bromine. Le Bel examined this product, and found it to consist of bromides of the olefines C_2H_4, C_3H_6, C_4H_8, C_5H_{10}, C_6H_{12}, and that there are isomeric compounds of the higher members of the series. They have been separated either by fractionating the bromides obtained in this way, or by their different behaviour towards cold HCl. Acetylene and crotonylene are also formed, and other less hydrogenised hydrocarbons. When the vapour of petroleum ether, or the fraction (50°–80°) and containing chiefly C_5H_{12}, C_6H_{14}, and C_7H_{14}, is passed through a red-hot tube it yields C_2H_4 and C_3H_8 and hydrocarbons absorbable by bromine. These, according to Prunier, are acetylenes consisting of crotonylene C_4H_6 and traces of C_5H_8, C_6H_{10}, and C_7H_{12}.

Petroleum spirit (70°–120°) contains the hydrocarbons C_6H_{14}, C_7H_{16}, and C_8H_{18}, and the rectified oil (150°–280°) the paraffins from C_9H_{20} to $C_{16}H_{34}$; the crude fraction, however, contains hydrocarbons which are dissolved by sulphuric acid. The heavy oil (above 400°), used for lubricating purposes, has not been carefully examined. Vaseline is the next product obtained on distilling the crude oil, the distillation for heavy oil being stopped as soon as acid vapours begin to be evolved. Little is known as to the constitution of its hydrocarbons. When vaseline is not manufactured the distillation is continued until solid paraffin distils over. The solid residue, rich in carbon, also contains hydrocarbons, and in it or in the solid paraffin have been found, besides the higher paraffins, anthracene, phenanthrene, chrysene, pyrene, chrysogen (Fritzsche, *C. R.* 54, 910), parachrysene (Rasenack), benzerythrene (Schultz), and fluoranthrene (Prunier, *Bl.* [2] 31, 293). A hydrocarbon $C_{12}H_8$, isomeric with acenaphthalene, has also been isolated, and there are indications of the presence of quinones. From the coke Prunier and Varetine have also succeeded, by the action of solvents, in extract-

ing small quantities of hydrocarbons containing a very high percentage of carbon.

From a green solid [190°–240°] obtained from Pittsburg, and called 'petrocene' or the 'new product,' formed by the distillation of the residue after the ordinary paraffin had come over, Prunier isolated hydrocarbons which are called carbozene, carbopetrocene, and thallene. Analysis shows that they contain 96–97·7 p.c. of carbon, and have formulæ, therefore, ranging from $(C_4H_2)_n \ldots (C_7H_2)_n$, where n is variable but higher than 4.

Gustavson has studied *the action of* Al_2Br_6 and HBr on the different fractions of petroleum ether. The fraction (67°–70°), and chiefly hexane, gave by this treatment a solid from which he obtained an orange liquid $C_4H_8AlBr_3$, which decomposes above 120° and on addition of water. It is insoluble in the hydrocarbons from which it is derived, and in CS_2, but soluble in EtBr. The other fractions give similar results, but not such a good yield.

Beilstein and Kurbatoff, by the action of HNO_3 on the fraction (95°–100°), obtained a nitro- compound $C_7H_{15}(NO_2)$ (195°), and soluble in KOH. The fraction (115°–120°) similarly treated also gave acid nitro- products, called by the authors trinitro-isoxylene.

Russian petroleum. The Baku oil has been the subject of much investigation, and it apparently is a more complicated mixture than the American product. Its density, according to Mendeléeff, varies from ·881–·886 at 15°, and its variation with temperature is given by the equation $\frac{d\Delta}{dt} = -[0{\cdot}00635d - 0{\cdot}0000015d^2 - 1{\cdot}44]$, since the co-efficient of variation of density with temperature can be considered constant for any given hydrocarbon. The densities d range between ·750 and ·900.

Baku petroleum gives off a large volume of inflammable gas, and leaves on distillation a vaseline having all the properties of the American product save that its density is higher. The low-boiling portions of the oil contain some hydrocarbons of the C_nH_{2n+2} series, and marsh gas is evolved in the neighbourhood of the Caspian Sea; but Schutzenberger and Ionine found that the major portion of the hydrocarbons present were characterised by great inertness, and had a composition represented by the formula C_nH_{2n}, being isomerides of the olefine series of hydrocarbons. The hydrocarbons were called paraffenes (*C. R.* 91, 823), and were found not to form addition products with Br, fuming HNO_3, nor H_2SO_4. They found that the vapours, when passed through a red-hot tube, produced aromatic hydrocarbons, and at a dull redness gave products which unite energetically with Br, and are converted into resins by H_2SO_4. Chlorine and a little iodine convert them into unstable chloro- compounds, which cannot be distilled without decomposition. Of the several hydrocarbons present they isolated two, (221°) and (231°), and found that the latter had a V.D. corresponding to the formula $C_{14}H_{28}$. Subsequent investigators have concluded that these paraffenes are the hexahydrides of the benzene series of hydrocarbons which are now called naphthenes, similar to those obtained synthetically by Wreden (*A.* 187, 161), who described the following:—

C_6H_{12}, hexahydrobenzene, S.G. ·76 (69°);
C_7H_{14}, hexahydrotoluene, S.G. ·772 (97°);
and C_8H_{16}, hexahydroisoxylene, S.G. ·771 (117°).

Beilstein a. Kurbatoff have found the isomeric hexahydrometaxylene (*B.* 13, 1820; *C. J.* 40, 159; also Markownikoff a. Spady, *B.* 20, 1850) in Russian petroleum, and subsequent investigations have established the presence of a series of naphthenes from C_9H_{18} to $C_{15}H_{30}$. Markownikoff (*A.* 234, 89–115) has also obtained similar results, and has shown that the naphthenes are the chief constituents of the oil boiling below 300°. The fraction distilling (210°–330°) under 20 mm. also contains a large percentage of these C_nH_{2n} hydrocarbons. In addition, he isolated in the fraction (85°–250°) the following aromatic hydrocarbons: C_6H_6, $C_6H_5(CH_3)$, C_8H_{10} isoxylene, *p*-xylene, C_9H_{12} pseudo-cumene and mesitylene, $C_{10}H_{14}$ durene, isodurene and another (diethylbenzene?), $C_{11}H_{16}$ diethyl-toluene and isomerides, and hydrocarbons of the formulæ $C_{11}H_{14}$ (styrene?), $C_{11}H_{12}$, $C_{12}H_{14}$, and $C_{13}H_{14}$. Markownikoff and Oglobine, from the fraction (210°–330°) under 20 mm. obtained evidence of the presence of oxygenated compounds of both acid and neutral characters (*Bl.* [2] 41, 258), and obtained a denser naphthene $C_{15}H_{30}$. Engler has also confirmed the presence of mesitylene and pseudo-cumene (*B.* 18, 2234) in Caucasian petroleum (*v.* also Le Bel, *C. R.* 103, 1017–1019).

Aschan has isolated from the Baku oil, acids of low carbon percentage derived from hexa-, hepta-, and octo-naphthenes. From the heptanaphthene carboxylic acid by P and HI he has prepared an octonaphthene (117°) under 742 mm. S.G. $\frac{0}{}$ 0·7706, identical with that obtained by Markownikow from the Caucasian oil (*B.* 24, 2710; and Zaloziecki, *B.* 24, 1808). On the formation of acid compounds in petroleum *v.* Zaloziecki, *Z. f. Angew. C.* 1891. 410.

The oil of still higher boiling-point consists of naphthines C_nH_{2n-2}, or hydrocarbons probably derived from the naphthenes by the high temperature, together with C_nH_{2n-4} hydrocarbons and about 10 p.c. of true benzene compounds, which are homologues of styrene. When the naphtha residues are distilled at temperatures above 400°, dissociation of the high boiling products takes place, and fresh low-boiling hydrocarbons are formed. According to Lissenko a. Rosenbladt, the best yield of low-boiling products is obtained at a temperature 434°–437° (Berg, *J. R.* 1887, 349), but Nobel gives 400° as the best temperature for maximum dissociation (*D. P. J.* 266, 226). The Nobel brothers obtain benzene, naphthalene, and anthracene from their petroleum residues at Baku (*D. P. J.* 246, 429–432). Beilstein a. Kurbatoff have studied *the action of nitric acid* upon Russian petroleum. They find that the fraction (95°–100°) is oxidised to succinic and several volatile acids, and at the same time a nitro-compound $C_6H_{11}(NO_2)$ (212°) is formed. The corresponding fraction of American petroleum under like treatment yields a nitro- body $C_7H_{15}(NO_2)$ (195°). The fraction (115°–120°) gives crystals of trinitro-isoxylene. Markownikoff a. Oglobine isolated the above-mentioned

hydrocarbons chiefly by treating the several fractions of the oil with concentrated H_2SO_4 and separating the sulphonates produced. About 15-20 per cent. of the fraction (180°-280°) is converted into these sulphonates. Chiefly mono- and di- acids derived from the hydrocarbons C_nH_{2n-2}, C_nH_{2n-4}, C_nH_{2n-6}, C_nH_{2n-10} and C_nH_{2n-12}. The naphthenes are not attacked by conc. H_2SO_4, but fuming acid converts them into resins. The principal sulphonates isolated are $C_{11}H_{15}SO_3H$, 2 isomers $C_{10}H_{13}SO_3H$, $C_{13}H_{13}SO_3H$, $C_{12}H_{12}SO_3H$, $C_{11}H_{13}SO_3H$, and $C_{12}H_{13}SO_3H$. Schutzenberger has shown that a bright-red heat dissociates the low-boiling naphthenes into benzene derivatives, while a dull heat determines the formation of butylene, and crotonylene and its homologues. The oil obtained from Tiflis appears to be intermediate in character to that of the American and Baku products. Beilstein a. Kurbatoff (*C. J.* 40, 1020) isolated from samples of this petroleum, *n*-pentane, isopentane, and a butane in the (30°-35°) fraction, a hexane and naphthenes in the (70°-75°) fraction, and a heptane, benzene, and toluene in the (95°-100°) fraction. They also obtained from this oil, by the action of HNO_3, a dinitro- compound $C_4H_8(NO_2)_2$ [95°] (*v.* also Le Bel, *C. R.* 103, 1018).

The petroleum found in Germany and Galicia is characterised by a large amount of aromatic hydrocarbons, and Kraemar a. Böttcher hold that the hydrocarbons of German petroleum and Baku oil differ from coal tar and shale tar oils only in the relative proportions of those hydrocarbons which are attacked by conc. H_2SO_4 and HNO_3 (*B.* 20, 595-609).

Engler has made a very systematic investigation into the composition of the German oils, and has isolated or identified the following substances: gases CH_4, CO, CO_2, N, C_2H_4, and homologues; in the first fraction (below 150°) C_5H_{12}, C_6H_{14}, and C_9H_{20}; in the fraction (160°-182°) pseudo-cumene and mesitylene; and in the higher-boiling portion solid paraffin. The oil from Oelheimer and Wietzer contains saturated hydrocarbons, naphthenes, but no solid paraffin nor volatile products below 150°. The Tegernsee oil is especially rich in aromatic hydrocarbons (Engler, *D. P. J.* 267, 550-570; 592-597; 268, 76-90). Engler has also detected phenols and fatty and oleic acids in many specimens. Boussingault has also isolated from Alsatian petroleum, petrolene, and a black colouring matter similar to that found in Alsatian bitumen and in Galician oil (Le Bel, *Bl.* 1888, 359).

Galician petroleum contains hydrocarbons of the C_nH_{2n+2} and C_nH_{2n-6} series (Freund, *A.* 115, 91). It has also been examined by Lachowicz (*A.* 220, 168), who finds in the low-boiling fraction (30°-125°) the following hydrocarbons: isopentane (30°), *n*-pentane (37°), hexane (60°), *n*-heptane (99°), ennane (148°), S.G. $\frac{12}{4}$ ·742, two decanes (152°), S.G. $\frac{21}{}$ ·7187 and (162°). S.G. $\frac{20}{}$ ·7324; benzene, toluene, xylene, and mesitylene, but no olefines. From the high S.G. of the benzene fractions he also infers the presence of naphthenes (hexahydro-toluene and hexahydro-isoxylene). Pawlewski has also found 2 p.c. of aromatic hydrocarbons, principally benzene and *p*-xylene, in Galician oil. According to Bandrowski, this petroleum contains a small quantity of a basic body resembling the alkaloids (*M.* 8, 225), and Weller has also detected the presence of bases in the yellow oil (S.G. 85) obtained from Saxon petroleum (*B.* 20, 2098). On the Galician petroleum industry *v.* Redwood, *S. C. I.* 1892.

Burmese petroleum has only been imperfectly examined. Romanis has found gases, benzene, and solid paraffin in the crude oil and 5 p.c. of solid paraffin in that refined at Rangoon. It solidifies at 24°, and has a S.G. ·85-·9. From another district in Burma (Arracan) a mineral oil is obtained which contains benzene and its homologues, but does not solidify. Its S.G. is also lower, ·825 (*C. N.* 59, 292).

The origin of petroleum.—Mendeléeff has given considerable attention to this subject, and has advanced strong reasons for believing that mineral oils have not been produced like coal from the decomposition of past vegetation. He believes that it is formed in the depths of the earth beneath the very site on which it is found, since it cannot be water-borne. The absence of any large masses of organic matter in the oil districts negatives the vegetable origin of petroleum. In Europe the oil wells belong to Tertiary and late geological periods, but in America and Canada the oil-bearing sands are found in the Devonian and Silurian formations, and hence below the carboniferous beds. The oil beds also always run parallel to mountain ranges, and Mendeléeff believes that water has found its way through the fissures formed at the upheaval of these ranges to the heated metallic carbides below, resulting in the formation of metallic oxides and hydrocarbons, the chemical composition of which depends upon the conditions of temperature and pressure under which they are formed. This origin of petroleum is supported by the frequent presence of sulphur in crude oils, by the asphaltene containing a mineral ash consisting of oxides of Fe, Al, Cu, Ca (Ag), and by the non-saturated nature of many of the hydrocarbons. The occurrence of petroleum in the lavas of Etna lends additional support to this theory (Silvestri, *G.* 1877, 1). Hoefer, Engler, Leopold v. Buch, Sterry Hunt, and many geologists believe that petroleum has been formed by the decomposition of organic matter of animal origin, and advance the presence of nitrogen compounds and direct experiments with animal fats in support of their view. On the origin of petroleum see *Neues Wörterbuch*, iii. 39; Byasson (*M. S.* 1876, 1077); Mendeléeff (*Revue Scientif.* 1877, 409); Anderson (*B. A. address*, 1889); Engler (*B.* 21, 1816-1827); Hoefer ('*Mineralölindustrie*' in *Bolley's Technologie*); Zaloziecki (*D. P. J.* 280, 69, 85, 133); Watson Smith (*S. C. I.* 10, 979). S. R.

PETROLEUMIC ACID *v.* Hendecenoic acid.

PETTENKOFER'S REACTION. A blood-red colour on warming with cane-sugar and conc. H_2SO_4. The colour is produced by the bile acids, cholic acid, and many other bodies. Furfuraldehyde may be used instead of sugar (Mylius, *H.* 11, 492; *v.* also vol. i. p. 508).

PEUCEDANIN *v.* Imperatorin.

PEWTER. An alloy of Pb and Sn; *v.* this vol. p. 125.

PHACONIN *v.* Proteïds.

PHASEOMANNITE *v.* Inosite.

PHASOL $C_{15}H_{24}O$. [190°]. $[\alpha]_D = 30\cdot6°$ in a 4 p.c. chloroform solution. Found in the husks of peas (*Pisum sativum*) (Likernik, *B.* 24, 188). Groups of tables (from alcohol), insol. water, v. sol. hot alcohol and ether. Gives a purple colour on shaking its chloroform solution with H_2SO_4 of S.G. 1·76.

PHELLANDRENE. A dextrorotatory modification of this terpene occurs in oil of elemi, a lævorotatory variety in Australian eucalyptus oil (Wallach, *A.* 246, 234). The dextrorotatory variety occurs also in the seeds of *Phellandrium aquaticum*, and in oil of fennel (*v.* TERPENES).

PHENACETURIC ACID $C_{10}H_{11}NO_3$, *i.e.* $CH_2Ph.CO.NH.CH_2.CO_2H$. [143°]. S. ·7 at 11°. Occurs in horses' urine (Salkowski, *B.* 17, 3010). Found in urine after taking phenyl-acetic acid (Salkowski, *H.* 7, 162). Prepared by digesting phenyl-acetic anhydride with glycocoll and benzene (Hotter, *J. pr.* [2] 38, 97; *B.* 20, 84). White laminæ (from water) or cubes (from alcohol). On nitration it gives *p*-nitro-phenaceturic acid [173°].—CaA'_2 2aq. S. (of CaA'_2) 3 at 11°.—CuA'_2 aq.—AgA': amorphous insoluble pp.

Methyl ether MeA'. [86·5°]. Needles.

Ethyl ether EtA'. [79°]. Prisms.

n-Propyl-ether PrA'. [31°]. Plates.

Amide [174°]. Pearly tables.

PHENACONIC ACID. A name given by Carius to a mixture of maleic and fumaric acids.

PHENACYL. The radicle $C_6H_5.CO.CH_2$.

DI-PHENACYL-ACETIC ACID *v.* DI-BENZOYL-ISOBUTYRIC ACID.

DI-PHENACYL-ACETOACETIC ETHER $(CH_2Bz)_2CAc.CO_2Et$. [83°]. Made from aceto-acetic ether, NaOEt, and phenacyl bromide (Paal a. Hoermann, *B.* 22, 3225). Monoclinic crystals, sl. sol. cold alcohol, v. sol. CS_2. Alcoholic NH_3 at 125° forms two bodies [136°] and [192°].

Mono-oxim. [63°]. Flakes.

Di-oxim. [63°]. Flakes.

Tri-oxim. [68°]. Flakes.

Di-phenyl-di-hydrazide $C_{39}H_{34}N_4O_3$. [88°–92°]. From the ether and phenyl-hydrazine.

PHENACYL-*o*-AMIDO-BENZOIC ACID.

Formyl derivative $CH_2Bz.N(CHO).C_6H_4.CO_2H$. [184°]. Got by oxidising quinoline phenacylo-bromide with $KMnO_4$ (Bamberger, *B.* 20, 3342). Tables (from alcohol), sl. sol. cold water.

PHENACYLAMINE $C_6H_5.CO.CH_2.NH_2$. *ω-Amido-acetophenone.* Got by decomposing phenacyl-phthalamic acid [160°] with conc. HClAq (Goedeckemeyer, *B.* 21, 2687). Converted by NH_3 into di-phenyl-pyrazine.—B'HCl. [188°].—$B'_2H_2PtCl_6$. [c. 210°].—$B'C_6H_3N_3O_7$. [175°]. Yellow needles.

PHENACYL-ISOAMYL-MALONIC ACID $C_6H_5.CO.CH_2.C(C_5H_{11})(CO_2H)_2$. [160°]. Made from sodium isoamyl-malonic ether and phenacyl bromide, the product being saponified (Paal a. Hofmann, *B.* 23, 1500). Needles, v. sol. alcohol. Yields $CH_2Bz.CH(C_5H_{11}).CO_2H$ [103°] on heating. —$NH_4C_{16}H_{19}O_5$. [165°]. Needles.

Ethyl ether Et_2A''. Oil.

Amide. Crystalline.

PHENACYL-BENZOYL-ACETIC ETHER $CH_2Bz.CHBz.CO_2Et$. *Di-benzoyl-propionic ether.* [c. 58°]. Made from ω-bromo-acetophenone and sodium benzoyl-acetic ether (Kapf a. Paal, *B.* 21, 1485, 3053). Crystals (from ether), insol. water. With aqueous potash it gives benzoyl-propionic acid; while alcoholic potash yields CPh:C.CHBz.CO_2H [135°] and $CH_2Bz.CH_2Bz$ [145°].

PHENACYL BROMIDE *v.* ω-BROMO-ACETOPHENONE.

PHENACYL CHLORIDE *v.* ω-CHLORO-ACETOPHENONE.

PHENACYL CYANIDE *v.* BENZOYL-ACETONITRILE.

DI-PHENACYL-MALONIC ACID *v.* DI-BENZOYL-DI-METHYL-MALONIC ACID.

PHENACYL-PHTHALAMIC ACID $CO_2H.C_6H_4.CO.NH.CH_2.CO.C_6H_5$. [160°]. Made by the action of alcoholic potash on phenacyl-phthalimide (Goedeckemeyer, *B.* 21, 2686). Needles, insol. water. Decomposed by boiling HClAg into phthalic acid and amido-acetophenone.

Phenacyl-phthalimide $C_6H_4{:}C_2O_2{:}N.CH_2Bz$. [167°]. Made by heating ω-bromo-acetophenone with potassium phthalimide at 150° (Goedeckemeyer, *B.* 21, 2685). Dimetric plates, sol. alcohol and ether, almost insol. water and ligroïn.

Phenyl-hydrazide $C_8H_4O_2.N.CH_2.C(N_2HPh).C_6H_5$. [155°]. Orange needles, insol. water.

PHENACYL SULPHIDE $S(CH_2.CO.C_6H_5)_2$. [77°]. Made by adding ω-bromo-acetophenone (100 pts.) in alcohol (400 pts.) to a solution of Na (12 pts.) in alcohol (400 pts.) saturated with H_2S (Tafel a. Moritz, *B.* 23, 3474). Prisms (from hot alcohol). Reduces Fehling's solution. Yields a di-oxim [151°] and a diphenyldihydrazide [147°].

PHENACYL SULPHOCYANIDE $C_6H_5.CO.CH_2.S.CN$. *Sulphocyanoacetophenone.* [74°]. Made by mixing alcoholic solutions of barium sulphocyanide and ω-bromo-acetophenone (Arapides, *A.* 249, 10). Needles or prisms, v. sol. ether, insol. water. Hot HCl converts it into $CH_2Bz.S.CONH_2$ and finally oxy-phenyl-thiazole.

PHENACYL THIOCARBAMATE $CH_2Bz.S.CONH_2$. A very unstable body got by boiling phenacyl sulphocyanide with conc. HClAq until crystallisation begins (Arapides, *A.* 249, 12). Yields oxy-phenyl-thiazole on boiling with HClAq.—B'HCl. [c. 177°]. Silky needles.—$B'_2H_2PtCl_6$. [c. 200]. Yellow crystalline powder.

PHENACYL TOLUIDINE *v.* TOLYL-AMIDO-ACETOPHENONE.

Di-phenacyl-*p*-toluidine $C_6H_4Me.N(CH_2Bz)_2$. [255°]. Formed from *p*-toluidine and ω-bromo-acetophenone in alcohol (Lellmann a. Donner, *B.* 23, 168). Needles, v. sol. alcohol.

PHENAMYLAMINE *v.* AMIDO-AMYL-BENZENE.

Diphenamylamine $NH(C_6H_4.C_5H_{11})_2$. *Di-isoamyl-di-phenylamine.* (320°).

Formed, together with amido-isoamyl-benzene $C_6H_4(C_5H_{11}).NH_2$ (260°) by heating $C_6H_4(C_5H_{11}).OH$ with ammoniacal $ZnBr_2$ or with $ZnCl_2$ and NH_4Br or NH_4Cl; the yield being 18 to 25 p.c. (Lloyd, *B.* 20, 1257).—$B'_2H_2PtCl_6$.

Acetyl derivative $NAc(C_{11}H_{15})_2$. [81°]. White glistening plates.

PHENANTHRAQUINONE $C_{14}H_8O_2$ *i.e.* $\begin{matrix}C_6H_4.CO\\ |\\ C_6H_4.CO\end{matrix}$ or $\begin{matrix}C_6H_4.C.O\\ |\quad\ \ |\\ C_6H_4.C.O\end{matrix}$. Mol. w. 208. [202°]

(Hayduck, *A.* 167, 184). (above 360°). Formed by oxidising the residue left after evaporating the alcoholic washings from the distillate got in preparing anthracene from o-bromo-benzyl bromide and Na (Jackson a. White, *Am.* 2, 392).

Preparation.—1. By warming phenanthrene (1 pt.) with $K_2Cr_2O_7$ (1 pt.), water (3 pts.) and H_2SO_4 ($1\frac{1}{2}$ pt.) and crystallising the product from diluted HOAc (Fittig a. Ostermayer, *B.* 5, 933; *A.* 166, 365).—2. By adding a solution of CrO_3 in HOAc to a hot solution of phenanthrene in HOAc (Graebe, *B.* 5, 861; *A.* 167, 139). The product is purified by solution in aqueous $NaHSO_3$ followed by ppn. with HCl and crystallisation from HOAc.—3. By oxidising crude phenanthrene (310°–340°), the following bodies being obtained at the same time; methyl-anthraquinone, diphenic acid, carbazole, acridine, and diphenylene-ketone (Anschütz a. Schultz, *A.* 196, 32).

Properties.—Orange needles or prisms (from solvents) or tables (by sublimation), almost insol. cold water, sl. sol. hot water and cold alcohol, m. sol. hot alcohol, ether, HOAc, and benzene. Conc. H_2SO_4 forms a dark-green solution but does not sulphonate it, even at 100°. A solution of phenanthraquinone (·1 g.) in HOAc (20 c.c.) mixed with toluene (4 c.c.) containing methyl-thiophene gives on shaking with H_2SO_4 (16 c.c.) a bluish-green liquid which, when poured into water and extracted with ether, imparts a purple colour to the ether (Laubenheimer, *B.* 8, 224; V. Meyer, *B.* 16, 1624). The colouring matter $C_{19}H_{12}SO$ formed in this reaction gives anthraquinone on distilling with $PbCrO_4$ (Oderheimer, *B.* 17, 1338). A solution of phenanthraquinone in wet ether when exposed in closed tubes to direct sunshine is readily reduced to phenanthrahydroquinone, with formation of aldehyde (Klinger, *B.* 19, 1869).

Reactions.—1. Oxidised by *chromic acid* to diphenyl di-*o*-carboxylic acid. — 2. Alkaline $KMnO_4$ gives oxy-diphenylene-acetic acid and diphenylene-ketone (Anschütz a. Japp, *B.* 11, 212).—3. Reduced to dihydride by warming with aqueous SO_2.—4. *Sodium-amalgam* acting on its alcoholic solutions forms diphenic acid [226°] (A. a. S.).—5. Boiling aqueous NaOH yields $C_{12}H_8{:}C(OH).CO_2H$ (A. a. J.). Boiling baryta-water forms, besides oxy-diphenylene-acetic acid, diphenylene ketone and fluorene alcohol.—6. *Alcoholic potash* gradually forms diphenic acid, the solution meanwhile giving out phosphorescent light on shaking (Lachovitch, *B.* 16, 332).—7. By passing the vapour over *heated lead oxide* di-phenylene-ketone is formed (Wittenberg a. Meyer, *B.* 16, 502).—8. Distillation with dry *soda-lime* gives diphenyl. When the soda-lime is moist, fluorene, fluorene alcohol, and diphenylene ketone are also formed.—9. Distillation with *quick-lime* gives fluorene and diphenylene ketone (Anschütz a. Schultz, *B.* 9, 1400).—10. Distillation with *zinc-dust* yields phenanthrene.—11. An ethereal solution of $ZnEt_2$ decolourises it. On adding alcohol, boiling, and filtering, crystals of $C_{16}H_{14}O_2HOEt$, [77°], are formed. These are rectangular plates, insol. water. Ac_2O converts it into $C_{16}H_{13}O_2Ac$, [103°] (Japp, *C. J.* 35, 526).—12. With PCl_5 it gives $\begin{matrix} C_6H_4.CCl_2 \\ | \quad\;\; | \\ C_6H_4.CO \end{matrix}$; benzene may be used as diluent. The product 'di-chloro-phenanthrone' may be recrystallised from benzene. It melts at [165°], although at 140° it begins to get brown. Alkalis convert it into phenanthraquinone. Shaken with alcoholic potash, it is oxidised to diphenic acid, the solution phosphorescing meanwhile. Iron and acetic acid reduce it first to chloro-phenanthrone, $\begin{matrix} C_6H_4.CHCl \\ | \quad\;\; | \\ C_6H_4.CO \end{matrix}$ [123°], and then to phenanthrone $\begin{matrix} C_6H_4.CH_2 \\ | \quad\;\; | \\ C_6H_4.CO \end{matrix}$, [149°]. Chloro-phenanthrone may be recrystallised from glacial acetic acid, and is not decomposed even by boiling alkalis, but HNO_3 (S.G. 1·3) converts it into nitro-phenanthraquinone. Phenanthrone may be crystallised first from glacial acetic acid, then from butyl bromide (B. Lachovitch, *J. pr.* [2] 28, 168).—13. By exhaustive *chlorination* with $SbCl_5$ it yields perchloro-diphenyl together with a very small quantity of per-chloro-benzene (Merz a. Weith, *B.* 16, 2870).—14. *Benzoic aldehyde* (free from HCy) at 260° forms *benzalquin of phenanthrene* $C_{35}H_{24}O$ [329°], which crystallises from CS_2 in rectangular plates and yields benzoic acid and phenanthraquinone on oxidation. It gives off no gas with $ZnEt_2$, hence contains no hydroxyl (Japp a. Wilcock, *C. J.* 37, 661).—15. Heating with PCl_3 followed by addition of water forms $\begin{matrix} C_6H_4.C(OH).PO(OH)_2 \\ | \quad\;\; | \\ C_6H_4.CO \end{matrix}$ crystallising in flesh-coloured plates, sol. water, alcohol, and ether (Fossek, *M.* 7, 36).—16. *Acetone* at 200° forms acetone-phenanthraquinone $C_{17}H_{14}O_3$ (vol. i. p. 33). By the action of H_2SO_4 on this body a small quantity of $C_{34}H_{22}O_3$ [238°] is formed (Wadsworth, *C. J.* 59, 105).—17. *Ammonia* passed into an alcoholic solution forms phenanthraquinonimide $C_{14}H_9NO$. On heating with alcoholic NH_3 in sealed tubes there are formed diphenanthrylene - azotide $C_{28}H_{16}N_2$, two compounds $C_{28}H_{19}N_3O$ [282°] and [over 300°] and a compound $C_{14}H_{10}N_2$ [above 285°] (Schmidt, *B.* 7, 1365; Anschütz a. Schultz, *A.* 196, 49; Zincke, *B.* 12, 1641; Sommaruga, *M.* 1, 146; Japp, *C. J.* 49, 845; 51, 98).—18. *Benzoic aldehyde* and aqueous NH_3 at 100° quickly forms $C_{21}H_{13}NO$ or $C_{12}H_8{:}C_2{<}^{O}_{N}{>}CPh$. This 'benzenyl-amido-phenanthrol' crystallises from benzene in tufts of silky needles, [202°], v. sl. sol. alcohol, sol. conc. HClAq and conc. H_2SO_4 without change. It yields benzoic acid and phenanthraquinone on oxidation. HClAq at 200° forms benzoic acid. It does not act on $ZnEt_2$ (Japp, *C. J.* 37, 666; 39, 225).—19. *Cuminic aldehyde* and NH_3 forms, in like manner, cumenyl-amido - phenanthrol $C_{14}H_8{<}^{O}_{N}{>}C.C_6H_4.C_3H_7$ [186°], crystallising from benzene-ligroïn in silky needles, and forming in conc. H_2SO_4 a yellowish-green fluorescent liquid (Japp a. Wilcock, *C. J.* 39, 226).—20. *Furfuraldehyde* and aqueous NH_3 give $C_{14}H_8{<}^{O}_{N}{>}C.C_4H_3O$ [231°], crystallising from isoamyl alcohol in needles (J. a. W.).—21. *Salicylic aldehyde* (1 mol.) and conc. NH_3Aq form, on warming, *o*-oxy-benzenyl-di-amido - phenanthrene $\begin{matrix} C_6H_4.C.NH \\ | \quad\;\; \| \\ C_6H_4.C{-}N \end{matrix}{>}C.C_6H_4.OH$ (Japp a. Streatfeild, *C. J.* 41, 146). This body crystallises from HOAc in slender needles [270°–

276°], and is sl. sol. alcohol, v. sol. HOAc. It dissolves in boiling KOHAq, and is ppd. by CO_2. Boiling alcoholic potash gives salicylic acid. HClAq at 200° has no action. BzCl yields a benzoyl derivative [220°].—22. o-*Methoxy-benzoic aldehyde* (15 g.) heated with phenanthraquinone (30 g.) and excess of NH_3Aq at 100° deposits yellow crystals of $C_{14}H_8{:}N_2H{:}C.C_6H_4OMe$ [208°], while the mother-liquor contains $C_{14}H_8<\substack{O\\N}>C.C_6H_4OMe$, which crystallises in white needles, v. sol. hot benzene (Japp a. Streatfeild, *C. J.* 41, 154).—23. *p-Oxy-benzoic aldehyde* and aqueous NH_3 form *p*-oxy-benzenyl-di-amido-phenanthrene [above 350°], crystallising from HOAc in slender needles. It yields an acetyl derivative [205°–210°] (J. a. S.).—24. *Aldehyde-ammonia* yields an amorphous base (J. a. W.).—25. Alcoholic *methylamine* forms, on warming, yellow crystals. The mother-liquor deposits $C_{16}H_{14}N_2$ or $C_{14}H_8(NMe)_2$, crystallising in colourless prisms [186°], and yielding B′HCl, v. sol. water, and $B'HNO_3$, $B'_2H_2SO_4$, $B'_2H_2C_2O_4$, all crystallising in needles (Zincke, *B.* 12, 1643). — 26. *Ethylene-diamine* and HOAc form the azine $C_{14}H_8<\substack{N\\N}>C_2H_4$, which crystallises from alcohol in needles [181°]. It yields a platinochloride $B'_2H_2PtCl_6$, nearly insol. alcohol (Mason, *B.* 19, 112; 20, 268).—27. *Propylene-diamine* yields $C_{17}H_{12}N_2$, crystallising in needles [128°], and yielding $B'_2H_2PtCl_6$ (Strache, *B.* 21, 2362).—28. *Trimethylene-diamine* forms $C_{26}H_{27}NO_2$, a lemon-yellow powder, not melted at 250°. Its alcohol solution is coloured violet by acids. 29. *Tetra-amido-phenazine* and HOAc give

$$C_{14}H_8<\substack{N\\N}>C_6H_2<\substack{N\\N}>C_6H_2<\substack{N\\N}>C_{14}H_8,$$

a green crystalline pp., forming a bluish-green solution in H_2SO_4, changing on dilution through red to orange (Nietzki a. Müller, *B.* 22, 450).—30. *Phenylene-o-diamine* gives phenanthrazine $C_{14}H_8<\substack{N\\N}>C_6H_4$, [217°], insol. water, v. sol. alcohol (Hinsberg, *A.* 237, 340).—31. *Tolylene-o-diamine* forms $C_{14}H_8<\substack{N\\N}>C_6H_3Me$ [213°].—32. Heating with *acetamide* and HOAc forms the azine $C_{14}H_8<\substack{N\\N}>C_{14}H_8$, crystallising in yellowish-brown flat needles, [400°], sol. aniline, nitro-benzene, and phenol (Mason, *C. J.* 55, 108).—33. *Naphthylene-(1,2)-diamine* yields $C_{14}H_8<\substack{N\\N}>C_{10}H_6$ [264°] (Leuckart, *B.* 19, 174).—34. *Phenyl-naphthylene-(1,2)-diamine* boiled with HOAc and phenanthraquinone forms, on adding HNO_3, a pp. of $C_{30}H_{19}(NO_3)N_2O$, whence boiling potash separates $C_{14}H_8<\substack{N.C_{10}H_6\\NPh(OH)}>$ which forms a yellow solution in ether. It forms a blue solution in H_2SO_4, turned orange by dilution (Witt, *B.* 20, 1185).—35. *Nitro-o-phenylene-diamine* and HOAc give, on heating, $C_{20}H_{11}N_3O_2$ [251°] (Heim, *B.* 21, 2301). — 36. *Isobutyl-phenylene-diamine* in HOAc forms $C_{14}H_8<\substack{N\\N}>C_6H_3.C_4H_9$ [147°], crystallising in pale-yellow needles, coloured cherry-red by H_2SO_4 (Gelzer, *B.* 20, 3253; 21, 2951). The compound $C_{14}H_8{:}N_2{:}C_6H_2Br.C_4H_9$ [154°] also forms yellow needles. (β)-*Isobutyl-phenylene-diamine* gives an isomeric azine [144°].—37. (6,4,2,1)-*Bromo-tolylene-diamine* in HOAc forms $C_{14}H_8{:}N_2{:}C_6H_2MeBr$ [210°] crystallising in yellow needles (Hartmann, *B.* 23, 1050).—38. *i-Tri-amido-benzene* (from chrysoidine) yields $C_{14}H_8{:}N_2{:}C_6H_3NH_2$ as brown crystals [179°] (Witt, *C. J.* 49, 402; Heim).—39. *Aceto-acetic ether* forms, in presence of KOH, phenanthroxylene acetoacetic ether $C_{18}H_{11}EtO_4$ [185°] crystallising in white needles (Japp a. Streatfeild, *C. J.* 43, 27).—40. *Acetone* and NH_3Aq form $C_{17}H_{15}NO_2$ crystallising in colourless laminæ [c. 130°]. This body forms a yellow solution in HClAq, which deposits a dark-blue substance and gives, on addition of water to the filtrate, needles of $C_{17}H_{14}O_3$ (Japp a. Streatfeild, *C. J.* 41, 272).

Combinations.—$C_{14}H_8O_2NaHSO_3$2aq. Small colourless plates, v. e. sol. water, which slowly decomposes it.—$(C_{14}H_8O_2)_2HgCy_2$. [223°]. Red crystals with green lustre, deposited from a hot saturated solution of phenanthraquinone and $HgCy_2$ in acetone (Japp a. Turner, *C. J.* 57, 7).—$(C_{14}H_8O_2)_2HgCl_2$. [223°]. Red prisms (from boiling acetone).—$C_{14}H_8O_2ZnCl_2$. Dark reddish-brown needles got by adding a hot solution of $ZnCl_2$ in HOAc to a hot solution of phenanthraquinone in HOAc (Japp a. Turner, *C. J.* 57, 5).

Hydrocyanide $C_{14}H_8O_2(HCN)_2$: tufts of needles, formed by action of 30 p.c. HCN solution. Decomposed by heat into its components. Conc. HCl decomposes it, giving off CO_2 and forming $C_{15}H_9NO$ [241°] and $C_{15}H_{11}NO_2$ [183°]. The latter separates from benzene in slender needles. Both dissolve in sodium carbonate, expelling CO_2; the compound [241°] producing $C_{15}H_{10}NaNO_2$4aq, and also the corresponding $(C_{15}H_{10}NO_2)_2Ba$ 7aq whence HCl liberates $C_{15}H_9NO$ (Japp a. Miller, *C. J.* 51, 29).

Mono-oxim $C_{14}H_9NO$ *i.e.* $\begin{array}{l}C_6H_4.C{:}NOH\\ C_6H_4.CO\end{array}$ [158°]. Formed by boiling phenanthraquinone with alcoholic hydroxylamine hydrochloride for an hour (Goldschmidt, *B.* 16, 2178). Small yellow needles, v. sol. hot alcohol. Forms coloured pps. with metallic salts (Kostanecki, *B.* 22, 1347). Boiling NaOHAq forms a green liquid. Conc. H_2SO_4 forms a blood-red solution and at 100° converts it into diphenylene ketone carboxylic amide. HCl, Ac_2O, and HOAc at 100° convert it, by intra-molecular change, into a weak base [217°], probably $\begin{array}{l}C_6H_4.CO\\ C_6H_4.CO\end{array}>NH$, and also form prisms [92°] (Wegerhoff, *A.* 252, 17). Ac_2O forms $C_{28}H_{16}N_2O$ crystallising in small brownish tables [247°] nearly insol. alcohol and ether (Zincke).

Di-oxim $\begin{array}{l}C_6H_4.C{:}NOH\\ C_6H_4.C{:}NOH\end{array}$. [202°]. Formed by heating an alcoholic solution of phenanthraquinone (1 mol.) with hydroxylamine hydrochloride (4 mols.) for 30 hours at 100° (Auwers a. V. Meyer, *B.* 22, 1993). Minute yellow prisms (from alcohol or HOAc), insol. water, sl. sol. hot alcohol and ether. Conc. H_2SO_4 forms a blood-red solution. NaOHAq forms a yellow solution, depositing the Na salt as pearly plates. Alcohol at 150° forms the anhydride $\begin{array}{l}C_6H_4.C{:}N\\ C_6H_4.C{:}N\end{array}>O$ [183°] which crystallises in long yellow needles, insol. NaOHAq. A solution of the dioxim in HOAc

and Ac_2O saturated with HCl in the cold gives the acetyl derivative $\begin{matrix}C_6H_4.C{:}NOAc\\C_6H_4.C{:}NOAc\end{matrix}$ separating from alcohol in minute crystals [184°].

Phenyl-hydrazide $C_{20}H_{14}N_2O$. [165°]. Formed by warming an alcoholic solution of phenanthraquinone with aqueous phenyl-hydrazine hydrochloride (Zincke, *B.* 16, 1564). Red needles or plates (from alcohol). Gives a violet solution in H_2SO_4.

Di-bromo-phenanthraquinone $C_{14}H_6Br_2O_2$. [230°] (H.); [233°] (Ostermayer, *B.* 7, 1090). Made by heating the quinone with Br and a little water for six hours at 180° (Hayduck, *A.* 167, 185). Yellow nodules (from HOAc), sl. sol. alcohol. Yields di-bromo-diphenyl dicarboxylic acid on oxidation by chromic acid mixture.

Nitro-phenanthraquinone $\begin{matrix}[1{:}2]C_6H_4 - - - CO\\ [1{:}4{:}2]C_6H_3(NO_2).CO\end{matrix}$. [257°]. Formed from the quinone and boiling HNO_3 (S.G. 1·4) (Anschütz a. Schultz, *B.* 9, 1404; Strasburger, *B.* 16, 2346). Orange plates (from HOAc) yields nitro-diphenyl dicarboxylic acid [217°] on oxidation. By oxidation of (α)-, (β)-, and (γ)-nitro-phenanthrene with CrO_3 and HOAc there are formed (α)-, (β)-, and (γ)-**nitro-phenanthraquinones** [215°-220°], [260°-266°], and [263°] respectively (Schmidt, *B.* 12, 1156).

Nitro-phenanthraquinone. [282°]. Made by warming chloro-phenanthrone with nitric acid (S.G. 1·3) (Lachovitch, *J. pr.* [2] 28, 172). Orange plates, sl. sol. HOAc.

Di-nitro-phenanthraquinone $\begin{matrix}C_6H_3(NO_2).CO\\C_6H_3(NO_2).CO\end{matrix}$. [294°]. Made by boiling phenanthrene with fuming HNO_3 or with a mixture of HNO_3 and H_2SO_4. Obtained also, together with a more soluble isomeride, by nitration of phenanthraquinone and of nitro-phenanthraquinone [257°] (Graebe, *A.* 167, 144; Schultz, *A.* 203, 108; Strassburger, *B.* 16, 2346). Yellow plates, v. sl. sol. alcohol. Yields di-nitro-diphenyl dicarboxylic acid [253°] on oxidation.

Amido-phenanthraquinone $\begin{matrix}[1{:}2]C_6H_4 ——— CO\\ [1{:}4{:}2]C_6H_3(NH_2).CO\end{matrix}$. [c. 200°]. Formed by reduction of nitro-phenanthraquinone [257°] with tin and HCl (Anschütz a. Meyer, *B.* 18, 1943). Violet-black needles, sl. sol. hot water, forming a reddish-violet solution.—B′HCl: yellowish-red feathery needles.

Di-amido-phenanthraquinone $\begin{matrix}[1{:}4{:}2]C_6H_3(NH_2).CO\\ [1{:}4{:}2]C_6H_3(NH_2).CO\end{matrix}$. Formed by reduction of the di-nitro-compound with tin and HCl (A. a. M.; Kleemann a. Wense, *B.* 18, 2168). Violet-black needles, not melted at 310°. The hydrochloride forms yellow plates.

Oxy-phenanthraquinone $\begin{matrix}C_6H_4 ——— CO\\C_6H_3(OH).CO\end{matrix}$. *Phenanthrolquinone.* Formed by the action of nitrous acid on amido-phenanthraquinone. Brownish-red needles. May be sublimed. Forms a yellowish-green solution in NaOHAq.

Acetyl derivative. [200°-210°].

Di-oxy-phenanthraquinone $C_{14}H_6(OH)_2O_2$. Formed by the action of nitrous acid on di-amido-phenanthraquinone (A. a. M.). Minute dark-brown needles. Yields a di-acetyl derivative crystallising in yellowish-red needles.

Hydro-phenanthraquinone $C_{14}H_{10}O_2$ *i.e.* $\begin{matrix}C_6H_4.C.OH\\C_6H_4.C.OH\end{matrix}$. *Phenanthraquinone dihydride. Phenanthrenehydroquinone.* Mol.w. 210. Formed by heating phenanthraquinone with aqueous SO_2, or by passing SO_2 into a warm alcoholic solution of the quinone (Graebe, *A.* 167, 146). Colourless needles, m. sol. hot water, v. e. sol. alcohol, ether, and benzene. Absorbs oxygen when moist, or in aqueous solution, forming the quinhydrone $C_{28}H_{18}O_4$, which crystallises in black needles [169°], and finally phenanthraquinone. $FeCl_3$, HNO_3, and CrO_3 oxidise it in the same way.

Mono-acetyl derivative $C_{14}H_8(OH)(OAc)$. [170°]. Got by boiling phenanthraquinone with HOAc, HI, and red P (Japp a. Klingemann, *C. J. Proc.* 6, 31). Formed by the action of sunlight on phenanthraquinone in aldehyde (Klinger, *A.* 249, 138). Flat needles.

Di-acetyl derivative $C_{14}H_8(OAc)_2$. [202°]. Formed from the dihydride and Ac_2O. Colourless plates (from benzene), not oxidised by boiling chromic acid mixture. Not attacked by heating with KOHAq, unless the solution has a higher S.G. than 1·3.

Benzoyl derivative $C_{14}H_8(OH)(OBz)$. [178°]. Got by action of sunlight on phenanthraquinone and benzoic aldehyde (K.). White needles (from HOAc).

Valeryl derivative $C_{14}H_8(OH)(O.C_5H_9O)$. [149°]. Got by using isovaleric aldehyde.

Ethyl derivative $C_{14}H_8(OH)(OEt)$. [80°]. On treatment of phenanthraquinone with $ZnEt_2$ and alcohol successively the compound $C_{16}H_{14}O_2EtOH$ [77°] is got, from which EtOH can be removed by standing for some months *in vacuo* over H_2SO_4 (Japp, *C. J.* 37, 408). Gives a mono-acetyl derivative $C_{16}H_{13}AcO_2$ [103°].

Isomeride of hydro-phenanthraquinone $C_{14}H_8(OH)_2$. [143°]. Got by heating its diacetyl derivative with alcoholic NH_3 (Fischer a. Gerichten, *B.* 19, 792). Needles; very oxidisable; its alkaline solution turning green and finally red.

Acetyl derivative $C_{14}H_8(OAc)_2$. [159°]. Made by boiling morphine methylo-iodide with Ac_2O, adding dry AgOAc, filtering, and heating the filtrate at 180°. Needles (from ether).

Di-amido-hydro-phenanthraquinone $C_{14}H_6(NH_2)_2(OH)_2$. Formed by reduction of di-nitro-phenanthraquinone with $SnCl_2$ (Kleemann a. Wense, *B.* 18, 2168). Very readily oxidised by air, $FeCl_3$, or CrO_3 to violet-black needles of di-amido-phenanthraquinone.—$B''H_2Cl_2$ 3aq.

Tetra-acetyl derivative $C_{14}H_6(NHAc)_2(OAc)_2$. Colourless needles, solid at 300°, sl. sol. alcohol and HOAc.

Phenanthraquinone carboxylic acid $\begin{matrix}C_6H_4 ——— CO\\C_6H_3(CO_2H).CO\end{matrix}$. [315°]. Made by oxidation of phenanthrene carboxylic acid with CrO_3 in HOAc (Japp a. Schultz, *B.* 10, 1661; *A.* 196, 14). Orange substance, sol. $NaHSO_3$Aq.

Phenanthraquinone sulphonic acid $C_{14}H_7(SO_3H)O_2$. Formed from phenanthraquinone and SO_3 (Graebe). Gives a colouring matter resembling alizarin when fused with potash.

Phenanthrone $C_{14}H_{10}O$. [149°]. Formed as above (*Reaction* 12). Brownish-red plates, v.

sol. alcohol and ether; does not combine with $NaHSO_3$. Its alkaline solution is green.

Diphenanthrylene-azotide $C_{14}H_8:N_2:C_{14}H_8$. [above 400°]. Formed from phenanthraquinone and alcoholic NH_3 at 100°, and also by heating tetraphenylazine with soda-lime to a red heat (Japp a. Burton, *C. J.* 49, 845; 51, 98). Yellow crystalline powder or yellow needles (by sublimation), v. sl. sol. ether. Its solution in H_2SO_4 is deep blue, becoming orange on dilution.

Isophenanthraquinone $C_{14}H_8O_2$. [156°]. Formed by the further action of CrO_3 and HOAc on an oil formed in the oxidation of phenanthrene, which remains in the alcoholic liquid from which phenanthraquinone has separated (Hayduck, *A.* 167, 185). Yellow crystals (from alcohol), sl. sol. water, v. sol. hot alcohol.

PHENANTHRAZINE *v.* PHENANTHRAQUINONE, *Reaction* 29.

PHENANTHRENE $C_{14}H_{10}$ *i.e.* $\begin{matrix}[1:2]\ C_6H_4.CH \\ [1:2]\ C_6H_4.CH\end{matrix}$. Mol. w. 178. [100°] (Graebe; Schiff); [103°] (Reissert, *B.* 23, 2244). (340° i.V.). S. (alcohol) 2·62 at 16°, 10·08 at 78°. S. (toluene) 33 at 16·5° (Bechi, *B.* 12, 1978). S.V.S. 167·05 (Schiff). S.V. 186·2 (Lossen, *A.* 254, 54); 196·7 (Ramsay). H.F. (from diamond) −39,400 (Berthelot a. Vieille, *A. Ch.* [6] 10, 446; *Bl.* [2] 47, 864); −32,500 (Stohmann, *J. pr.* [2] 40, 94). H.C.v. 1,699,000 (B. a. V.); 1,692,000 (S.). H.C.p. 1,700,400 (B. a. V.); 1,693,500 (S.). Occurs in coal-tar oil (Graebe, *B.* 5, 861; *A.* 167, 131; Fittig a. Ostermayer, *B.* 5, 933; *A.* 166, 361; Hayduck, *B.* 6, 532; *A.* 167, 177) and in 'idryl' got by distillation of an Idrian ore of mercury.

Formation.—1. Together with toluene by passing *s*-di-phenyl-ethylene through a red-hot tube (Graebe).—2. From *s*-di-phenyl-ethane, from toluene (Graebe, *B.* 7, 48), from a mixture of diphenyl and ethylene, from di-methyl-diphenyl, and from phenyl-tolyl-methane (Barbier, *C. R.* 79, 121) by passing the vapours through red-hot tubes. Other hydrocarbons are also formed in these reactions.—3. Together with anthracene in the action of sodium on [1:2] $C_6H_4Br.CH_2Br$ (Jackson a. White, *Am.* 2, 391).—4. By heating coumarone and benzene to a high temperature (Kraemer a. Spilker, *B.* 23, 85).

Preparation.—By fractional distillation of the portion of hydrocarbons (310°–360°) from coal-tar oil, followed by crystallisation from alcohol. A solution of crude phenanthrene (3 pts.) in hot toluene mixed with picric acid (4 pts.) deposits on cooling the picric acid compound in golden needles, which may be subsequently decomposed by alkalis. The mixture of phenanthrene and anthracene may also be crystallised from toluene, when anthracene separates first (Wense, *B.* 19, 761). Chromic acid mixture attacks anthracene more readily than phenanthrene, so that a small quantity of anthracene may be removed by its means (Anschütz a. Schultz, *A.* 196, 35).

Properties.—Small colourless plates (from alcohol), sl. sol. cold alcohol, v. sol. ether, benzene, HOAc, and CS_2. May be sublimed. Exhibits slight blue fluorescence. Its absorption spectrum in the ultra-violet has been studied by Hartley (*C. J.* 39, 164). Not reduced in alcoholic solution by sodium-amalgam.

Reactions.—1. Oxidised by *chromic acid mixture* and by CrO_3 in HOAc to phenanthraquinone.—2. HIAq and P at 200° form a tetrahydride.—3. *Bromine* added to its solution in ether or CS_2 forms unstable $C_{14}H_{10}Br_2$, crystallising in four-sided prisms (F. a. O.; Hayduck, *A.* 167, 180). This dibromide melts with effervescence at 98°, and its alcoholic solution gives a pp. of AgBr on adding $AgNO_3$. By alcoholic KCy it is reconverted into phenanthrene (Anschütz, *B.* 11, 1217).—4. By exhaustive *chlorination* with $SbCl_5$ it yields per-chloro-benzene (Merz a. Weith, *B.* 16, 2869).

Combinations.—$C_{14}H_{10}C_6H_3N_3O_7$. [143°]. S. (95 p.c. alcohol) 2·7 at 15°. Golden prisms.—$C_{14}H_{10}C_6H_3Cl(NO_2)_2$ [1:2:4] [44°]. Orange needles. (Willgerodt, *B.* 11, 604).—$C_{14}H_{10}C_6H_2Cl(NO_2)_3$. [88°]. Lemon-yellow needles (Liebermann, *B.* 8, 378).

Tetrahydride $C_{14}H_{14}$. [0°]. (310° i.V.). S.G. $\frac{10}{}$ 1·067. Got by reducing phenanthrene with HIAq and P, or by isoamyl alcohol and sodium (Bamberger a. Lodter, *B.* 20, 3076). Liquid, v. sol. hot alcohol. Yields phenanthraquinone on oxidation by CrO_3 and HOAc.

Octohydride $C_{14}H_{18}$. (below 300°). Got by heating phenanthrene with HIAq and P at 240° (Graebe). Liquid.

Perhydride $C_{14}H_{24}$. [−3°]. (270°–275°). S.G. $\frac{20}{20}$ ·933. Made, together with a hydride (290°), by heating phenanthrene with HIAq and red P at 250° (Liebermann a. Spiegel, *B.* 22, 779). Yields phenanthrene and anthracene when distilled with zinc-dust. Not attacked by H_2SO_4, HNO_3, or Br.

Chloro-phenanthrenes. By passing chlorine into a solution of phenanthrene in HOAc the compound $C_{14}H_8Cl_6$ [170°] is formed, together with oily $C_{14}H_9Cl$ and $C_{14}H_8Cl_2$. Alcoholic potash converts $C_{14}H_8Cl_6$ into $C_{14}H_6Cl_4$. By heating phenanthrene with $SbCl_5$ the compounds $C_{14}H_6Cl_4$ [172°], $C_{14}H_4Cl_6$ [250°], and $C_{14}H_2Cl_8$ [270°–280°] may be obtained (Zetter, *B.* 11, 165), the final products being C_6Cl_6 and CCl_4.

Bromo-phenanthrenes. Bromine acting on phenanthrene dissolved in ether forms $C_{14}H_{10}Br_2$, which at 100° splits up into HBr and $\begin{matrix}C_6H_4.CH \\ C_6H_4.CBr\end{matrix}$, [63°], (above 360°). Bromo-phenanthrene crystallises in thin prisms, v. sol. HOAc and CS_2, and is converted by oxidation into phenanthraquinone (Zetter; Hayduck; Anschütz). Bromine (4 mols.) acting on phenanthrene in ethereal solution also forms two di-bromo-phenanthrenes $C_{14}H_8Br_2$ [148°] and [156°]. A third di-bromo-phenanthrene [202°] is a crystalline powder insol. ether. By heating phenanthrene with bromine the compounds $C_{14}H_7Br_3$ [126°] and $C_{14}H_6Br_4$ [185°] may be got. By heating phenanthrene with bromine and iodine the compounds $C_{14}H_4Br_6$ [245°] and $C_{14}H_3Br_7$ [above 270°] are obtained. All these bromo-phenanthrenes crystallise in needles.

(α) - **Nitro - phenanthrene** $C_{14}H_9NO_2$. [75°]. Made, together with the two following isomerides, by nitration of phenanthrene (Schmidt, *B.* 12, 1153). Yellow needles. Gives (α)-nitro-phenanthraquinone [215°–220°] on oxidation.

(β) - **Nitro - phenanthrene.** [127°]. Less soluble than the (α)- isomeride. Yields nitro-phenanthraquinone [260°–266°] on oxidation.

(γ) - **Nitro - phenanthrene.** [171°]. Small yellow leaflets. Less sol. alcohol than either of its isomerides. Yields on oxidation a nitro-phenanthraquinone [263°].

Di-nitro-phenanthrene $C_{14}H_8(NO_2)_2$. [150°–160°]. Made by prolonged action of HNO_3 on phenanthrene (Graebe). Yellow crystals.

Bromo-nitro-phenanthrene $\begin{matrix} C_6H_4 & \text{——} & CH \\ C_6H_3(NO_2) & . & CBr \end{matrix}$. [196°]. Made by nitration of bromo-phenanthrene (Anschütz, *B.* 11, 1218). Long spikes.

(α)-**Amido-phenanthrene** $C_{14}H_9NH_2$. Got by reduction of (α)-nitro-phenanthrene (Schmidt, *B.* 12, 1156). Small leaflets, insol. water.—B′HCl: crystalline pp.—$B'_2H_2SO_4$: powder.

(β)-**Amido-phenanthrene.** Small leaflets.—B′HCl: sl. sol. water.

(γ)-**Amido-phenanthrene.** Got, like the preceding bodies, by reduction of the corresponding nitro-phenanthrene.—B′HCl: glistening needles.

Oxy-phenanthrene *v.* PHENANTHROL.

Di-oxy-phenanthrene *v. Hydro-phenanthraquinone.*

Pseudophenanthrene $C_{16}H_{12}$. [115°]. Occurs in crude anthracene (Zeidler, *A.* 191, 295). Large white plates, yielding on oxidation a quinone [170°] which is v. sol. alcohol and benzene. The picric acid compound [147°] separates in bright-red needles on mixing saturated alcoholic solutions of pseudophenanthrene and picric acid.

A hydrocarbon $C_{13}H_{10}$ or $C_{14}H_{10}$, [104°], possibly a mixture of phenanthrene with pseudophenanthrene, was got by Zeidler (*A.* 191, 292) from crude anthracene. It yields an orange picrate [142°], a quinone [205°–209], insol. $NaHSO_3$ (difference from phenanthraquinone), and a bromide [95°] which changes on fusion to a compound [83°], and on boiling with alcoholic potash forms yellow needles [250°]. The quinone gives Laubenheimer's reaction.

(α)-**PHENANTHRENE CARBOXYLIC ACID** $\begin{matrix} CO_2H.C_6H_3.CH \\ C_6H_4.CH \end{matrix}$. [266°]. Formed by the action of alcoholic potash on the nitrile which is got by distilling sodium phenanthrene (α)-sulphonate (2 pts.) with K_4FeCy_6 (3 pts.) (Japp a. Schultz, *B.* 10, 1661; *C. J.* 37, 86). Colourless curved blades (from HOAc) or fern-shaped leaves (by sublimation), almost insol. water. Yields phenanthraquinone carboxylic acid on oxidation by CrO_3 and HOAc.—NaA′4aq. S. (of NaA′) 6·8 at 20°.—$BaA'_2$7aq. S. (of BaA'_2) ·066 at 20°, ·56 at 100°.

Phenanthrene (β)-**carboxylic acid** $\begin{matrix} C_6H_4.C.CO_2H \\ C_6H_4.CH \end{matrix}$. [c. 252°]. Formed in like manner from a calcium phenanthrene sulphonate contained in the mother-liquid from which its (α)- isomeride has crystallised (Japp). Stellate groups of straight needles (from HOAc), insol. water, sol. alcohol, ether, and HOAc. Yields phenanthraquinone on oxidation.—NaA′5aq: laminæ. S. (of NaA′) 6·2 at 20°; v. e. sol. boiling water.—$BaA'_2$6aq: rectangular laminæ. S. (of BaA'_2) ·27 at 20°; 3·7 at 100°.

PHENANTHRENE (α)-**SULPHONIC ACID** $\begin{matrix} SO_3H.C_6H_3.CH \\ C_6H_4.CH \end{matrix}$. Made, together with a (β)-acid which forms more soluble salts, by heating phenanthrene (1 pt.) with H_2SO_4 (1 pt.) at 100° (Graebe, *A.* 167, 152; Japp, *C. J.* 37, 83; *B.* 11, 213). Crystalline mass, m. sol. water. Yields phthalic acid on oxidation.—$CaA'_2$4aq: small plates, v. sol. hot water.—$PbA'_2$2aq: crystalline.

Phenanthrene sulphonic acid $C_{14}H_9.SO_3H$. Got by heating phenanthrene (3 pts.) with H_2SO_4 (2 pts.) at 170° (Morton a. Geyer, *A. C. J.* 2, 203; *B.* 13, 1870). Pearly needles, sol. water and alcohol. Its salts are less soluble than those of the (α)- acid.—KA′.—$BaA'_2$3aq.—$PbA'_2$3aq.

Phenanthrene disulphonic acid $C_{14}H_8(SO_3H)_2$. Formed by heating phenanthrene with fuming H_2SO_4 (E. Fischer, *B.* 13, 314; Hazura a. Julius, *M.* 5, 188). Syrup.—$K_2A''xaq$: powder, v. sol. water.—BaA″.—Ag_2A'': yellowish powder.

Bromo-phenanthrene sulphonic acid $C_{14}H_8Br(SO_3H)$. Made by sulphonating bromo-phenanthrene (Anschütz a. Siemensky, *B.* 13, 1179).—KA′: needles, sl. sol. water.—BaA'_2: insoluble pp.—AgA′: glistening needles.

PHENANTHRIDINE $C_{13}H_9N$ *i.e.* $\begin{matrix} C_6H_4.CH \\ C_6H_4.N \end{matrix}$. V.D. 6·5. [104°]. (360°). Made by passing the vapour of benzylidene-aniline through a red-hot tube (Pictet a. Ankersmit, *B.* 22, 3339). White needles, v. e. sol. alcohol, sl. sol. hot water. Its aqueous solution shows blue fluorescence. $NaNO_2$ gives a bulky pp. of the nitrite. Tin and HCl give a hydride crystallising in needles [100°].—B′HCl: needles, v. sol. water.—$B'_2H_2PtCl_6$: needles.—B′HAuCl₄.—$B'HHgCl_3$. [190°].—$B'C_6H_3N_3O_7$: needles.—$B'H_2Cr_2O_7$.

Methylo-iodide B′MeI. [201°].

Oxy-phenanthridine $\begin{matrix} C_6H_4.CO \\ C_6H_4.NH \end{matrix}$. Got by reducing *o*-nitro-*o*-phenyl-benzoic acid with zinc-dust and ammonia. It yields phenanthridine on distillation with zinc-dust.

PHENANTHROL $C_{14}H_9.OH$. [112°]. Formed by potash-fusion from phenanthrene sulphonic acid (Rehs, *B.* 10, 1253). Thin laminæ (from benzene-ligroïn), with bluish fluorescence. V. sol. alcohol and ether, sl. sol. water, v. sol. alkalis.

Acetyl derivative $C_{14}H_9.OAc$. [118°].

PHENANTHROLINE $C_{12}H_8N_2$ *i.e.* $\begin{matrix} CH:CH.C.CH:CH.C.\ N:CH \\ CH:\ N\ .C \text{ ——— } C.CH:CH \end{matrix}$. [78°]. (above 360°). Prepared by heating *m*-phenylene-diamine or (*B.* 3)-amido-quinoline with nitro-benzene, glycerin, and H_2SO_4 (Skraup, *B.* 15, 895; *M.* 3, 578; 5, 532; La Coste, *B.* 16, 674). Got also by heating its carboxylic acid [209°] (Gerdeissen, *B.* 22, 252). Colourless anhydrous four-sided tables [78°] or needles (containing aq) [66°]. M. sol. hot water, v. sol. alcohol, v. sl. sol. ether. Bromine gives in a solution of its hydrochloride a crystalline pp. $C_{12}H_8N_2Br_2$ [149°], converted by hot alcohol into $C_{24}H_{17}N_2Br_3$ [178°]. $KMnO_4$ oxidises it to dipyridyl dicarboxylic acid.

Salts.—$B''H_2Cl_2$2aq: colourless prisms. Its aqueous solution yields on evaporation long prisms of B′HCl aq.—B′HBr ½aq. [280°].—$B'_2H_2Cr_2O_7$: golden needles.—$B'C_6H_3N_3O_7$. [238°].—$B''H_2PtCl_6$aq.—$B'HNO_3$: prisms, m. sol. hot water.

Methylo-iodide B′MeI2aq. Golden prisms, sol. water, sl. sol. alcohol, insol. ether.

Oxy-phenanthroline $C_{12}H_8N_2O$. [160°]. Formed in small quantity, together with phenanthroline, by heating *m*-nitro-aniline with glycerin, nitro-benzene, and H_2SO_4 (La Coste). Needles (from benzene).—$B'_2H_2PtCl_6$aq.

Methyl-phenanthroline *v.* p. 355.

Di-methyl-phenanthroline
CH :CH.C.CH:CH.C. N :CMe
CMe: N .C————C.CH:CH · [98°]. Formed by the action of paraldehyde and HClAq at 100° on *m*-phenylene-diamine or (*B.* 3)-amido-(*Py.* 3)-methyl-quinoline (Von Miller a. Niederländer, *B.* 24, 1740; Schiff, *B.* 24, 2127). Colourless needles (from water). Melts at 78° when containing water of crystallisation. V. sol. alcohol, volatile with steam. Yields on reduction a base whence BzCl forms $C_{14}H_{19}BzN_2$ [164°]. —$B'_2H_2PtCl_6$.

Di-hexyl-di-amyl-phenanthroline
C_5H_{11}.C:CH.C.CH:CH.C. N :C.C_6H_{13}
C_6H_{13}.C: N .C————C.CH:C.C_5H_{11} · [51°].
Formed by the action of œnanthol on an alcoholic solution of *m*-phenylene-diamine or of amido-hexyl-amyl-quinoline at 100° (Von Miller a. Gerdeissen, *B.* 24, 1731; *cf.* Schiff, *A.* 253, 322). Needles. Its alcohol solution does not fluoresce.—B′HCl.—$B'H_2PtCl_6$2aq. [201°–210°]. Orange powder.—$B'C_6H_3N_3O_7$. [104°]. Needles.

Pseudo-phenanthroline $C_{12}H_8N_2$ *i.e.*
CH: N .C.CH:CH.C. N :CH
CH:CH.C————C.CH:CH · [173°]. Made from *p*-phenylene-diamine, glycerin, H_2SO_4, and nitrobenzene (Skraup a. Vortmann, *M.* 4, 569), and from $Ph.N_2.C_6H_4NH_2$, glycerin, and H_2SO_4 (Lellmann a. Lippert, *B.* 24, 2623). Obtained also as a by-product in the preparation of (*B.* 3)-nitroquinoline from *p*-nitro-aniline (Bornemann, *B.* 19, 2377). Crystallises from water in needles (containing 4aq), v. sol. alcohol, sl. sol. ether. Oxidised by $KMnO_4$ to dipyridyl dicarboxylic acid.

S a l t s. — B″HCl 2aq : plates. — $B''H_2Cl_2$: monoclinic prisms.—$B''H_2PtCl_6$ 2½aq.—$B''H_2Br_2$. — $B''H_2Br_4$. — $B''Br_4$. — $B''I_2$. — $B''HI_3$. — $B''H_2Cr_2O_7$ 2½aq : orange needles, sl. sol. cold Aq.

Methylo-iodides B″MeI aq : lemon-yellow needles.—$B''Me_2I_2$ aq : red tables.

PHENANTHROLINE - (*B.*) - CARBOXYLIC ACID $C_{12}H_7(CO_2H)N_2$. [277°]. Formed by oxidation of (*B.*)-methyl-phenanthroline with chromic acid (Skraup a. Fischer, *M.* 5, 527). Minute needles, sl. sol. water and alcohol, sol. alkalis and acids.—$Ca_2HA'_5$ 10aq : needles. Yields phenanthroline on distillation with alkalis.

Phenanthroline-(*Py.* 3)-carboxylic acid $C_{12}H_7(CO_2H)N_2$[N:CO_2H = 1:2]. [209°]. Formed by oxidation of (α)-methyl-phenanthroline with $KMnO_4$ and H_2SO_4 (Gerdeissen, *B.* 22, 250). Pale-yellow needles (containing aq), v. sl. sol. cold water.

Phenanthrone *v.* PHENANTHRAQUINONE.

PHENANTHROXYLENE - ACETOACETIC ACID. *Ethyl ether* $C_{20}H_{16}O_4$ *i.e.*
C_6H_4.C:CAc.CO_2Et.
C_6H_4.CO · Mol. w. (by Raoult's method) 287 (calc. 320). [185°]. Formed by heating phenanthraquinone with acetoacetic ether and NH_3Aq or KOHAq (Japp a. Streatfeild, *C. J.* 43, 27; Japp a. Klingemann, *C. J.* 59, 2). White silky needles, v. sol. hot benzene and alcohol.

Reactions. — 1. *Alcoholic potash* forms $C_{17}H_{12}O_2$ crystallising from alcohol, after solution at 100° in sealed tubes, in needles [259°].—2. *Alcoholic ammonia* at 100° yields lustrous yellow laminæ [168°] of $C_{40}H_{38\text{ or }40}N_4O_5$.—3. *Alcoholic* HCl yields $C_{20}H_{15}ClO_3$ [146°], whence alcoholic NH_3 produces $C_{40}H_{31}NO_6$. — 4. Heating with HOAc forms three compounds, $C_{20}H_{14}O_3$, decomposing at 285° without melting, $C_{20}H_{15}AcO_4$ [165°–171°], and $C_{41}H_{34}O_9$ [227°].—5. *Propionic acid* at 140° yields silky needles $C_{20}H_{14}O_3$ and crystalline $C_{23}H_{20}O_5$, which body is also got by heating with propionic anhydride at 150°.—6. HI and P yield $C_{20}H_{16}O_3$ [123°], whence potash forms an acid $C_{18}H_{14}O_4$ [295°], which gives BaA″2aq and Ag_2A''.—7. Heated on the water-bath with alcohol containing a few drops of H_2SO_4, it forms $C_{17}H_{10}O(OEt)(CO_2Et)$ [144°], which yields, with phenyl - hydrazine, $C_{17}H_{10}(N_2HPh)(OEt)(CO_2Et)$ [220°] and, on hydrolysis, $C_{16}H_{11}(OEt)(CO_2H)_2$ [203°], crystallising in colourless needles.—8. Alcohol containing a large quantity of H_2SO_4 forms $C_{22}H_{20}O_4$ [144°], sol. boiling alcohol, and $C_{17}H_{12}O_2$ [277°], insol. alcohol.

Isophenanthroxylene-acetoacetic acid $C_{18}H_{12}O_4$. [269°]. Formed by saponifying its ether with NaOH (Japp a. Klingemann, *C. J.* 59, 14). Flat needles (from alcohol). Conc. KOHAq at 150° yields $C_{17}H_{10}O$. Ac_2O at 150° forms $C_{17}H_{10}O$, insol. alcohol, and $C_{19}H_{14\text{ or }16}O_4$ [226°].—$CuA'_2$9aq.

Ethyl ether EtA′. [177°]. Formed from phenanthroxylene-acetoacetic ether by heating with formic acid (S.G. 1·22) at 130° for an hour, or by boiling with H_2SO_4 diluted with twice its weight of water (Japp a. Klingemann, *C. J.* 59, 3). Colourless triclinic prisms (from EtOAc); $a:b:c$ = ·964:1: ·507 ; α = 78° 6′ ; β = 72° 0′ ; γ = 83° 18′; sol. alcohol, benzene, and light petroleum.

Reactions.—1. Ac_2O at 150° forms the acetyl derivative $C_{20}H_{15}AcO_4$ [165°–170°], crystallising from benzene in needles.—2. *Phenyl-hydrazine* in alcoholic solution at 135° yields the compound $C_{20}H_{16}(N_2HPh)O_3$ crystallising in yellow needles [212°].—3. *Zinc* and HCl yield a crystalline compound [165°–170°], and also $C_{20}H_{16}O_3$ [123°], a body which yields a phenyl-hydrazide $C_{20}H_{16}(N_2HPh)O_2$.—4. *Bromine* in $CHCl_3$ yields $C_{20}H_{15}BrO_4$ [212°] crystallising in yellow prisms and tables.—5. HIAq at 100° forms $C_{17}H_{12}O$ [215°] crystallising in slender flat needles.

PHENAZINE $C_{12}H_8N_2$ *i.e.* $C_6H_4\!<\!{N \atop N}\!>\!C_6H_4$. *Azophenylene.* [171°]. (above 360°). S. (alcohol) 2 in the cold.

Formation.—1. By distilling *m*- or *p*- azobenzoic acid with excess of lime (Claus, *B.* 5, 367, 610; 6, 723; 8, 39, 600; 10, 1303; *A.* 168, 1).—2. By passing aniline over red-hot PbO (Schichutzky, *J. R.* 6, 248), or merely through a red-hot tube (Bernthsen, *B.* 19, 3256).—3. By heating equal weights of pyrocatechin and o-phenylene-diamine at 205°, followed by atmospheric oxidation of the resulting dihydride (Ris, *B.* 19, 2206).—4. By heating o-amidophenol and oxidising in the same way (Ris).—5. From di-amido-phenazine by the diazo- reaction (O. Fischer a. Hepp, *B.* 22, 358; Nietzki, *B.* 23, 1855).

Properties.—Long yellowish needles (by sub-

limation), v. sol. hot alcohol and ether, v. sl. sol. hot water. H_2SO_4 forms a blood-red solution, becoming yellow on dilution. Volatile with steam. Combines with bromine, forming $C_{12}H_8N_2Br_2$, which separates from benzene in yellow needles; and with chlorine, forming $C_{12}H_8N_2Cl_2$ as unstable red crystals (from alcohol).

Salts.—B'HCl. Tables (from HClAq), decomposed by hot water.—$B'HAuCl_4$: crystals.—$B'_2H_2HgCl_4$.—$B'_2H_2PtCl_6$ 2aq: yellow plates.—B'HI. Dark-green needles.—B'HBr. Brown crystals.—$B'C_6H_3N_3O_7$. [180°–190°]. Long yellow needles, sol. cold alcohol.—$B'Hg(NO_3)_2$: ruby-red crystals (from HNO_3).—$B'2AgNO_3$.

Dihydride $C_{12}H_{10}N_2$ *i.e.* $C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{NH}{>}C_6H_4$. Formed by reduction of phenazine with alcoholic NH_3 and H_2S (Claus, *A.* 168, 8). Trimetric laminæ; almost insol. water and benzene; v. sl. sol. cold alcohol. Conc. H_2SO_4 forms a green solution, turning red on further addition of H_2SO_4, and green on cautious addition of water; in this reaction an unstable base $C_{24}H_{18}N_4$ appears to be formed, giving the salts $B''H_2Cl_2$ and $B''H_2PtCl_6$, the latter forming in green needles.

Di-chloro-phenazine $C_{12}H_6Cl_2N_2$. [144°]. Made from phenazine and PCl_5.

Nitro-phenazine $C_{12}H_7(NO_2)N_2$. [210°]. Made by nitration. Yellowish green needles.

Amido-phenazine $C_6H_4{<}\genfrac{}{}{0pt}{}{N}{N}{>}C_6H_3(NH_2)\left[\genfrac{}{}{0pt}{}{1}{2}\ 3\right]$. [265°]. Got by sublimation from a mixture of di-amido-phenazine and zinc-dust (O. Fischer a. Hepp, *B.* 22, 357). Long red needles with bronze lustre (from alcohol). Strong base. Its dilute solution shows orange-red fluorescence.—$B'_2H_2PtCl_6$ $2\frac{1}{2}$aq.

u-**Di-amido-phenazine** $C_{12}H_{10}N_4$ *i.e.* $C_6H_4{<}\genfrac{}{}{0pt}{}{N.C.CH:C.NH_2}{N.C.CH:C.NH_2}$. A product of oxidation of o-phenylene-diamine by $FeCl_3$ (Fischer a. Hepp, *B.* 22, 355; 23, 841, 2788; *cf.* Griess, *B.* 5, 202; Rudolph, *B.* 12, 2211; Wiesinger, *A.* 224, 353). Formed also from *o*-phenylene-diamine and CyI (*cf.* Hübner, *B.* 9, 777; 10, 1715), and by boiling o-phenylene-diamine hydrochloride (2·5 g.) with amido-azo-benzene (3 g.) and acetic acid (30 g. of 75 p.c.) for two hours. Long brownish-yellow needles or yellow plates (by sublimation). Conc. H_2SO_4 forms a grass-green solution, turned red on dilution. Its solution in benzene or alcohol fluoresces greenish-yellow. Alcoholic solutions of the salts fluoresce dark orange-red. Yields with benzil the quinoxaline $C_{26}H_{16}N_4$.—B'HCl 3aq.—$B'_2H_2SO_4$ 3aq.

Di-acetyl derivative $C_{12}H_8Ac_2N_4$. [c. 270°]. Yellow needles.

Di-formyl derivative. Reddish-yellow mass.

i-**Di-amido-phenazine** $\left[1\ \genfrac{}{}{0pt}{}{3}{4}\right]$ $C_6H_3(NH_2){<}\genfrac{}{}{0pt}{}{N}{N}{>}C_6H_3NH_2$ $\left[\genfrac{}{}{0pt}{}{3}{4}\ 1\right]$. [280°]. Got by heating the tin double salt of tri-amido-diphenylamine with water, $CaCO_3$, and MnO_2 (Nietzki, *B.* 23, 1854). Long dark-yellow needles, v. e. sol. alcohol, ether, and hot water. Yields phenazine on elimination of amidogen.—$B''HNO_3$: greenish needles.—$B''C_6H_3N_3O_7$.

Di-acetyl derivative $C_{16}H_{14}N_4O_2$. [c. 330°].

Tri-amido-phenazine $C_{12}H_{11}N_5$ *i.e.* $\left[4\ \genfrac{}{}{0pt}{}{1}{2}\right]$ $C_6H_3(NH_2){<}\genfrac{}{}{0pt}{}{N}{N}{>}C_6H_2(NH_2)_2\left[\genfrac{}{}{0pt}{}{1\ \ 3}{2\ \ 4\text{ or }6}\right]$. Made by passing a current of oxygen through a solution of *i*-triamidobenzene hydrochloride (10 g.) and NaOAc (18 g.) (E. Müller, *B.* 22, 856; *cf.* Witt, *B.* 10, 658). Brown needles, m. sol. hot alcohol and water, the solutions showing yellow fluorescence. Conc. H_2SO_4 gives a yellow solution, changing violet, red, and finally yellow on dilution. It decomposes when heated to 100°.—$B''(HNO_3)_2$ 2aq: needles with green lustre. Forms a crimson solution with yellow fluorescence. The solution becomes yellow on dilution.

Tri-acetyl derivative $C_{12}H_8Ac_3N_5$.

Tetra-amido-phenazine $\genfrac{}{}{0pt}{}{NH_2.C:CH.C.N.C.CH:C.NH_2}{NH_2.C:CH.C.N.C.CH:C.NH_2}$. Formed by passing air through a hot solution of tetra-amido-benzene hydrochloride (10 g.) and NaOAc (20 g.) (Nietzki a. E. Müller, *B.* 22, 447). Brown needles (from hot water or alcohol), or yellow needles containing aniline of crystallisation (from aniline). Its solutions exhibit yellowish green fluorescence. Conc. H_2SO_4 forms a yellow solution, passing, on dilution, through blue, violet, and red, to yellow.—$B''(HNO_3)_2$ 2aq: lustrous green needles giving a crimson solution.

References.—METHYL-PHENAZINE and DI-OXY-PHENAZINE.

Tolylene red $C_6H_3(NMe_2){<}\genfrac{}{}{0pt}{}{N}{N}{>}C_6H_2Me(NH_2)$ is also a phenazine derivative (Bernthsen, *A.* 236, 332).

PHENTRIAZINE $C_6H_4{<}\genfrac{}{}{0pt}{}{N.CH}{N.N}$. [66°]. (235°–240°). Formed from the formyl derivative of o-nitro-phenyl-hydrazine, alcohol, HOAc, and sodium-amalgam (Bischler, *B.* 22, 2806), and by the action of P_2O_5 on o-amido-phenyl-methyl-hydrazine (Hempel, *J. pr.* [2] 41, 174). Yellow needles, v. sol. warm water and cold alcohol, very volatile with steam.

TRIPHENAZINE DIHYDRIDE $C_{18}H_{12}N_4$ *i.e.* $C_6H_4{<}\genfrac{}{}{0pt}{}{N}{N}{>}C_6H_2{<}\genfrac{}{}{0pt}{}{NH}{NH}{>}C_6H_4$ or $C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{N}{\geqslant}C_6H_2{\leqslant}\genfrac{}{}{0pt}{}{N}{NH}{>}C_6H_4$. *Homofluorindine.* Formed by heating *u*-di-amido-phenazine hydrochloride (4 pts.) with o-phenylene-diamine at 205° for 15 minutes (Fischer a. Hepp, *B.* 23, 2791). Bluish-violet powder or lustrous-green needles, v. sl. sol. alcohol, forming a violet-red solution with yellowish-red fluorescence. Solutions of its salts are blue, with brownish-red fluorescence.

PHENAZOXINE $C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{O}{>}C_6H_4$. *Oxy- or oxido-diphenyl-amine.* [148°]. Obtained by heating together equal quantities of o-amido-phenol and pyrocatechin at 260°–280°. Silvery scales. V. sol. alcohol, ether, chloroform, and benzene. Sublimable. Distils, in great part undecomposed. By nitration and reduction the leuco-base of a violet dye-stuff is obtained (Bernthsen, *B.* 20, 942).

PHENBUTYL- COMPOUNDS *v.* BUTYL-PHENYL- COMPOUNDS.

PHENISOBUTYL CYANIDE *v.* ISO-BUTYL BENZONITRILE.

PHENISOBUTYL - PHENETHYL - THIO - UREA *v.* Ethyl-phenyl-isobutyl-phenyl-thio-urea.

PHENCAPRYLAMINE *v.* Amido-phenyl-octane.

PHENENYL TRIBENZOIC ACID $C_{27}H_{18}O_6$. [261°]. Got by potash-fusion from tri-benzoyl-ene-benzene (Gabriel a. Michael, *B.* 11, 1008). Prisms, v. sol. alcohol, ether, and HOAc. Yields $C_6H_3Ph_3$ when distilled with lime.—Na_3A'''.—Ag_3A'''.

PHENENYL TRI-METHYL TRIKETONE $C_6H_3(CO.CH_3)_3$. [163°]. Formed by the spontaneous condensation of acetoacetic aldehyde (Claisen a. Stylos, *B.* 21, 1144). Small needles, v. sol. HOAc, sl. sol. alcohol, ether, and water. Oxidised by nitric acid to trimesic acid.

PHENETHYLAMINE *v.* Amido-phenyl-ethane.

PHENETHYL - PHENISOBUTYL - THIO - UREA *v.* *p*-Ethyl-phenyl-*p*-isobutyl-phenyl-thio-urea.

PHENETIDINE *v.* *Ethyl derivative* of Amido-phenol.

PHENETOL *v.* *Ethyl ether* of Phenol.

DIPHENIC ACID *v.* Diphenyl dicarboxylic acid.

PHENNAPHTHAZINE $C_{16}H_{10}N_2$ *i.e.* $C_{10}H_6{<}{\overset{N}{\underset{N}{}}}{>}C_6H_4$. ($\alpha\beta$)-*Naphthophenazine.* [142°].

Formation.—1. By mixing equal mols. of *o*-phenylene-diamine and (β)-naphthoquinone in 50 p.c. acetic acid.—2. By oxidation of equal mols. of *o*-phenylene-diamine and (β)-naphthol with alkaline potassium ferricyanide.—3. By the decomposition of sulpho-benzene-azo-(β)-naphthyl-phenyl-amine by treatment with boiling dilute mineral acids: $C_6H_4(SO_3H).N_2.C_{10}H_6.NHC_6H_5 = C_{10}H_6{:}N_2{:}C_6H_4 + C_6H_4(NH_2)SO_3H$.

Preparation.—Fifty grms. of the dyestuff are dissolved in 500 c.c. of boiling water, and 125 c.c. of conc. H_2SO_4 is slowly added to the hot solution; the colour-acid, which is first precipitated, re-dissolves, and on cooling the sulphate of the azine crystallises out in red needles, whilst sulphanilic acid remains in solution.

Properties.—Glistening yellow needles or prisms. Sublimes at about 200° in long flat needles. Distils undecomposed above 360°. Sl. sol. alcohol, ether, and cold benzene; v. sol. hot benzene. Dissolves in conc. H_2SO_4 with a brownish-red colour, becoming yellow on dilution.

S a l t s.—With each acid it forms two different salts.—$B'HCl^{\times}$: long reddish-yellow needles and warty crystals.—$B'_2H_2SO_4^{\times}$: red needles and thick garnet-red prisms.—$B'HNO_3^{\times}$: yellow and red needles, both sparingly soluble (Witt, *B.* 20, 572).

PHENOCYANIN C_6H_5NO or $C_6H_7NO_2$. Dark-blue mass with coppery lustre, got by atmospheric oxidation of a mixture of phenol and NH_3 (Phipson, *B.* 6, 823). Insol. water, sol. alcohol. Coloured red by acids.

PHENOL C_6H_6O *i.e.* C_6H_5OH. *Carbolic acid. Phenyl hydrate.* Mol. w. 94. [41°]. (181·5°) (Dale a. Schorlemmer); (182·9°) (Pinette, *A.* 243, 32). S. 6·6 at 17°. S.G. $\frac{20}{4}$ 1·0702 (Brühl); $\frac{0}{0}$ 1·0906 (P.). S.V. 101·8. C.E. (0°–10°) ·00083 (P.). μ_β 1·5636 (B.). R_∞ 45·71. H.C.v. 736,500 (Berthelot, *A. Ch.* [6] 10, 452; 13, 329). H.C.p. 737,100. H.F. 47,341 (Stohmann, *J. pr.* [2] 33, 471; 28,000 (Von Rechenberg). Occurs in castoreum (Wöhler, *A.* 67, 360), and in small quantities in urine of cows, horses, and men (Städeler, *A.* 77, 18; Lieben, *A. Suppl.* 7, 240; Hoppe-Seyler, *C. J.* 25, 628; Munk, *B.* 9, 1596; Salkowski, *B.* 9, 1595; Baumann, *B.* 9, 54, 1389, 1715). Contained in considerable quantity in coal-tar (Runge, *P.* 31, 69; 32, 308; Laurent, *A. Ch.* [3] 3, 195), and in the products of the dry distillation of gum benzoïn, quinic acid, wood, and bones.

Formation.—1. By distilling *o*-, *m*- or *p*-, oxy-benzoic acid alone or with lime (Gerhart, *Rev. scient.* 10, 210; Rosenthal, *Z.* [2] 5, 627).—2. A product of the distillation of glycerin with $CaCl_2$ (Linnemann a. Zotte, *A.* 174, 87; *Suppl.* 8, 254).—3. By heating anisole with conc. HIAq or HClAq at 140° (Graebe, *A.* 139, 149).—4. From aniline by the diazo- reaction (Griess, *A.* 137, 39).—5. From benzene sulphonic acid by potash-fusion (Wurtz, *Bl.* [2] 8, 197; *cf.* Degener, *J. pr.* [2] 17, 394).—6. From phenol *p*-sulphonic acid by distillation with dilute H_2SO_4 and superheated steam at temperatures above 116° (Armstrong a. Miller, *C. J.* 45, 148).—7. By heating acetylene with fuming H_2SO_4 and fusing the product with potash (Berthelot, *C. R.* 68, 539).—8. By shaking benzene with palladium that has absorbed hydrogen and air (Hoppe-Seyler, *B.* 12, 1552).—9. By the direct action of hydrogen-peroxide on benzene (Leeds, *B.* 14, 975).—10. In small quantity by the action of dry oxygen on boiling benzene containing $AlCl_3$ (Friedel a. Crafts, *A. Ch.* [6] 14, 435; *C. R.* 86, 884).—11. A product of fermentation of proteïds (Baumann, *B.* 10, 685; Weyl, *H.* 1, 339; Brieger, *J. pr.* [2] 17, 134).

Preparation.—The aqueous solution got by stirring coal-tar oil with NaOHAq is diluted with water as long as naphthalene separates. The liquid is then exposed to the air, with frequent stirring, for several days, and then fractionally ppd. by acid (*e.g.* CO_2), the last fraction being nearly pure phenol. The phenol is dried by heating to boiling in a current of air, and further purified by crystallisation (Hugo Müller, *Z.* [2] 1, 270; *cf.* Williamson a. Scrugham, *C. J.* 7, 232). Phenol may also be dried by distilling over dried $CuSO_4$ (Bickerdike, *C. N.* 16, 188; *cf.* Gladstone, *C. N.* 2, 98).

Properties. — Long deliquescent needles, with strong smell, m. sol. water, miscible with alcohol and ether. Attacks the skin. Does not redden litmus. Nearly insol. Na_2CO_3Aq, m. sol. NH_3Aq, v. sol. KOHAq and NaOHAq. Antiseptic. Not affected by distillation with P_2O_5, lime, or BaO. A solution of phenol even in 43,000 pts. of water gives a pp. of tri-bromo-phenol on addition of bromine-water (Landolt, *B.* 4, 770). $FeCl_3$ gives a violet colour to an aqueous solution; the reaction is prevented by acetic acid and by alcohol (Hesse, *A.* 182, 161). Conc. H_2SO_4 poured beneath a solution containing phenol and nitric acid (·1 p.c.) gives an intense red ring; with nitrous acid, red and green rings are got; with chlorates, a pale-yellow ring with blue below (Lindo, *C. N.* 58, 1, 15). An aqueous solution of phenol (4 vols.) mixed with ammonia (1 vol.) gives on warming with a few drops of bleaching-powder solution a blue colour

which becomes red on addition of acids (Salkowski, *Fr.* 11, 316). Boiling aqueous mercurous nitrate gives a deep-red colour (Plugge, *Fr.* 11, 173). Millon's reagent gives on boiling a yellow pp. which dissolves in nitric acid forming a deep red liquid; salicylic acid behaves in like manner (Almén, *J.* 1878, 1079). On adding *p*-oxy-benzoic aldehyde and an equal volume of H_2SO_4 a yellow liquid is got, turned crimson by potash (aurin). Phenol is poisonous (Wöhler, *A.* 65, 344; Duplay a. Carin, *C. R.* 112, 627).

Reactions. — 1. Decomposed by passing through a *red-hot tube* yielding benzene, toluene, xylene, naphthalene, anthracene, and phenanthrene (Kramers, *A.* 189, 129). When crude phenol is used the product deposits a crystalline hydrocarbon $C_{10}H_{12}$ [32·9°], S.G. $\underline{17\cdot5}$ 1·012 (63° at 9 mm.). This hydrocarbon is volatile in the cold, smells like camphor, and is sol. alcohol, ether, and petroleum-spirit. It is resinified by atmospheric oxygen. It absorbs bromine, yielding a liquid bromide. By heating for 4 hours at 100° *in vacuo* the hydrocarbon is polymerised, yielding a solid [200°–220°] (Roscoe, *C. J.* 47, 669).—2. *Chlorine* forms *o*- and *p*-chloro-phenol (4,2,1)-di-chloro-phenol, (6,4,2,1)-tri-chloro-phenol, and tetra-, pent-, and hexa-chloro-phenols. Exhaustive chlorination gives C_6Cl_6, CCl_4, C_2Cl_6, and CO_2 (Ruoff, *B.* 9, 1483). An intermediate body is $C_{12}Cl_8O_2$ [323°] (Hugounenq, *C. R.* 109, 309). $KClO_3$ and HCl yield tri-chloro-phenol and tri- and tetra- chloro-quinone.—3. Chlorine acting on phenol in alkaline solution forms the acid $\left.\begin{matrix}\ddot{C}(OH).CCl_2\\ \ddot{C}Cl{-}{-}CH_2\end{matrix}\right>C(OH).CO_2H$ (Hantzsch, *B.* 20, 2780; 22, 1238).—4. *Bromine-water* forms tri-bromo-phenol. Heat (68492 units) is given out in the reaction. Br in excess gives $C_6H_2Br_4O$ (Werner, *C. R.* 100, 799; *Bl.* [2] 46, 280).—5. *Iodine* and alkali at 60° form $C_6H_3I_3O$ [157°], which is violet-red, insol. water, and forms a red solution in alcohol and ether. It is converted into tri-iodo-phenol by boiling with KOHAq (Messinger a. Vortmann, *B.* 22, 2313). — 6. *Chloride of iodine* forms mono- and di-, iodo-phenol (Schützenberger, *C. R.* 54, 197).—7. Oxidised by *nitro-benzene* and dilute NaOH in the cold to oxalic acid and CO_2 (Siegfried, *J. pr.* [2] 31, 542).—8. If a rapidly *alternating electric current* be passed through a solution containing phenol, magnesic sulphate, and magnesic bicarbonate, the following bodies are formed, owing to the rapidly alternating oxidation and reduction: pyrocatechin, hydroquinone, di-oxy-diphenyl, formic acid, succinic acid, and oxalic acid (E. Drechsel, *J. pr.* [2] 29, 249). Another product is $C_6H_{10}O$, an oil (153°–178°) with aromatic smell which forms a phenyl hydrazide $C_{12}H_{13}N$ [108°]. By continuing the alternating current this oil is converted in *n*-hexoic acid.—9. *Electrolysis* with carbon electrodes in aqueous solution rendered slightly alkaline by KOH yields a di-oxy-benzoic acid $C_7H_6O_4$ [93°] and an amorphous acid $C_{65}H_{48}O_{22}$ insol. water and ether, sol. alcohol. The amorphous acid yields picric acid with HNO_3, and on protracted boiling with dilute HClAq it yields amorphous infusible $C_{44}H_{30}O_{15}$ and amorphous $C_{21}H_{20}O_8$ [60°], sol. water, alcohol, and ether. In like manner NaOPh yields on electrolysis $C_{20}H_{20}O_5$ separable by hot HClAq into infusible $C_{17}H_{10}O_5$, insol. water and ether, and $C_{12}H_{10}O_3$ [73°], sol. water (Bartoli a. Papasogli, *G.* 14, 90).—10. Taken internally it is partly oxidised to hydroquinone and pyrocatechin (Nencki a. Giacoso, *H.* 4, 325).—11. H_2O_2 oxidises it to pyrocatechin, hydroquinone, and quinone (Martinon, *Bl.* [2] 43, 156). When treated in aqueous solution with NH_3, H_2O_2, Na_2CO_3, and hydroxylamine hydrochloride it yields phenolquinonimide, which colours the liquid bright blue (Wurster, *B.* 20, 2934).—12. CrO_2Cl_2, followed by water, gives $O(C_6H_4.OH)_2$ (Etard). CrO_2Cl_2 and HOAc give tri- and tetra- chloro-quinone (Carstenjen, *J. pr.* [2] 2, 82).—13. Fusion with NaOH yields resorcin, pyrocatechin, and phloroglucin. *Potash-fusion* gives *o*- and *m*- oxybenzoic acids and two di-oxy-diphenyls (Borth a. Schreder, *B.* 11, 1332; 12, 417).—14. PCl_3 forms $PCl_2(OPh)$, $PCl(OPh)_2$, and $P(OPh)_3$, which may be separated by fractional distillation *in vacuo* (Noack, *A.* 218, 85; Anschütz a. Emery, *A.* 239, 310; *A.* 253, 110). The compound $PCl_2(OPh)$, (90° at 11 mm.), (216° at 760), S.G. $\frac{20}{4}$ 1·354, is converted by chlorine into $PCl_4(OPh)$, whence SO_2 produces $POCl_2(OPh)$ (122° at 11 mm.). Bromine converts $PCl_2(OPh)$ into $PCl_2Br_2(OPh)$, which is crystalline but very unstable. Sulphur at 190° converts $PCl_2(OPh)$ into $PSCl_2(OPh)$, a colourless liquid (120° at 11 mm.), S.G. $\frac{20}{4}$ 1·4059. The compound $PCl(OPh)_2$ (172° at 11 mm.) (295° at 760 mm.) is converted by chlorine into $PCl_3(OPh)_2$, which is crystalline, and insol. ether. Bromine converts $PCl(OPh)_2$ in ether into orange-yellow crystals of $PClBr_2(OPh)_2$. Sulphur and $PCl(OPh)_2$ at 190° yield $PSCl(OPh)_2$, crystallising in colourless needles [64°], (194° at 11 mm.). Tri-phenyl phosphite $P(OPh)_3$ combines with chlorine, forming $PCl_2(OPh)_3$, whence water produces tri-phenyl-phosphate $PO(OPh)_3$ [45°] (245° at 11 mm.). $P(OPh)_3$ with sulphur at 190° yields $PS(OPh)_3$ [50°] (245° at 11 mm.). S.G. $\frac{20}{4}$ 1·2341.—15. PCl_5 forms hardly any chloro-benzene (Otto, *A.* 145, 317; *cf.* Glutz, *A.* 143, 181).—16. P_2S_5 forms, on heating, phenyl mercaptan, di-phenylenedisulphide $C_{12}H_8S_2$, and some Ph_2S (Kekulé, *C. R.* 64, 752; Graebe, *B.* 7, 51, 397; Geuther, *A.* 221, 57). P_2S_3 forms benzene, Ph_3PO_4, and H_2S.—17. Aqueous $KMnO_4$ oxidises it to oxalic acid and CO_2 (Tollens, *Z.* [2] 4, 715). — 18. Distillation over heated zinc-dust yields benzene.—19. H_2SO_4 (1 pt.) forms *o*- and *p*- sulphonic acids (Kekulé, *Z.* [2] 3, 197). H_2SO_4 ($1\frac{1}{2}$ pts.) at 160° forms di-oxy-di-phenyl sulphone (Glutz, *A.* 147, 52). $K_2S_2O_7$, heated with a solution of KOC_6H_5 at 65°–70°, forms $C_6H_5O.SO_2.OK$, which crystallises in tables, S. 14 at 15°, sol. hot alcohol. This salt occurs in urine. It is decomposed by boiling with water and dilute acids into phenol and H_2SO_4. At 150° the dry salt changes to the isomeric potassium phenol *p*-sulphonate. Phenyl sulphuric acid is also a product of the passage of a rapidly-alternating electric current through a solution of phenol, $MgSO_4$, and magnesium bicarbonate. The free acid is very unstable (Baumann, *B.* 11, 1907; Brieger, *H.* 8, 311; Drechsel, *J. pr.* [2] 29, 240).—20. SO_2Cl_2 at 150° forms chloro-phenol (Dubois, *Z.* [2] 2, 705). $S_2O_5Cl_2$ forms *o*- and *p*- chloro-phenols and their sulphonic acids (Armstrong a. Pike, *C. N.* 29, 283).—21. *Nitric acid* forms *o*- and *p*- nitro-, di-nitro, and tri-nitro- phenols.—

22. *Potassium* and *sodium* dissolve, giving off hydrogen and forming phenylates. These absorb CO_2, forming $PhO.CO_2K$ and $PhO.CO_2Na$, which yield oxy-benzoates when strongly heated (*v.* *o*-OXY-BENZOIC ACID) (Kolbe, *J. pr.* [2] 10, 89).—23. CrO_3 forms phenoquinone $C_{18}H_{14}O_4$ (Wichelhaus, *B.* 5, 248, 846).—24. *Nitrous acid* forms nitroso-phenol, the mono-oxim of quinone (Baeyer, *B.* 7, 967). H_2SO_4, to which 6 p.c. of KNO_2 has been added, gives when shaken with a mixture of phenol (1 vol.) and H_2SO_4 (1 vol.) a brown colour, changing to green, and finally to a magnificent blue. On pouring into water brown flakes are deposited (Liebermann, *B.* 7, 248, 1098). In the action of H_2SO_4 and nitrous acid on phenol there is formed (α)-phenol-dichroïn $C_{18}H_{15}NO_3$ or $C_6H_4(OH)N(OPh)_2$?, a brown powder, sol. ether, and also phenoloxychroïn $C_{18}H_{15}NO_4$, which is black and insol. ether (Krämer, *B.* 17, 1877; Brunner a. Chuit, *B.* 21, 250). (α)-Phenol-dichroïn is also formed from quinone mono-oxim and H_2SO_4 (Baeyer a. Caro, *B.* 7, 966). Each body yields an amorphous acetyl derivative. Phenol-dichroïn forms a blue solution in alkalis and H_2SO_4. Phenol-oxychroïn forms a green solution in H_2SO_4, and a brown solution in alkalis.—25. NOCl gives chlorinated quinones (Tilden, *C. J.* 27, 851).—26. Distillation with PbO yields diphenylene oxide $C_{12}H_8O$ and $C_{13}H_8O_2$, crystallising in needles [174°] (Graebe, *B.* 7, 396; Behr a. Van Dorp, *B.* 7, 398).—27. $COCl_2$ at 150° forms $CO(OPh)_2$ and COCl(OPh) (Kempf, *J. pr.* [2] 1, 402).—28. *Ammoniacal zinc chloride* at 290° forms aniline, diphenylamine, and Ph_2O (Merz a. Weith, *B.* 13, 1299). 29. *Hydrazine* solution in excess forms a white unstable substance [57°], possibly $C_6H_6O(N_2H_4)$ (Curtius a. Thun, *J. pr.* [2] 44, 190).—30. $TiCl_4$ acting on a benzene solution of phenol forms dark-red crystals of $Ti(OPh)_4HCl$, decomposed by water into phenol, titanic acid, and HCl (Schumann, *B.* 21, 1079).—31. $AlCl_3$ gives the solid $Al_2Cl_3(OPh)_3$, v. sol. hot CS_2, insol. ligroïn, decomposed at once by water into phenol, alumina, and HCl (Claus a. Merklin, *B.* 18, 2933). On heating phenol (2 pts.) with $AlCl_3$ (1 pt.), benzene, Ph_2O, and diphenylene-methane oxide are formed (Merz a. Weith, *B.* 14, 191). Phenol (5 g.) added to $AlBr_3$ (10 g.) forms amorphous $Al_2Br_3(OPh)_3$, which is quickly decomposed by water (Gustavson, *J. R.* 16, 242).—32. $AlCl_3$ and CCl_3NO_2 followed by water give aurin.—33. Heating with oxalic acid and H_2SO_4 gives rosolic acid. 34. *Cyanic acid vapour* is absorbed by dry phenol forming phenyl allophanate, which crystallises from hot alcohol in unctuous crystals (Tuttle, *J.* 1857, 451).—35. *Benzyl chloride* and zinc form $PhCH_2.C_6H_4OH$ on heating (Paterno, *G.* 2, 1).—36. Phenol (10 g.) boiled with Ac_2O (20 g.) and $ZnCl_2$ (20 g.) forms phenacetein, a red dye $C_{16}H_{12}O_2$, which is insol. benzene, sol. alcohol, ether, and HOAc. Its solution in alkalis is raspberry-red (Rasiński, *J. pr.* [2] 26, 54).—37. $C_6H_5.CCl_3$ forms benzaurin.—38. *Phthalic anhydride* and H_2SO_4 form phenol-phthaleïn $C_{20}H_{14}O_4$ on heating (Baeyer, *B.* 4, 658).—39.—*Acetamide* and *benzamide* on heating form respectively PhOAc and PhOBz, while NH_3 is given off (Guareschi, *A.* 171, 140).—40. Heated in alcoholic solution with CCl_4 and KOH or NaOH it yields *o*- and *p*- oxy-benzoic acids.—41. *Paraldehyde* and stannic chloride form $CH_3.CH(C_6H_4OH)_2$.—42. *Benzoic aldehyde*, alcohol, and a few drops of HCl form white resinous $C_{26}H_{20}O_2$, whence amorphous $C_{26}H_{18}Ac_2O_2$ may be got (Michael a. Ryder, *Am.* 9, 130).—43. *Benzene sulphochloride* added to a slightly-alkaline solution of phenol forms $C_6H_5SO_2.OPh$ as very stable colourless crystals [36°], sol. alcohol, sl. sol. ether, saponified by alcoholic potash (Georgesen, *B.* 24, 417).—44. *Acetoacetic ether* and H_2SO_4 form (β)-methyl-coumarin.—45. *Chloro-acetal* and alcoholic NaOPh at 160° form $C_6H_5.O.CH_2.CH(OEt)_2$ (255°) (Autenrieth, *B.* 24, 162).—46. $CCl_3.COCl$ and $AlCl_3$ give diphenyl carbonate (Heutschel, *J. pr.* [2], 36, 315). 47. *o-Oxy-benzoic aldehyde*, HOAc, and H_2SO_4 form, on warming, oxyaurin $C_{19}H_{14}O_4$, which greatly resembles aurin (Liebermann, *B.* 9, 801; 11, 1436). Zulkowsky (*M.* 5, 111) obtained a dyestuff $C_{26}H_{20}O_4$ soluble in aqueous $NaHSO_3$, and another dyestuff insol. $NaHSO_3Aq$.—48. $CH_3.CCl_3$ and dilute caustic soda form $CH_3.C(OPh)_3$ [98·5°] crystallising in plates, v. sl. sol. water (Heiber, *B.* 24, 3678).

Estimation.—1. Titrated by adding bromine water till the solution is yellow, or by adding excess of bromine, KI, and starch, then titrating with $Na_2S_2O_3$. The bromine solution contains 40 grms. Br and 20 grms. KBr per litre (Degener, *J. pr.* [2] 17, 380; *cf.* Landolt, *B.* 4, 770; Koppeschaar, *Fr.* 15, 233; Weinreb a. Bondi, *M.* 6, 506; Giacosa, *H.* 6, 45).—2. 14 to 15 grms. of pure KOH are dissolved in 1 litre of water and 10 grms. of bromine gradually added; the solution is then diluted till 50 c.c. corresponds to 0·05 grm. of pure phenol. To ascertain the strength of any phenol solution 50 grms. of the above solution are taken and the phenol added till a drop of the solution ceases to give a blue colouration with KI and starch (Chandelon, *Bl.* [2] 38, 69).—3. 2 or 3 grms. phenol are dissolved in three times the molecular proportion of caustic soda. The solution is made up to 500 c.c., and 10 c.c. are put into a small flask warmed to 60°, and one-tenth normal iodine solution is allowed to flow in until it is coloured strongly yellow by excess of iodine; by shaking, a red pp. is formed. The excess of iodine is estimated by sodium thio-sulphate. The quantity of iodine taken up by the phenol multiplied by 0·123518 gives the amount of pure phenol (Messinger a. Vortmann, *B.* 23, 2753).—4. To separate phenol from mixtures in poisoning cases the substance is triturated with dilute H_2SO_4 and extracted with alcohol, the alcohol evaporated, and the residue extracted with benzene (Dragendorff a. Jacobson, *C. C.* 1886, 828); or the alcoholic extract may be mixed with NaOHAq, evaporated to a small bulk, filtered, and the phenol ppd. by HClAq in a graduated tube (Muter a. De Koningh, *An.* 12, 191; *cf.* Staveley, *Chem. Zeit.* 13, 1126).—5. Phenol may be titrated by adding standard NaOH to a solution containing *s*-tri-nitro-benzene as indicator until a red colour appears (Bader, *Fr.* 31, 58).

Salts.—Phenol behaves as a very weak acid. It dissolves in KOHAq, but does not expel CO_2 from sodium carbonate in the cold.—C_6H_5OK. White hygroscopic needles, v. sol. alcohol, ether, and water. Oxidises rapidly in air.—$C_6H_5ONa^{\times}$. Yields Ph_2O and $C_{13}H_{10}O$ when distilled with $NaPO_3$ (Niederhäusern, *B.* 15,

1123). Sulphur at 200° gives $S_2(C_6H_4OH)_2$.—$Ba(OC_6H_5)_2$3aq. Crystalline crusts, got by boiling phenol with baryta-water and evaporating *in vacuo*. — $Ca(OC_6H_5)_2{}^x$. Yields diphenylene oxide and a little benzene on distillation.—$Pb(OH)OC_6H_5$. Made by boiling phenol with litharge (Calvert, *C. J.* 18, 68). — $TlOC_6H_5$. Crystals, sl. sol. cold water (Kuhlmann, *J.* 1864, 254).—$Hg(OC_6H_5)_2Hg_2Cl_2$4aq. Pp. got by adding mercurous chloride to a solution of NaOPh (Pouchet, *C. R.* 106, 276).—$Al(OC_6H_5)_3$. Made by heating phenol with aluminium and AlI_3, and pouring off the liquid product (Gladstone a. Tribe, *C. J.* 39, 9; 41, 5; Hodgkinson, *C. N.* 1877, 237). Split up on distillation into Al_2O_3 and Ph_2O, other products being phenol and a ketone $C_{13}H_{10}O$ [97°] (c. 280°), V.D. 182·2.—Aniline salt $C_6H_5ONH_3Ph$. [37°]. (181°). Formed by boiling aniline with phenol (Dale a. Schorlemmer, *A.* 217, 388; Dyson, *C. J.* 43, 466; Mylins, *B.* 19, 1002). Tables (from alcohol).—*p*-Toluidine salt $C_6H_5ONH_3C_6H_4Me$. [31°]. Needles (from ligroïn) (Dyson).

Combinations.—1. With SO_2 phenol forms an unstable compound which may be distilled at 140° (best in a current of SO_2), and which crystallises in rectangular tablets. If exposed to air it absorbs water and gives off SO_2. The compound melts between 25° and 30° (A. Hölzer, *J. pr.* [2] 25, 463).—2. With CO_2. If salicylic acid be heated in a sealed tube for two hours at 260° it is resolved into phenol and CO_2, but on cooling crystals resembling common salt with sides like staircases are formed. These melt at 37°. They are decomposed by heat, and also by water, alcohol, ether, and chloroform, into phenol and CO_2 (A. Klepl, *J. pr.* [2] 25, 464). The same compound is got from phenol and liquid CO_2 (Barth, *A.* 148, 49).

Formyl derivative $C_6H_5O.CHO$. Liquid, boiling with decomposition at 180° (Seifert, *J. pr.* [2] 31, 467).

Acetyl derivative C_6H_5OAc. *Phenyl acetate.* (195°) at 733 mm. (Orndorff, *Am.* 10, 368). Formed by boiling an alcoholic solution of phenyl phosphate with KOAc (Williamson a. Scrugham, *A.* 92, 317; Kreysler, *B.* 18, 1716) and by the action of AcCl on phenol (Cahours, *A.* 92, 316) or of $POCl_3$ (1 mol.) on phenol (3 mols.) mixed with HOAc (3 mols.) (Nencki, *J. pr.* [2] 25, 282; Seifert, *J. pr.* [2] 31, 467). Obtained also by boiling phenol with acetamide (Guareschi, *A.* 171, 142). Heavy oil, saponified by KOHAq. *Reactions.*—1. Sodium acts violently, giving off and forming EtOAc, phenol, salicylic acid, $C_{15}H_{12}O_3$ [48°] crystallising from alcohol in needles, and $C_{18}H_{14}O_4$ [138°] nearly insol. alcohol, but crystallising therefrom in yellow needles (Hodgkinson a. W. H. Perkin, jun., *C. J.* 37, 487, 721).—2. Benzyl chloride after heating for 14 days leaves an oil with strong blue fluorescence which when saponified by alcoholic potash forms $C_{10}H_{10}O$ [39°] (c. 295°) and benzylphenol $C_{13}H_{12}O$ [81°] (321°) (H. a. P.).—3. Benzyl chloride and $AlCl_3$ give HCl, toluene, anthracene, Ac_2O, and $CH_2Ph.C_6H_4OAc$.—4. NaSEt forms PhONa and EtSAc (Seifert).—5. PCl_5 at 100° gives phenyl phosphate and $C_6H_5O.CCl:CCl_2$ [26°] (Michael, *Am.* 9, 207).—6. Chlorine in the cold forms AcCl, *p*-chloro-phenol, and $C_6H_4Cl(OAc)$. Chlorine at 160° yields AcCl, $C_6H_3Cl_2(OAc)$, and mono- and di- chloro-phenols (Seelig, *J. pr.* [2] 39, 175).—7. Bromine forms AcBr and $C_6H_4Br.OAc$. Excess of Br gives $C_6H_2Br_3OH$ and $C_6H_2Br_3OAc$ (Seelig).—8. BzCl and a little $ZnCl_2$ give PhOBz (Doebner, *A.* 210, 255).

Propionyl derivative $C_6H_5O.CO.Et$. [20°]. (211°). S.G. $\frac{4}{4}$ 1·0643; $\frac{15}{15}$ 1·0542. Formed by distilling phenol with excess of propionyl chloride (Perkin, *C. J.* 55, 546). Large transparent prisms. PCl_5 at 100° followed by water gives oily $C_9H_8Cl_2O$ (116°) (Michael, *Am.* 9, 212).

Butyryl derivative $C_6H_5O.CO.C_3H_7$. (228°). S.G. $\frac{4}{4}$ 1·0364; $\frac{15}{15}$ 1·0269. Formed from phenol and butyryl chloride (Perkin).

Benzoyl derivative $C_6H_5.OBz$. *Phenyl benzoate.* [69°]. (314° cor.). H.F. 61,804 (Stohmann, *J. pr.* [2] 36, 7). Made by melting benzoic acid (11 g.) with phenol (10 g.) and gradually adding $POCl_3$ (13 g.). The product is washed with dilute KOH and crystallised from dilute alcohol, the yield being fair (12 g.) (Rasiński, *J. pr.* [2] 26, 62; *cf.* Ettling, *A.* 53, 87; Stenhouse, *A.* 53, 91; Laurent a. Gerhardt, *A.* 75, 75; List a. Limpricht, *A.* 90, 190). Formed also by boiling phenol with benzamide (Guareschi, *A.* 171, 141) and from phenyl phosphate and NaOBz (Kreysler, *B.* 18, 1719). Monoclinic prisms (from ether-alcohol). Not saponified by boiling aqueous KOH, but saponified by alcoholic potash.

Salicyl derivative v. *o*-OXY-BENZOIC ACID.

Methyl derivative $C_6H_5.O.Me$. *Anisole.* Mol. w. 108. (155°). V.D. 3·79 (calc. 3·73). S.G. $\frac{0}{0}$ 1·0110 (Pinette, *A.* 243, 34); $\frac{15}{4}$ ·997 (Vincent, *Bl.* [2] 40, 106). C.E. (0°–10°) ·00083. S.V. 125·2 (R. Schiff, *A.* 220, 105). S.H. ·405 at 0° (Schiff, *A.* 234, 300). R_∞ 55·33 (Nasini a. Bernheimer, *G.* 15, 93). H.F.p. 15,860. H.F.v. 13,830 (Thomsen, *Th.*); 32,718 [C,O_2 = 94,000; H_2,O = 69,000] (Stohmann, *J. pr.* [2] 35, 23). Formed by distilling anisic acid or the methyl derivative of salicylic acid with baryta (Cahours, *A. Ch.* [3] 2, 274; 10, 353; 27, 439). Made also by heating PhOK with MeI at 110° (Cahours, *A.* 78, 225). Prepared by heating NaOPh at 200° in a rapid current of MeCl (Vincent, *Bl.* [2] 40, 106). Oil with pleasant odour, v. sol. alcohol and ether. Conc. HIAq at 140° splits it up into phenol and MeI (Graebe, *A.* 139, 149). At 400° it decomposes into phenol and ethylene (Bamberger, *B.* 19, 1820). Chlorine in the cold gives rise to [1:2]$C_6H_4Cl.OMe$ (c. 200°), [1:3:6]$C_6H_3Cl_2.OMe$, [28°], (233°), and [1:3:5:6]$C_6H_2Cl_3.OMe$ [60°] (249°). In presence of iodine, chlorine forms [1:2:3:5:6]$C_6HCl_4.OMe$ [100°] (279°) and also $C_6Cl_5.OMe$ [107°] (c. 289°). Chlorine with I at 60° forms C_6Cl_6 [220°], C_6HCl_5 [87°] and $C_6H_2Cl_4$ [136°]. Chlorine with I acting on boiling anisole forms C_6Cl_6, $COCl_2$, HCl, and some CCl_4. Chlorine with $SbCl_3$ forms $C_6Cl_5.OH$ [187°] and CCl_4. Chlorine with $SbCl_5$ at 100° gives C_6Cl_6O [107°] (Hugounenq, *A. Ch.* [6] 20, 504). AcCl in CS_2 in presence of $AlCl_3$ forms $CH_3.CO.C_6H_4OMe$ (Gattermann, *B.* 22, 1129); BzCl acts in like manner.

Ethyl derivative C_6H_5OEt. *Phenetole.* (172°). S.G. $\frac{0}{0}$ ·9822 (Pinette, *A.* 243, 35). V.D. 4·27 (calc. 4·21). C.E. (0°–10°) ·00087. S.V. 148·5 (R. Schiff, *A.* 220, 105). S.H. ·429 (Schiff,

A. 234, 300). H.F.p. 39,775 (Stohmann). Formed by distilling barium ethyl-salicylate and by the action of EtI on C_6H_5OK (Cahours, *A. Ch.* [3] 27, 463; Baly, *A.* 70, 269). Formed also by the action of alcohol and $ZnCl_2$ on phenol (Kastropp, *B.* 10, 1685) and by the action of dry alcohol on diazobenzene nitrate or sulphate (Remsen a. Orndorff, *Am.* 9, 392).

Preparation.—Equal volumes of H_2SO_4 and alcohol are mixed and allowed to cool. The liquid is then neutralised with soda and evaporated until Na_2SO_4 begins to crystallise out. The liquid is poured off from the crystals, mixed with a strong solution of sodium phenylate, and heated in an autoclave at 150° under 7 atmospheres' pressure. The sodic phenylate is made by dissolving phenol in caustic soda solution (S.G. 1·33). In calculating the amount of phenol it is assumed that half the alcohol forms sodic ethyl sulphate (Kolbe, *J. pr.* [2] 27, 425).

Properties.—Oil. Yields with fuming HNO_3 a di-nitro- derivative [87°]. At 400° it yields phenol and ethylene. BzCl in CS_2 in presence of $AlCl_3$ forms $C_6H_5.CO.C_6H_4.OEt$; AcCl acts in like manner (Gattermann, *B.* 22, 1129).

Propyl derivative $C_6H_5.OPr$. (191°). S.G. $\frac{0}{0}$ ·9639. C.E. (0°–10°) ·00086. S.V. 172 (Pinette, *A.* 243, 35). H.F.p. 46,574 (Stohmann).

Isopropyl derivative PhOPr. (176°). S.G. $\frac{0}{}$ ·958 (Silva, *Z.* 1870, 249).

Butyl derivative $C_6H_5.O.C_4H_9$. (210°). S.G. $\frac{0}{0}$ ·95. C.E. (0°–10°) ·00089. S.V. 195·3.

Isobutyl derivative $C_6H_5.O.CH_2Pr$. (198°). S.G. $\frac{16}{}$ ·939 (Riess, *B.* 3, 780).

Isoamyl derivative $C_6H_5.O.C_5H_{11}$. (225°). Formed from PhOK and isoamyl iodide (Cahours, *C. R.* 32, 61). Oil, lighter than water.

Heptyl derivative $C_6H_5.O.C_7H_{15}$. (267°). S.G. $\frac{0}{0}$ ·9319. C.E. (0°–10°) ·00091. S.V. 270·8.

Octyl derivative $C_6H_5.O.C_8H_{17}$. (283°). S.G. $\frac{0}{0}$ ·9221. C.E. ·00084. S.V. 296·1 (Pinette, *A.* 243, 36).

Vinyl derivative $C_6H_5.O.C_2H_3$. (c. 155°). S.G. $\frac{0}{}$ ·992. From the bromo-ethyl derivative and alcoholic potash (Sabanéeff, *Bl.* [2] 41, 253).

Bromo-vinyl derivative $C_6H_5.O.C_2H_2Br$. Formed from $C_2H_2Br_2$, phenol, and alcoholic potash (Sabanéeff, *A.* 216, 277). Oil, decomposed by distillation.

Di-bromo-vinyl derivative $C_6H_5O.C_2HBr_2$. [38°]. Got from phenol, C_2HBr_3, and alcoholic potash. Gives $PhO.C_2HBr_4$ [59°].

Tri-chloro-vinyl derivative $C_6H_5O.CCl:CCl_2$. [26·5°]. (106° at 12 mm.). Formed by the action of PCl_5 upon phenyl acetate. Also obtained by the action of potassium phenol upon per-chloro-ethylene. Crystalline solid. Volatile with steam (Michael, *B.* 19, 845; *Am.* 9, 207).

Bromo-ethyl derivative $PhOC_2H_4Br$. [39°]. (240°–250°). Made from ethylene bromide and sodium phenol in alcoholic solution by digesting for 3 hours at 100°. Separated from the ethylene-ether, $(PhO)_2C_2H_4$, by distilling with steam, in which it is much more volatile. Colourless crystals with characteristic odour, partly decomposes on boiling. V. sol. alcohol and ether (Weddige, *J. pr.* [2] 24, 242). *Reactions.*—1. Heated at 110° with alcoholic NH_3 it gives crystals of $HN(C_2H_4.OPh)_2HBr$, [216°], sl. sol. alcohol. Alkalis liberate from this salt the free base imido-di-ethylene-di-phenyl ether as an alkaline oil. With HCl it forms a salt, $HN(C_2H_4OPh)_2HCl$ [213°]. It also forms a nitrate [197°].—2. With o-nitro-phenol potassium it forms $Ph.O.C_2H_4.OC_6H_4NO_2$, crystallising in prisms, [86°].—3. Heated with potassium *p*-oxybenzoic ether in alcoholic solution it forms $C_6H_5.O.C_2H_4.O.C_6H_4.CO_2Et$ [81°], which, when saponified by alcoholic potash, yields the acid, $C_6H_5.O.C_2H_4.O.C_6H_4.CO_2H$ melting at [196°] (Wagner, *J. pr.* [2] 27, 227).

Chloro-ethyl derivative $PhO.C_2H_4Cl$. [25°]. (221°). Made from C_2H_4ClBr and KOPh. Reacts with KOEt forming $PhO.C_2H_4.OEt$ (230°), S.G. $\frac{11}{}$ 1·018 (Henry, *C. R.* 96, 1233), or (252°), S.G. $\frac{0}{}$ 1·037 (Sabanéeff, *Bl.* [2] 41, 253).

Penta-bromo-ethyl derivative $PhOC_2Br_5$. [103°–106°]. From the di-bromo vinyl derivative by successive treatment with alcoholic potash and Br (Sabanéeff, *A.* 216, 282).

Methylene derivative $CH_2(OPh)_2$. (294°) (Henry); (299°) (Arnhold, *A.* 240, 201). S.G. $\frac{18}{}$ 1·114 (H.); $\frac{20}{}$ 1·092 (*A.*). Formed from CH_2Br_2 and KOPh (Henry, *A. Ch.* [5] 36, 269).

Ethylene derivative $C_2H_4(OPh)_2$. [98·5°] (Burr, *Z.* [2] 5, 165); [95°] (Lippmann, *C. C.* 1870, 45). Made from $C_2H_4Br_2$ and KOPh at 140°. Crystals, sl. sol. alcohol. Br yields $C_{14}H_{14}Br_4O_2$ [c. 100°]. H_2SO_4 yields a disulphonic acid, whence $C_2H_4(O.C_6H_4SO_3)_2Pb$ may be got, crystallising from hot water in laminæ.

Bromo-propyl derivative $C_6H_5O.CH_2.CH_2.CH_2Br$. (246°–256°). Formed from phenol, trimethylene bromide, and NaOEt (Lohmann, *B.* 24, 2632). Oil. Alcoholic NH_3 at 100° forms $(PhO.C_3H_6)_2NH$ which distils above 300° and gives B'HCl [206°], and the nitrosamine $(PhO.C_3H_6)_2.N.NO$ [61°]. Aniline forms $PhO.C_3H_6.NHPh$ [32°] which gives B'HCl [170°]. With NaOMe in MeOH it yields $PhO.C_3H_6.OMe$ (231°), while alcoholic potash solution forms $PhO.C_3H_6.OEt$ (329°, or probably 239°). The compound $PhO.C_3H_6.OH$ (250°) is formed by the action of nitrous acid on $PhO.C_3H_6.NH_2$ (242°) which is itself obtained by the hydrolysis of $PhO.C_3H_6.NH.CO.C_6H_4.CO_2H$.

Trimethylene derivative $CH_2(CH_2OPh)_2$. [61°]. A by-product in the preparation of the bromo-propyl derivative.

Allyl derivative $PhO.C_3H_5$. (194°). From C_3H_5Br and NaOPh (Henry, *B.* 5, 455).

Di-chloro allyl derivative $PhO.C_3H_3Cl_2$ (114°–118° *in vacuo*). Got from PhO.CO.Et and PCl_5 (Michael).

Bromo-allyl derivative $PhO.C_3H_4Br$. (240°). Got from $CH_2:CHBr.CH_2Br$ and KOPh (Henry, *Bl.* [2] 40, 324). Alcoholic potash forms the propargyl derivative (210°).

Benzyl derivative v. Phenyl ether of Benzyl alcohol.

Glucoside $C_6H_5O.C_5H_6(OH)_4.CHO$. [172°]. Formed by adding acetochlorhydrose to an alcoholic solution of PhOK (Michael, *C. R.* 89, 355; *Am.* 1, 306). Long needles (from hot water), v. sol. water, sol. alcohol and HOAc. H_2SO_4 forms a yellow solution. Acetic anhydride and NaOAc at 100° yield the tetra-acetyl derivative $C_6H_5O.C_5H_6(OAc)_4.CHO$, which crystallises from alcohol in long white needles.

References. — Amido-, Amido-di-imido-, Bromo-, Bromo-amido-, Bromo-iodo-nitro-,

BROMO-NITRO-, CHLORO-, TRI-CHLORO-IODO-, CHLORO-NITRO-, IODO-, DI-IODO-AMIDO-, IODO-NITRO-, and NITRO- phenols.

Diphenol *v.* DI-OXY-DIPHENYL.

Tetraphenol *v.* FURFURANE.

PHENOL-AZO- COMPOUNDS *v. Oxy-benzene-* AZO- COMPOUNDS.

Phenol-bidiazo- compounds *v.* DISAZO- COMPOUNDS.

PHENOL-BLUE *v. Di-methyl-amido-phenyl-imide* of QUINONE.

PHENOL CARBOXYLIC ACID *v.* OXY-BENZOIC ACID.

Phenol dicarboxylic acid *v.* OXY-PHTHALIC, OXY-ISOPHTHALIC, and OXY-TEREPHTHALIC ACIDS.

Phenol triearboxylic aeid *v.* OXY-TRIMESIC ACID.

PHENOLISATIN *v.* DI-OXY-DIPHENYLOXINDOLE.

PHENOL-PHTHALEÏN $C_{20}H_{14}O_4$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{C(C_6H_4OH)_2}{CO.O}$. [c. 253°]. Formed by heating phenol with phthalic anhydride and conc. H_2SO_4. Obtained also from di-amido-di-phenyl-phthalide by the diazo- reaction (Baeyer, *A.* 202, 36; *B.* 9, 1230; 12, 642). Small crystals (from alcohol), v. sol. hot alcohol, sl. sol. water. Its solutions in alkalis and alkaline carbonates are red, but become colourless on neutralisation, and also on addition of exeess of KOHAq but not by NH_3. The red colour of a solution in very dilute ammonia disappears on standing (Long, *Am.* 11, 84). Aniline does not give any colour with phenol-phthaleïn. $AgNO_3$ gives a violet pp.

Reactions.—1. H_2SO_4 at 100° forms a sulphonic acid, but at 200° it yields oxy-anthraquinone.—2. PCl_5 yields di-chloro-di-phenyl-phthalide [156°].—3. *Zinc-dust* and NaOHAq yield phenol-phthalin $CO_2H.C_6H_4.CH(C_6H_4OH)_2$. —4. *Potash-fusion* gives dioxybenzophenone and benzoic acid.—5. NH_3Aq at 170° forms $C_{20}H_{16}N_2O_2$ [266°].

Di-acetyl derivative $C_{20}H_{12}Ac_2O_4$. [143°]. Colourless tables (from wood-spirit).

Anhydride $C_{20}H_{12}O_3$. [175°]. A by-product in the preparation of phenol-phthaleïn (Baeyer, *A.* 212, 347). Needles, insol. NaOHAq. Conc. H_2SO_4 forms a solution with green fluorescence. Bromine yields $C_{20}H_{10}Br_2O_3$ [258°]. Alcoholic potash and zinc-dust reduco it to phthalin $C_{20}H_{14}O_3$.

Tetra-bromo-phenol-phthaleïn $C_{20}H_{10}Br_4O_4$ *i.e.* $C_6H_4:C_2O_2(C_6H_2Br_2OH)_2$. [220°–230°]. Formed by adding Br in HOAc to a solution of phenol-phthaleïn in alcohol. Colourless needles (from ether), sl. sol. alcohol and HOAc. Alkalis form violet solutions, decolourised by excess. H_2SO_4 produces di-bromo-oxy-anthraquinone on heating to 150°. Ac_2O yields a di-acetyl derivative [134°]. H_2SO_4 containing KNO_3 forms bromorosoquinone $C_{12}H_4Br_4O_2$, separating from alcohol-chloroform in red crystals with steel-blue lustre, insol. water, forming a violet solution in H_2SO_4, and oonverted by boiling alcoholic potash into $C_{12}H_6Br_4O_2$ [264°]. NH_3Aq at 170° forms $C_{20}H_{12}Br_4N_2O_2$ [above 280°], whence nitrous acid produces $C_{20}H_{12}Br_2N_4O_6$, and Ac_2O yields $C_{20}H_8Ac_4Br_4N_2O_2$ [241°].

PHENOL-PHTHALIDEÏN $C_{20}H_{14}O_4$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{C(OH)(C_6H_4OH)}{CO}>C_6H_3OH$. *Di-oxy-phenyl-oxanthranol.* [212°]. Formed by oxidation of phenol-phthalidin by dilute alkaline $KMnO_4$ (Baeyer, *A.* 202, 100). Monoclinic tables (from HOAc); $a:b:c = {\cdot}46:1:{\cdot}49$; $\beta = 69°\ 5'$, v. sol. alcohol and acetone. It forms a pale-yellow solution in KOHAq, and is reppd. by HCl. Conc. H_2SO_4 forms a violet solution, and on heating produces oxyanthraquinone and phthalic acid. Reduced by zinc-dust and NaOHAq to phenol-phthalidin. PCl_5 yields di-chloro-phenyl-oxanthranol $C_{20}H_{12}Cl_2O_2$ [156°]. Bromine gives $C_{20}H_{10}Br_4O_4$ [above 280°], whence $C_{20}H_8Ac_2Br_4O_4$ [182°] may be obtained. On adding phenol to a solution of phenol-phthalideïn in H_2SO_4, the violet colour changes to blood-red, and on addition of water a red amorphous pp. is thrown down. This pp. forms a deep-violet solution in alkalis, and yields a crystalline bromo- derivative. A mixture of NH_3Aq and alcohol at 160° converts the red pp. into $C_{20}H_{15}NO_3$ [260°], crystallising in yellow needles.

Acetyl derivative $C_{20}H_{12}Ac_2O_4$. [109°]. Monoclinic prisms, $a:b:c = 2{\cdot}78:1:1{\cdot}44$; $\beta = 77°\ 2'$.

PHENOL-PHTHALIDEÏN CHLORIDE *v.* DI-CHLORO-PHENYL-OXANTHRANOL.

PHENOL-PHTHALIDIN *v.* DI-OXY-PHENYL-ANTHRANOL.

PHENOL-PHTHALIN $C_{20}H_{16}O_4$ *i.e.* $CO_2H.C_6H_4.CH(C_6H_4OH)_2$. *Di-oxy-tri-phenyl-methane carboxylic acid.* [225°]. Formed by reduction of phenol-phthaleïn with zinc-dust and NaOHAq (Baeyer, *A.* 202, 80; 212, 350). Small needles. Forms a colourless solution in potash, coloured red by K_3FeCy_6 through formation of phenol-phthaleïn. Yields a di-acetyl derivative [146°]. Sodium-amalgam yields phenol-phthalol $CH_2(OH).C_6H_4.CH(C_6H_4OH)_2$ [190°], which gives a tri-acetyl derivative [40°].

Anhydride $C_{20}H_{14}O_3$. [217°]. Formed by reducing the anhydride of phenol-phthaleïn. Small needles (from dilute alcohol).

Di-chloro-phenol-phthalin. *Anhydride* $O<\genfrac{}{}{0pt}{}{C_6H_3Cl}{C_6H_3Cl}>CH.C_6H_4.CO_2H$. [226°–230°]. Got by the action of zinc and NaOHAq on the compound $C_{20}H_{10}Cl_2O_3$ derived from fluoresceïn (*v.* vol. ii. p. 558). Small needles (from dil. alcohol).

Tetra-bromo-phenol-phthalin $CO_2H.C_6H_4.CH(C_6H_2Br_2OH)_2$. [205°]. Formed by bromination. Crystals (from benzene). Yields a di-acetyl derivative [166°] (Baeyer, *A.* 202, 80). Conc. H_2SO_4 converts it into tetra-bromo-phenol-phthalidin $C_{20}H_{10}Br_4O_3$, which crystallises from alcohol in golden needles, and is converted by oxidising agents into tetra-bromo-phthalideïn $C_{20}H_{10}Br_4O_4$. Tetra-bromo-phenol-phthalidin is tetra-bromo-di-oxy-phenyl-anthranol, and its di-acetyl derivative crystallises in needles [256°].

PHENOL-QUINOLINE *v.* OXY-PHENYL-QUINOLINE.

PHENOLS. Compounds containing hydroxyl united to carbon, which forms part of a benzene nucleus (*v.* BENZENE and ALCOHOLS). They much resemble the tertiary fatty alcohols, being more acid in character than primary alcohols. Thus phenols and tertiary alcohols form hardly any acetate on heating with HOAc. Phenols in which hydrogen in the o- or *p*- position has been displaced by NO_2 or by a halogen are even more strongly acid in character (*e.g.* picric acid).

Formation.—1. By potash-fusion from sul-

phonic acids.—2. By the diazo- reaction from amido- compounds (*v.* DIAZO-COMPOUNDS).—3. By distillation of oxyacids either alone or with lime.—4. Halogens in a benzene nucleus may sometimes be displaced by hydroxyl by heating with KOHAq in sealed tubes; thus *o*- and *p*-chloro-nitro-benzenes give *o*- and *p*- nitro-phenols by this treatment.

Properties of Phenol and its homologues.—Dissolve in NaOHAq but not in Na_2CO_3Aq. Phenols do not give rise on oxidation to an acid or aldehyde containing the same number of atoms of carbon in the molecule. They do not exchange H for K on treatment with KSH, nor do they form ammonium salts. They do not react (like alcohol) with HCl. $FeCl_3$ colours aqueous solutions of phenols, and products of oxidation are often produced. H_2SO_4 to which 6 p.c. of KNO_2 has been added gives with a solution of a phenol in H_2SO_4 a brown colour, changing on warming to green and blue (Liebermann, *B.* 7, 248, 806, 1098).

Reactions.—1. Readily undergo bromination, chlorination, and nitration.—2. H_2SO_4 forms sulphonic acids, the isomeric sulphuric acids being very unstable.—3. *Sodium* and CO_2 form oxyacids on heating (Kolbe).—4. *Chloroform* and NaOHAq form, on boiling, oxy-aldehydes (Tiemann a. Reimer, *B.* 9, 824).—5. CCl_4 and *alcoholic potash* at 100° form oxyacids.—6. Ammoniacal $ZnCl_2$ at 200°–300° converts phenols into amines (Merz a. Weith, *B.* 13, 1298; 20, 544).—7. Solutions of $NaHCO_3$ and $(NH_4)HCO_3$ yield oxyacids on heating with dioxyphenols (Kostanecki, *B.* 18, 3203).—8. Distillation over *zinc-dust* reduces the hydroxyl to hydrogen, forming the corresponding hydrocarbons.—9. *Alkoyl chlorides* and *anhydrides* yield alkoyl derivatives of phenols, especially if a little powdered zinc be added (Schiaparelli, *G.* 11, 69). When an alkoyl chloride is used oxy-ketones are also often formed through the alkoyl entering the benzene nucleus.—10. *Organic acids* mixed with phenols readily yield alkoyl derivatives of the phenols on adding $POCl_3$ or on heating in presence of $ZnCl_2$ (Rasinski, *J. pr.* [2] 26, 62; Nencki, *M.* 10, 906). Alcohols in presence of $ZnCl_2$ form alkyl ether and higher homologous phenols.—11. *Alkyl derivatives* of phenols split up on distillation into phenols and olefines (Bamberger, *B.* 19, 1819).—12. The acid sulphuric ethers of the form $C_6H_4X.O.SO_3H$ derived from *o*- and *p*- alkyl-phenols are oxidised by alkaline $KMnO_4$ to *o*- and *p*- oxy-benzoic acids (Heymann, *B.* 19, 704).—13. Alkaline solutions of phenols absorb atmospheric *oxygen*, forming dark-coloured products.—14. Homologues of phenol frequently yield oxyacids on *fusion with potash*, the alkyl side-chain being oxidised to carboxyl. 15. *Aldehydes* in presence of dehydrating agents form compounds of the form $XCH(OY)_2$, which change to $XCH(Y''.OH)_2$. Thus (β)-naphthol and benzoic aldehyde give $PhCH(OC_{10}H_7)_2$ changing to $PhCH(C_{10}H_6OH)_2$, which is at once converted into the anhydride $PhCH\langle{C_{10}H_6 \atop C_{10}H_6}\rangle O$ (Baeyer, *B.* 5, 26; Claisen, *B.* 19, 3316).—16. *Phthalyl chloride* usually forms phthalic ethers (R. Meyer, *B*, 24, 2600).—17. *Iodine* and *potash* give di- and tri- iodo- derivatives (Messinger a. Vortmann, *B.* 22, 2315).—18. *Nitrous acid* displaces hydrogen in the *o*- or *p*- position by nitrosyl. The products are identical with the mono-oxims formed by warming quinones with hydroxylamine hydrochloride, but yield nitrophenols on oxidation with alkaline K_3FeCy_6.—19. *Diazo-salts* readily form AZO-COMPOUNDS (*q.v.*). 20. *Diazo-amido- compounds* form oxy-azo- compounds. Thus $C_6H_4Cl.N_2.NHC_6H_4Cl$ heated with phenol on a water-bath yields $C_6H_4Cl.N_2.C_6H_4OH$ and $C_6H_4ClNH_2$ (Heumann a. Oeconomides, *B.* 20, 904).—21. *Benzotrichloride* acting on phenols in which there is an atom of hydrogen in the *p*- position to hydroxyl yields colouring matters related to aurin (Doebner, *A.* 217, 223; 257, 56).

PHENOL *o*-SULPHONIC ACID $C_6H_6SO_4$ *i.e.* $C_6H_4(OH).SO_3H$. Formed, together with the *p*- acid, by the action of H_2SO_4 on phenol, especially in the cold (Kekulé, *Z.* 1867, 199; *B.* 2, 330; Faust, *Z.* 1871, 339; Armstrong, *C. J.* 24, 1112; 25, 12, 857). Prepared by dropping H_2SO_4 on dry phenol at −10°, allowing the product to stand for a week, and then distilling, treating with $BaCO_3$ and $KHCO_3$ successively, and crystallising the K salt (Allain le Canu, *C. R.* 109, 225). Crystals (containing 1½ aq), melting at 50° and decomposing at a higher temperature, with liberation of H_2SO_4. Sol. ether. When heated with water it changes to phenol *p*-sulphonic acid (Post, *A.* 205, 64). Possesses powerful antiseptic properties (Serrant, *C. R.* 102, 1079).

Reactions.—1. *Potash-fusion* gives some pyrocatechin. The action begins about 280° and attains a maximum (20 p.c.) at 320°. *Soda-fusion* also gives pyrocatechin. The action begins at 310°. At 330° the yield is 6 p.c. Fusion with a mixture of potash and soda gives a still smaller yield (1 p.c.) of pyrocatechi (Degener, *J. pr.* [2] 20, 308).—2. *Bromine-vapour* acting at −8° on the K salt yields bromo- and di-bromo- derivatives.—3. BzCl forms PhOBz on heating with the K salt (Solommanoff, *Z.* [2] 5, 296).—4. Heated with dilute HCl at 140° it is split up into phenol and H_2SO_4 (Armstrong).

Salts.—KA′ 2aq. [235°–240°]. Colourless trimetric prisms, sol. water.—NaA′ 1½aq.—BaA'_2 aq: needles. S. 25 at 100°.—BaA'_2 2aq.—PbA'_2 aq: tables, sl. sol. water.—The aniline salt yields phenol and amido-benzene *p*-sulphonic acid on distillation (Kopp, *B.* 4, 978).

Methyl derivative $C_6H_4(OMe).SO_3H$. Formed from the acid, KOH, MeI, and MeOH (Kekulé).—KA′ aq: needles, more soluble than its *p*- isomeride (Haitinger, *M.* 4, 173). Yields a chloride [55°].

Ethyl derivative. Forms a K salt crystallising in plates.

Phenol *m*-sulphonic acid $C_6H_4(OH).SO_3H$. Formed by potash-fusion from benzene *m*- or *p*-disulphonic acid (Barth a. Senhofer, *B.* 9, 969). Needles (containing 2aq). $FeCl_3$ gives a violet colour. Yields resorcin on fusion with potash.—NaA′ aq.—KA′ aq. [200°–210°]. Efflorescent needles.—$K_2C_6H_4SO_4$ aq.—PbA'_2 3aq: tables, v. sol. water.—BaA'_2 ½aq.—CuA'_2 6aq: green tables.

Ethyl derivative $C_6H_4(OEt).SO_3H$. Got by the action of KOH and EtI on the acid (Delisle a. Lagai, *B.* 23, 3393). Deliquescent needles. Yields a chloride [33°] and an amide [131°], and is reduced by zinc-dust and dilute H_2SO_4 to $C_6H_4(OEt)SH$ (239°).—Salts: KA′ aq. BaA'_2 4aq: needles (from water).—CaA'_2 3aq.

Phenol *p*-sulphonic acid $C_6H_4(OH).SO_3H$. Formed by warming phenol with H_2SO_4 or $ClSO_3H$. Formed also from amido-benzene *p*-sulphonic acid by the diazo- reaction. Highly deliquescent hydrated needles (Le Canu, *C. R.* 103, 385).

Reactions.—1. *Bromine* acting on a cold solution forms mono- and di-bromo- derivatives and finally tri-bromo-phenol (Le Canu).—2. Boiling HIAq gives phenol (Benedikt a. Bamberger, *M.* 12, 4).—3. *Potash-fusion* forms a little resorcin (Lincke, *J. pr.* [2] 8, 43).—4. PCl_5 gives *p*-di-chloro-benzene and $C_6H_4Cl.O.POCl_2$ (Kekulé, *B.* 5, 875; 6, 943).—5. MnO_2 and H_2SO_4 yield quinone (Schrader, *B.* 8, 759).—6. Dilute HCl at 150° forms phenol and H_2SO_4.

Salts.—KA'. [400°]. Six-sided trimetric lamellæ: $a:b:c = \cdot879:1:1\cdot002$.—NaA' 2aq: monoclinic prisms (Shadwell, *J.* 1881, 874).—BaA'_2 3aq. S. 50 at 100°.—$BaC_6H_4SO_4$ 2aq.—PbA'_2 2aq.—CoA'_2 8aq (Freund, *A.* 120, 85).—NiA'_2 8aq.—CuA'_2 10aq.—AgA'.—Aniline salt. Plates. [170°]. Decomposed at 190° into phenol and amido-benzene *p*-sulphonic acid.—o-Toluidine salt. [c. 192°]. S. 10·7 at 14° (Lecco, *J.* 1874, 747).—*p*-Toluidine salt. [202°]. S. 5·2 at 17°.

Benzoyl derivative $C_6H_4(OBz).SO_3H$. Formed from PhOBz and SO_3 (Engelhardt a. Latschinoff, *Z.* 1868, 76).—KA': long needles (from water).—CaA'_2.—BaA'_2.—PbA'_2 2aq.—CuA'_2 6aq.—AgA'.

Methyl derivative $C_6H_4(OMe).SO_3H$. Got by methylation. The K salt forms needles.

Ethyl derivative $C_6H_4(OEt).SO_3H$. Formed from the acid, KOH, and EtI (Kekulé, *Z.* 1867, 200), and also, together with the o- isomeride, by sulphonating phenetole (Lippmann, *C. R.* 68, 1332).—BaA'_2 4aq: crystals, v. sl. sol. hot water.—KA' aq: needles (from alcohol).

Phenyl ether PhA'. Formed from phenol (2 mols.) and $ClSO_3H$ (Engelhardt a. Latschinoff, *Z.* 1869, 298). Syrup, split up by water into phenol and phenol sulphonic acid.

Anhydride $C_{12}H_{10}S_2O_7$. Formed from the acid and $POCl_3$ (Schiff, *A.* 178, 171). Powder, v. sol. water, v. sl. sol. HClAq. Coloured violet-red by $FeCl_3$. Ppts. gelatin and alkaloids. Yields an acetyl derivative $C_{12}H_9AcS_2O_7$.

Phenol disulphonic acid $C_6H_3(OH)(SO_3H)_2$ [1:2:4]. Formed by warming phenol with H_2SO_4 and SO_3, and by allowing separate vessels of phenol and fuming H_2SO_4 (S.G. 1·85) to remain for six months *in vacuo*, the acid absorbing the vapour of phenol (Kekulé, *Z.* 1866, 693; Le Canu, *C. R.* 109, 442). Formed also from diazo-benzene sulphate and fuming H_2SO_4 (Griess, *A.* 137, 69; Armstrong a. Prevost, *B.* 6, 664). Nodular groups of deliquescent needles, v. e. sol. water and alcohol. HNO_3 yields picric acid. Potash-fusion gives pyrocatechin and its sulphonic acid; soda-fusion forms also protocatechuic acid (Barth a. Schmidt. *B.* 12, 1260). $FeCl_3$ gives a red colour (Städeler, *A.* 144, 299).

Salts.—K_2A''aq. Needles, decomposing about 270°. S. 33 at 100°.—BaA'' 4aq. S. 19·6 at 15°.—$Ba_3(C_6H_3S_2O_7)_2$ 6aq.—$Ba_3(C_6H_3S_2O_7)_2$ 3aq. Sl. sol. water.—$Pb_3(C_6H_3S_2O_7)_2$ 6aq. Sl. sol. water.—Ag_2A'': plates, v. sol. water.

Methyl derivative $C_6H_3(OMe)(SO_3H)_2$. Formed by sulphonation of anisic acid (Zervas, *A.* 103, 342), and also from $SO_2(C_6H_4OMe)_2$ and conc. H_2SO_4 at 170° (Annaheim, *A.* 172, 47).—BaA'' 4aq: monoclinic crystals.

Ethyl derivative $C_6H_3(OEt)(SO_3H)_2$ [1:2:4]. Formed from amido-benzene disulphonic acid by the diazo- reaction (Zander, *A.* 198, 25). Very deliquescent needles. Yields a chloride [108°] and an amide [233°].—KHA''aq.—BaA'' 2aq.—BaA'' 3aq: v. sol. water.

Ethylene derivative $C_2H_4(O.C_6H_4.SO_3H)_2$. Formed from $C_2H_4(OPh)_2$ and H_2SO_4 at 120° (Lippmann, *Z.* 1869, 447).—BaA'' *x*aq.—PbA'' *x*aq: plates, insol. cold water.

Phenol disulphonic acid. An unstable acid is formed by heating the trisulphonic acid with KOH (3 pts.) and some water at 150° (Senhofer, *J.* 1879, 749). Yields K_2A'' $3\frac{1}{2}$aq.—BaA'' 4aq.—PbA'' 4aq: long prisms, v. sol. water.

Phenol trisulphonic acid $C_6H_2(OH)(SO_3H)_3$ [1:2:4:6]. Formed by heating phenol (6 pts.) with H_2SO_4 (30 pts.) and P_2O_5 (15 pts.) at 180° (Senhofer, *A.* 170, 110). Formed also by heating $SO_2(C_6H_4.OH)_2$ with fuming H_2SO_4 at 190° (Annaheim, *A.* 172, 28). Needles or short prisms (containing $3\frac{1}{2}$aq). Coloured red by $FeCl_3$.—Na_3A''' 3aq.—K_3A''' 4aq.—$K_4C_6H_2S_3O_{10}$ 2aq.—$Ba_3A'''_2$ 4aq: scales.—$Ba_3A'''_2$ 10aq: plates.—$Cd_3A'''_2$ 7aq.—$Pb_4C_6H_2S_3O_{10}(OH)_4$ $4\frac{1}{2}$aq: crystalline powder.—Ag_3A''' $1\frac{1}{2}$aq: slender needles.

References.—Amido-, Bromo-, Bromo-nitro-, Di-iodo-, Iodo-nitro- phenol sulphonic acids.

PHENOQUINONE $C_{18}H_{16}O_4$. [71°]. Formed from phenol (1 mol.) and quinone (2 mols.), or by boiling phenol with aqueous CrO_3 (Wichelhaus, *B.* 5, 248, 846; Nietzki, *A.* 215, 134; Hesse, *A.* 200, 232; Erhart, *Ar. Ph.* [3] 8, 481). Red needles with green lustre, sol. cold water, alcohol, ether, and ligroïn. Reduced by SO_2 to hydroquinone. Bromine forms di-bromo-phenol.

PHENOSAFRANINE *v.* Safranine.

PHENOSE $C_6H_{12}O_6$. Formed by the action of aqueous ClOH on benzene in the dark, the resulting $C_6H_9Cl_3O_3$ [10°] being extracted with ether and heated with very dilute Na_2CO_3 (Carius, *A.* 136, 323). Formed also by the electrolysis of toluene mixed with alcohol and dilute H_2SO_4 (Renard, *C. R.* 92, 965). Deliquescent amorphous mass, v. sol. water and alcohol, insol. ether. Has a sweet taste. Decomposes above 100°. Turned brown by acids and alkalis. Prevents ppn. of cupric sulphate by potash, and reduces Fehling's solution. Does not undergo alcoholic fermentation. Reduced by HI to hexyl iodide. HNO_3 yields oxalic acid. Ammoniacal lead acetate ppts. $C_6H_6Pb_3O_6$.

PHENOXYACETIC ACID *v. Phenyl derivative* of Glycollic acid, vol. ii. p. 638, and Chloro-phenoxyacetic acid.

PHENOXYACETIC-ACRYLIC ACID *v. Carboxy-methyl derivative* of Coumaric acid.

PHENOXYACETIC-CARBOXYLIC ACID *v.* Carboxyphenoxyacetic acid.

γ-PHENOXY-BUTYRIC ACID $C_{10}H_{12}O_3$ *i.e.* $C_6H_5O.CH_2.CH_2.CH_2.CO_2H$. [60°]. Made from the nitrile and HClAq at 100°. Silvery plates, insol. water, v. sol. alcohol.—AgA': white crystalline powder, decomposing at 200°.

Nitrile $PhO.C_3H_6.CN$. [46°]. (288°). Formed from $PhO.C_3H_6Br$, alcohol, and aqueous KCy (Lohmann, *B.* 24, 2640), and from γ-chloro-butyronitrile and NaOPh (Gabriel, *B.* 24, 3231).

White needles. Conc. H_2SO_4 converts it into $C_6H_4(SO_3H).O.C_3H_6.CONH_2$ [211°], a crystalline powder which gives BaA'_2 as white crystals insol. Aq. Yields $PhO.C_4H_8.NH_2$ (256°) on reduction.

PHENPROPYL- COMPOUNDS *v.* PROPYL-PHENYL- COMPOUNDS.

PHENPROPYLAMINE *v.* AMIDO-PHENYL-PROPANE.

PHENUVIC ACID *v.* PHENYL-METHYL-FURFURANE CARBOXYLIC ACID.

PHENYL. The monovalent radicle C_6H_5. It is more chlorous in character than methyl and ethyl (V. Meyer, *B.* 20, 534).

Diphenyl $C_{12}H_{10}$ *i.e.* $C_6H_5.C_6H_5$. Mol. w. 154. [70°]. (254°) (Schultz, *A.* 174, 205); (253° at 716 mm.) (Bamberger a. Lodter, *B.* 20, 3077). H.C.v. 1,492,800 (Stohmann, *J. pr.* [2] 40, 86); 1,508,700 (Berthelot, *Bl.* [2] 47, 865; *A. Ch.* [6] 10, 448). H.C.p. 1,494,300 (S.); 1,510,100 (B.). H.F. −19,800 (S.); −37,100 (B.). S.V.S. 154·25 (Schiff). Occurs in the coal-tar oils boiling at 200°–300° (Büchner, *B.* 8, 22; Schulze, *B.* 17, 1203).

Formation.—1. By adding slices of sodium to bromo-benzene and distilling after 24 hours (Fittig, *A.* 121, 361; 132, 201; Schultz, *A.* 174, 201; Engelhardt a. Latschinoff, *Z.* [2] 7, 259).—2. From chloro-benzene and sodium-amalgam (Church, *C. J.* 16, 76).—3. With other hydrocarbons by passing benzene vapour through a red-hot tube (Berthelot, *Z.* 1866, 707), and formed consequently in many reactions in which benzene is produced at a high temperature.—4. By passing benzene vapour mixed with $SbCl_3$ or $SnCl_4$ through a red-hot tube (Watson Smith, *C. J.* 30, 30; Aronheim, *B.* 9, 1898).—5. A product of the passage of azobenzene through red-hot tubes (Claus, *B.* 8, 37).—6. By the action of red-hot zinc-dust on di-phenylene-ketone-oxide. 7. By heating diphenylene ketone dicarboxylic acid with lime (Bamberger a. Hooker, *A.* 229, 155).—8. From benzidine by the diazo-reaction (Griess, *Tr.* 1864 [3] 692).—9. By heating phenol with K at 240° and ppg. with water.—10. By subjecting bromo-benzene to an electric current, using zinc for the positive electrode (Christomanos, *G.* 5, 402).—11. In small quantity in the decomposition of diazobenzene salts by alcohol (Griess) and by $SnCl_2$ (Culman a. Gasiorowski, *J. pr.* [2] 40, 97).

Preparation.—1. By slowly passing benzene through a red-hot iron tube. By successive passage of the unchanged benzene through the tube the yield may be raised to 97 p.c. of the theoretical (Adam, *A. Ch.* [6] 15, 224; *cf.* Lüddens, *B.* 8, 870).—2. 31 g. aniline are dissolved in 40 g. conc. H_2SO_4 and 150 g. water, and diazotised with 31 g. $NaNO_2$. 100 g. 90 p.c. alcohol is then added, followed gradually by 50 g. finely-divided copper. After stirring for one hour it is finally distilled with steam. The yield is 6–7 grms. Iron and zinc-dust may also be used. The temperature must not rise above 30°–40° (L. Gattermann, *B.* 23, 1226).

Properties.—Iridescent nacreous scales (from alcohol), v. sol. hot alcohol and ether.

Reactions.—1. Readily yields di-bromo- and di-nitro- derivatives. Chlorine, in presence of $SbCl_5$, yields $C_{12}H_9Cl$ and $C_{12}H_8Cl_2$ (Kramers, *A.* 189, 142).—2. Heated in a stream of Cl in presence of I the product is $C_{12}Cl_{10}$ (Ruoff, *B.* 9, 1048; *cf.* Merz a. Weith, *B.* 16, 2881).—3. A mixture of diphenyl and ethylene passed through a red-hot tube yields benzene, styrene, anthracene, and phenanthrene (Barbier, *A. Ch.* [5] 7, 532).—4. CrO_2Cl_2 in HOAc oxidises it to benzoic acid (Carstanjen, *J. pr.* [2] 2, 79).—5. $AlCl_3$ yields, on heating, benzene and a pitchy mass (Friedel a. Crafts, *C. R.* 100, 692). Diphenyl (15 pts.) heated with $AlCl_3$ (1 pt.) and CH_2Cl_2 (10 pts.) yields diphenylene-methane (fluorene) [113°] and $(C_6H_5.C_6H_4)_2CH_2$ (310°–320°) (Adam, *Bl.* [2] 47, 686).—6. $AlCl_3$ and $COCl_2$ give $(C_6H_5.C_6H_4)_2CO$ [229°]. *Acetyl chloride* and $AlCl_3$ give $C_6H_5.C_6H_4.CO.CH_3$ [121°].—EtCl and $AlCl_3$ give $C_6H_5.C_6H_4.C_2H_5$ (285°) and $C_6H_5.C_6H_3Et_2$ (c. 307°). In all these cases the compounds are *m*-derivatives (Adam, *A. Ch.* [6] 15, 224).

Dihydride $C_{12}H_{12}$. (249°). Got by the action of boiling alcoholic potash on $C_{12}H_{14}Br_2$, which is formed from $C_{12}H_{14}$ and Br (Bamberger a. Lodter, *B.* 21, 843). Oil, volatile with steam, sol. ether. Yields $C_{12}H_{12}Br_2$.

Tetra-hydride $C_{12}H_{14}$. (245°) at 716 mm. Got by reducing diphenyl dissolved in amyl alcohol with sodium (Bamberger a. Lodter, *B.* 20, 3077). Liquid. Yields $C_{12}H_{14}Br_2$ and $C_{12}H_{13}Br_3$ [134°].

References.—AMIDO-, BROMO-, BROMO-AMIDO-, BROMO-NITRO-, CHLORO-, DI-CHLORO-DI-NITRO-, DI-IODO-, NITRO-, and OXY-, DIPHENYL.

PHENYL-ACETAMIDE *v. Acetyl derivative* of ANILINE and *Amide* of PHENYL-ACETIC ACID.

PHENYL-ACETAMIDINE $C_8H_{10}N_2$ *i.e.* $C_6H_5.CH_2.C(NH).NH_2$. Formed from the thioamide $CH_2Ph.CS.NH_2$ by the action of ammonia and atmospheric oxygen, or of ammonia and $HgCl_2$ (Bernthsen, *B.* 8, 1319; 9, 429; *A.* 184, 321). Formed also from $CH_2Ph.C(NH_2Cl).OEt$ and ammonia (Luckenbach, *B.* 17, 1423). Crystals, decomposed by heat, v. sol. alcohol, ether, and warm water. Absorbs CO_2 from the air. Decomposed by heating with water and alcohol into NH_3 and $CH_2Ph.CONH_2$.

Salts.—B'HCl aq.— $B'_2H_2PtCl_6$.—$B'H_2SO_4$: tables, v. sol. water and alcohol.—$B'_2H_2S_2O_3$. [198°]. Needles (from alcohol).—$B'HNO_3$. Monoclinic crystals (Lossen, *A.* 265, 165).—B'HOAc. [193°]. Stellate groups of needles (from alcohol).—$B'_2H_2C_2O_4$: prisms.

Di-acetyl derivative $C_6H_5.CH_2.C(NAc).NHAc$. [173°]. Four-sided tables (from water), sl. sol. alcohol and ether.

Phenyl - acetamidine $CH_3.C(NPh).NH_2$. Formed from acetonitrile and aniline hydrochloride at 170° (Bernthsen, *A.* 184, 358). Oil. $B'H_2C_2O_4$: v. e. sol. water.

s-Di-phenyl-acetamidine $C_{14}H_{14}N_2$ *i.e.* $CH_3.C(NPh).NHPh$. *Ethenyl-di-phenyl-amidine.* [132°]. *Formation.*—1. From aniline (3 pts.), HOAc (2 pts.) and PCl_3 (2 pts.) (Hofmann, *C. R.* 62, 729).—2. From acetanilide (2 mols.) and PCl_5 (1 mol.) (Lippmann, *B.* 7, 541; Wallach, *B.* 8, 1567).—3. From acetonitrile and aniline hydrochloride at 240° (Bernthsen).—4. By passing HCl into heated acetanilide (Wallach, *B.* 15, 210).—5. By-product in the preparation of thioacetanilide from acetanilide and P_2S_5.—6. By distillation of thioacetanilide (Jacobsen, *B.* 19, 1072).

Preparation.—By heating a mixture of equal weights of acetanilide and aniline hydrochloride.

Properties.—Slender needles or thin prisms, sl. sol. alcohol, forming a neutral solution, nearly insol. water, v. sol. ether. Conc. H_2SO_4 forms amido-benzene *p*-sulphonic acid and acetic acid. Tin and HCl reduce it to aniline and HOAc. Fuming HNO_3 forms the insoluble nitrate of a di-nitro- derivative $C_{14}H_{12}N_4O_4HNO_3$ [182°] (Biedermann, *B.* 7, 540). $COCl_2$ at 60° forms $C_{16}H_{12}N_2O_2Cl_2$, whence NaOEt yields $C_{20}H_{22}N_2O_4$ [91°] crystallising from ether (Loeb, *B.* 18, 2427; 19, 2340). Excess of $COCl_2$ in benzene yields $C_{15}H_{12}N_2O$ [118°], which is decomposed by dilute HCl into aniline and phenyl cyanate. Cyanogen passed into an ethereal solution forms $C_{16}H_{16}N_4O$, a white crystalline powder [165°]. EtI yields oily $CH_3.C(NPh).NPhEt$, whence MeI followed by moist Ag_2O produces strongly-alkaline $CH_3.C(NPh).NPhEtMe(OH)$. — B'HCl: tables, m. sol. water.—$B'_2H_2PtCl_6$.—$B'HNO_3$.

u-**Di-phenyl-acetamidine** $CH_3.C(NH).NPh_2$. [63°]. Formed from diphenylamine hydrochloride and acetonitrile by heating for a week at 150° (Bernthsen, *A.* 192, 25). Monoclinic tablets or thick prisms; $a{:}b{:}c = 1{\cdot}142{:}1{:}1{\cdot}222$. V. sol. alcohol, forming an alkaline solution. CS_2 at 100° gives di-phenyl-thioacetamide. The hydrochloride is v. e. sol. water.—$B'_2H_2PtCl_6$.—B'HNCS. Colourless tablets.

Di-phenyl-acetamidine $C_6H_5.CH_2.C(NPh).NH_2$. *Phenyl-phenyl-acetamidine.* [c. 128°]. Formed, with H_2S, by heating $C_6H_5.CH_2.CS.NH_2$ with aniline hydrochloride (B.). Formed also by heating phenyl-acetonitrile (benzyl cyanide) with aniline hydrochloride at 230° and by the action of iodine on a mixture of aniline and phenyl-thioacetamide. Small needles or laminæ, v. sl. sol. water, v. sol. alcohol and ether. May be sublimed. Boiling dilute alcohol decomposes it into aniline and $CH_2Ph.CONH_2$.

Tri-phenyl-acetamidine $C_6H_5.CH_2.C(NPh).NHPh$. [108°]. Formed from $C_6H_5.CH_2.C(NH_2Cl).OEt$ (1 mol.) and alcoholic aniline (3 mols.) (Luckenbach, *B.* 17, 1427). Plates (from alcohol).—$B'_2H_2PtCl_6$: plates.

Reference. — DI-BROMO-DI-PHENYL-ACETAMIDINE.

PHENYL ACETATE *v. Acetyl derivative* of PHENOL.

PHENYL-ACETCHLORAMIDE *v. Chloracetanilide* in the article ANILINE.

PHENYL-ACETIC ACID $C_8H_8O_2$ *i.e.* $C_6H_5.CH_2.CO_2H$. *Alphatoluylic acid.* Mol. w. 136. [77°]. (265·5° cor.). S.G. $\frac{83}{4}$ 1·0778; $\frac{135}{4}$ 1·0334. H.C.p. 933,200 (Stohmann, *J. pr.* [2] 40, 134). H.C.v. 932,600. H.F. 94,800 (Stohmann); 59,000 (von Rechenberg).

Formation.—1. By saponification of its nitrile (Cannizzaro, *A.* 96, 246; *C. R.* 52, 966; 54, 1225).—2. By boiling vulpic acid with baryta-water (Möller a. Strecker, *A.* 113, 64).—3. By reducing mandelic acid with conc. HIAq and P (Crum Brown, *Proc. Roy. Soc. Edinb.* 5, 409).—4. By the putrefactive fermentation of proteïds (Salkowski, *B.* 12, 649; *H.* 2, 420; 9, 507).

Preparation.—By converting benzyl chloride into the nitrile (benzyl cyanide), mixing 100 grms. of the cyanide with 300 grms. of a mixture of 3 vols. of H_2SO_4 and 2 vols. Aq, and heating till gas bubbles begin to rise. A violent reaction occurs, heat being again applied when this subsides, until no further reaction takes place. The acid partly crystallises out, and is partly extracted with ether (W. Slædel, *B.* 19, 1949).

Properties.—Thin laminæ, sl. sol. cold water, v. sol. hot water, alcohol, and ether.

Reactions.—1. Yields benzoic aldehyde, formic acid, and CO_2 when *oxidised* by chromic acid mixture.—2. HNO_3 yields o- and *p*- nitro-acids (Pirogoff, *B.* 5, 332).—3. *Electrolysis* of a dilute solution gives benzoic aldehyde and benzoic acid and two neutral substances [93°] and [115°] (Slawik, *B.* 7, 1051).—4. *Ozonised oxygen* yields $PhCH_2.CO.O.CH_2Ph$ (318°). — 5. When administered to animals it appears in the urine as phenyl-aceturic acid, and increases the amount of urea (Salkowski, *B.* 12, 653; *H.* 12, 222).—6. *Phthalic anhydride* and HOAc form benzylidene-phthalide on heating. Tetra-chloro-phthalic anhydride (40 pts.), phenyl-acetic acid (20 pts.), and NaOAc (1 pt.) form, in like manner, $CHPh{:}C_2O_2{:}C_6Cl_4$, melting above 360°, whence NaOH forms $CH_2Ph.CO.C_6Cl_4.CO_2H$ [175°] (Gabriel, *B.* 20, 2869). Di-chloro-phthalic anhydride forms the corresponding compound $CHPh{:}C_2O_2{:}C_6H_2Cl_2$ [210°], whence alkalis yield $C_{15}H_{10}Cl_2O_3$ [117°].—7. HIAq and P at 200° form $C_8H_{11}PO_3$ [136°], which crystallises from water in needles, and gives CaA'' 2aq, BaA'' 2aq, and Ag_2A'' (Guye, *J.* 1884, 468).

S a l t s.—CaA'_2 3aq.—CaA'_2 2aq.—BaA'_2 3aq: v. sol. water.—PbA'_2 aq.—AgA': small laminæ.

Methyl ether MeA'. [220°]. S.G. $\frac{16}{}$ 1·044. Liquid (Radziszewski, *Z.* [2] 5, 358).

Ethyl ether EtA'. (229° cor.). S.G. $\frac{18}{}$ 1·086. Converted by heating with sodium into acetic ether, sodium phenyl-acetate, a solid $C_{21}H_{18}O_3$ [175°] (? tri-phenyl-phloroglucin), and an oil (? $CH_2Ph.CO.CHPh.CO_2Et$) (Hodgkinson, *C. J.* 37, 481; *C. J. Proc.* 2, 189).

Amido-ethyl ether $CH_2(NH_2).CH_2A'$. Formed from $C_2H_4Br.NH.CO.CH_2Ph$ and hot water (Elfeldt, *B.* 24, 3222).—$B'C_6H_3N_3O_7$. [138°].

n-Propyl ether PrA'. (238° cor.). S.G. $\frac{18}{}$ 1·0142. Made by heating alcoholic potassium phenyl-acetate with PrI for two days. Sodium acts on it, forming propyl acetate, sodium phenyl-acetate, a yellow oil $C_{22}H_{20}O_2$, (335° at 50 mm.), and a small quantity of a solid, $C_{20}H_{24}O_3$, forming white needles (from petroleum), [170°], S.G. $\frac{17}{}$ 1·039. This solid is also formed by the action of sodium on the oil $C_{22}H_{20}O_2$, as well as on the corresponding oil $C_{18}H_{16}O_2$ formed from ethyl phenyl-acetate. The solid forms an acetyl derivative [100°] (Hodgkinson, *C. J.* 37, 483).

Iso-butyl ether $(CH_3)_2CH.CH_2.A'$. (147° cor.). Sodium gives isobutyl acetate and an oil (Hodgkinson, *C. J.* 37, 485).

Benzyl ether $PhCH_2A'$. (318°) (S.); (270° at 160 mm.). S.G. $\frac{17}{}$ 1·094. Got by heating benzyl chloride with alcoholic potassium phenylacetate for a week (H.). Heated with sodium it forms sodium phenyl-acetate, the salt of an acid $C_{15}H_{14}O_2$, [120°], possibly α-β-di-phenyl-propionic acid, and an oil, $C_{22}H_{20}O_2$ (320° at 60 mm.), possibly the benzyl ether of that acid.

Chloride $CH_2Ph.COCl$. (103° at 17 mm.). S.G. $\frac{20}{4}$ 1·1682 (Anschütz a. Berns, *B.* 20, 1389; Hinsberg, *B.* 23, 2962).

Anhydride $(CH_2Ph.CO)_2O$. [72·5°]. Formed from the chloride and the Ag salt (A. a. B.).

Amide $CH_2Ph.CO.NH_2$. [158°]. (283°). Formed from the nitrile by heating with alcoholic KSH (Weddige, *J. pr.* [2] 7, 99). Formed also by heating phenylacetamidine hydrochloride with oxalacetic ether and dilute (10 p.c.). NaOHAq (Pinner, *B.* 22, 1627), and by the action of yellow ammonium sulphide on acetophenone (Willgerodt, *B.* 21, 534). Plates, v. sol. hot water. Forms with HgO a compound crystallising in needles [208°] (Reimer, *B.* 13, 741). KBrO and HOAc give $CH_2Ph.CO.NHBr$ [124°], crystallising from benzene in needles, and yielding benzylamine on warming with potash (Hoogewerff a. Van Dorp, *R. T. C.* 6, 385). Aldehyde and a few drops conc. HClAq give $(C_6H_5.CH_2.CO.NH)_2CHMe$ [228°]. Chloral gives an analogous body.

Diethylamide $CH_2Ph.CO.NEt_2$. [86°]. (296° uncor.). Formed from the chloride and diethylamine in ether (Hausknecht, *B.* 22, 324).

Bromo-ethyl-amide $CH_2Ph.CO.NH.C_2H_4Br$. [85°]. Plates.

β-Bromo-propyl-amide $CH_2Ph.CO.NH.CH_2.CHMeBr$. [46°]. Formed from the chloride and $C_3H_6Br(NH_2)$. Needles.

γ-Bromo-propyl-amine $CH_2Ph.CO.NH.CH_2.CH_2.CH_2Br$. [44°]. Needles, converted by KOH into $CH_2{<}{\substack{CH_2.O\\CH_2.N}}{>}C.CH_2Ph$ (Elfeldt, *B.* 24, 3224).

Anilide $CH_2Ph.CO.NHPh$. [117°] (Hofmann, *B.* 13, 1225). Got, by intramolecular change, by the action of PCl_5 on the oxim of deoxybenzoïn (Günther, *A.* 252, 71).

Di-phenyl-amide $CH_2Ph.CO.NPh_2$ [72°]. Satiny needles (from ether) (Hausknecht).

Phenyl hydrazide $C_{14}H_{14}N_2O$. [167°]. White flakes (Bülow, *A.* 236, 196).

Nitrile $C_6H_5.CH_2.CN$. *Benzyl cyanide.* (232° cor.). S.G. $\frac{18}{}$ 1·015. H.C. 1,023,000. H.F. −27,900 (Berthelot a. Petit, *C. R.* 108, 1219). The chief constituent of the oils of garden cress (*Lepidium sativum*) and of nasturtium (*Tropæolum majus*) (Hofmann, *B.* 7, 1293). Formed by boiling benzyl chloride with alcoholic KCy (Cannizzaro, *A. Ch.* [3] 45, 468). *Preparation.*—By digesting benzyl chloride (1 kilo.), crude KCy (1 kilo.), and dilute alcohol for a week. Tribenzylamine remains in the retort after distilling off the benzyl cyanide below 300°. *Reactions.*—1. A specimen (200°–230°) treated with $ZnEt_2$, the temperature being kept below 130°, formed a product which, when decomposed by alcohol, gave cyanbenzine $(C_8H_7N)_n$ and benzacin, $C_{32}H_{27}N_3O$, an indifferent body [150°].—2. Reduced by *zinc* and HClAq to $C_6H_5.CH_2.CH_2.NH_2$ (Bernthsen, *B.* 8, 691).—3. Alcoholic ammonium sulphide forms $C_6H_5.CH_2.CS.NH_2$ [98°].—4. *Water* at 250° forms the amide; ammonium acetate acts in like manner (Bernthsen, *B.* 9, 429).—5. *Bromine* forms $C_6H_5.CHBr.CN$ and very sparingly soluble $C_6H_5.CHBr.CBr(NH)$ [c. 200°], which is crystalline, is decomposed by hot water and alcohol, and yields mandelic acid when heated with dilute HCl at 150° (Reimer, *B.* 14, 1797).—6. *Pyruvic acid* and H_2SO_4 in the cold form $C_{19}H_{20}N_2O_4$ [145°] (Böttinger, *B.* 14, 1600).

Paranitrile $(C_8H_7N)_n$. $n = 3$? *Cyanbenzine.* [171°] (F. a. T.); [221°] (P.). Obtained by extracting with alcohol the product of the action of $ZnEt_2$ on the isomeric nitrile (Frankland a. Tompkins, *C. J.* 37, 568). Occurs in small quantity in the product of the action of alcoholic KCy on benzyl chloride (Pinner, *B.* 17, 2010). Silky needles. Hardly sol. alcohol, sol. CS_2, and glacial acetic acid. Forms a gummy mass with warm dilute HCl, possibly a salt.

Di-phenyl-acetic acid $C_{14}H_{12}O_2$ *i.e.* $CHPh_2.CO_2H$. *Deoxybenzilic acid.* Mol. w. 212. [148°]. Formed by reducing benzilic acid with HIAq (Jena, *A.* 155, 84) and by heating $CHPhBr.CO_2H$ (1 mol.) with benzene (1 mol.) and zinc-dust (Symons a. Zincke, *B.* 6, 1188; *A.* 171, 122). Obtained also by saponifying its nitrile or amide. Needles (from water); sl. sol. cold water, v. sol. alcohol and ether. Yields benzophenone on oxidation, and di-phenyl-methane on distillation with soda-lime. Bromine forms $CPh_2Br.CO_2H$.

Salts.—BaA'_2 2aq. Efflorescent monoclinic crystals.—CaA'_2 2aq.—AgA′: amorphous pp.

Methyl ether MeA′. [60°]. Plates (from alcohol) (Rattner, *B.* 21, 1316).

Ethyl ether EtA′. [58°]. Prisms.

Amide $CHPh_2.CONH_2$. [166°]. Got by action of KOH (6 g.) in alcohol on the nitrile (2 g.) (Anschütz a. Romig, *A.* 233, 347), and by heating the ammonium salt under pressure at 230° (Neure, *A.* 250, 141). Plates (from alcohol).

Nitrile $CHPh_2.CN$. [76°]. (N.); [73°] (F. a. S.). (183° at 12 mm.). Formed by heating $CHPh_2Br$ with $HgCy_2$ for 18 hours at 165°, and extracting with benzene (Friedel a. Balsohn, *Bl.* [2] 33, 589) and by heating the acid with lead sulphocyanide at 170° (Freund a. Immerwahr, *B.* 23, 2845). Got also, together with a polymeride [168°], by nitrating di-phenyl-ethane and reducing the resulting $C_{14}H_{10}N_2O_4$ [148°] with $SnCl_2$ and alcoholic HCl (A. a. R.), and by treating the amide with PCl_5 in $POCl_3$ (N.). White needles (from ligroïn and ether). Alcoholic NaOEt and benzyl chloride form $CPh_2(CH_2Ph).CN$ [126°]. An ethereal solution of iodine (1 mol.) gradually added to an alcoholic solution of the nitrile (2 mols.) and NaOEt (1 mol.) forms $CN.CPh_2.CPh_2.CN$ [c. 230°].

Tri-phenyl-acetic acid $CPh_3.CO_2H$. [264°]. Formed by the action of fuming HClAq and HOAc on the nitrile at 200° (E. a. O. Fischer, *B.* 11, 1598; *A.* 194, 242). Prepared by heating $CCl_3.CO_2H$ (250 g.), benzene (340 g.), and $AlCl_3$ (250 g.), mixing the product with water and distilling with steam; the residue of aluminium triphenylacetate is decomposed by NH_3Aq and the filtrate ppd. by HCl; the yield being 5 p.c. (Elbs a. Tölle, *J. pr* [2] 32, 624). In this preparation two by-products $(C_8H_4O)_n$ [325°] and $(C_{12}H_8O)_n$ [75°] crystallising in yellow needles are also formed. Monoclinic prisms (from alcohol), sl. sol. HOAc. Very feeble acid. The NH_4 salt gives off NH_3 spontaneously. The K salt, ppd. as needles by conc. KOHAq, is decomposed by water. Fuming H_2SO_4 at 100° forms $SO_3H.C_6H_4.CPh_2.CO_2H$, which yields BaA″aq, an amorphous salt.—Salt: AgA′. Powder, not affected by light.

Nitrile $CPh_3.CN$. [127·5°]. Formed from $HgCy_2$ and CPh_3Cl at 160° and from KCy and CPh_3Br (Elbs, *B.* 17, 700). Monoclinic prisms

(from ligroïn or HOAc). Converted by alcoholic potash into a polymeride [210°] crystallising in colourless needles.

References.—Amido-, Bromo-, Bromo-amido-, Bromo-nitro-, Chloro-, Iodo-, and Oxy-phenyl-acetic acid.

PHENYL-ACETIC ALDEHYDE C_8H_8O *i.e.* $C_6H_5.CH_2.CHO$. (206°) (Radziszewsky, *B.* 9, 372); (194°) (Etard).

Formation.—1. By distilling calcium phenyl-acetate with calcium formate (Cannizzaro, *A.* 119, 254).—2. From α-bromo- (or chloro-) β-oxy-phenyl-propionic acid $CHPh(OH).CHBr.CO_2H$ by distilling with dilute Na_2CO_3; the yield being 75 p.c. (Lipp. *B.* 16, 1286; Erlenmeyer, *A.* 219, 179).—3. By boiling $PhCH(OH).CH_2OH$ (1 pt.) for an hour with H_2SO_4 (3 pts.) and water (12 pts.) (Zincke, *A.* 216, 301). Stronger H_2SO_4 yields $C_{16}H_{12}$ [101°].—4. From ethyl-benzene by successive treatment with CrO_2Cl_2 and water (Etard, *A. Ch.* [5] 22, 248).—5. By distilling phenyl-glycidic acid with dilute H_2SO_4 (Erlenmeyer, *B.* 13, 304).

Properties.—Oil. Forms a crystalline compound with $NaHSO_3$.

Reactions.—1. With *acetoacetic ether* and NH_3 it yields benzyl-di-methyl-pyridine di-carboxylic ether dihydride $C_5H_2N(C_7H_7)Me_2(CO_2Et)_2$ [1:3:5:2:6] [115°] (Jeaurenaud, *B.* 21, 1784).—2. HCy forms $CH_2Ph.CH(OH).CN$ [58°], S. 1 at 15°, crystallising in stellate groups of colourless needles, v. sol. alcohol.—3. HNO_3 (S.G. 1·49) at −12° give o- and *p*- nitro-benzoic aldehyde.

Phenyl-hydrazide $CH_2Ph.CH:N_2HPh$. [58°]. Prisms, v. sol. alcohol. Converted into phenyl-indole by heating with $ZnCl_2$ at 180° (Fischer a. Schmitt, *B.* 21, 1072).

ψ-Ethyl derivative $C_6H_5.CH:CH.OEt$. (217°). S.G. $\frac{0}{0}$ ·981. Formed from ω-chloro-styrene and alcoholic potash (Erlenmeyer, *B.* 14, 1868). Oil, easily decomposed by heating with water into alcohol and the aldehyde.

Di-phenyl-acetic aldehyde $CHPh_2.CHO$. (315°). Formed by heating hydrobenzoïn (1 pt.) or isohydrobenzoïn with (6 pts. of) dilute (20 p.c.) H_2SO_4 for 8 hours at 210° (Zincke a. Breuer, *B.* 9, 1769; *A.* 198, 182; Weise, *A.* 248, 38). Oil, v. sol. alcohol and ether. Yields benzophenone and CO_2 on oxidation. Forms a crystalline compound with $KHSO_3$. Alcoholic potash yields di-phenyl-carbinol and di-phenyl-methane. Nascent HCy yields $CHPh_2.CH(OH).CN$, upon which alcoholic hydrogen chloride reacts with formation of $CHPh_2.CH(OH).C(NH_2Cl).OEt$ [135°]. The aldehyde appears to form condensation products [168°] and [214°] on standing.

Phenyl hydrazide $CHPh_2.CH:N_2HPh$. Flat stellate needles (from hot alcohol), v. sol. ether (Rudolph, *A.* 248, 101).

Oxim $CHPh_2.CH:NOH$. [120°]. White needles, formed together with another body [145°] by the action of hydroxylamine in dilute alcohol (Auwers, *B.* 24, 1780).

PHENYL-ACETIC CARBOXYLIC ACID *v.* Carboxy-phenyl-acetic acid.

PHENYL-ACET-IMIDO-ACETATE $C_6H_5.CH_2.C(NH).OAc$. [129°]. White needles. V. e. sol. alcohol, sl. sol. cold water. Formed by boiling phenyl-acet-imido-ethyl-ether with Ac_2O (Luckenbach, *B.* 17, 1423).

PHENYL-ACETIMIDAMIDE *v.* Phenyl-acetamidine.

PHENYL-ACET-IMIDO-ETHYL ETHER $C_6H_5.CH_2.C(NH).OEt$. The hydrochloride B'HCl [c. 85°] is formed by passing dry HCl into a solution of phenyl-acetonitrile in absolute alcohol (Luckenbach, *B.* 17, 1421). The free base is a colourless liquid of aromatic odour, decomposed on distillation into alcohol and phenyl-acetonitrile. The hydrochloride is resolved on fusion into phenyl-acetamide and EtCl.

PHENYL-ACETONITRILE *v. Nitrile* of Phenyl-acetic acid.

PHENYL ACETONYL SULPHIDE $C_9H_{10}SO$ *i.e.* $PhS.CH_2.CO.CH_3$. [35°]. (144° at 15 mm.). Formed from chloro-acetone and NaSPh (Delisle, *B.* 22, 308). Large tables (from ether), turned dark violet by hot H_2SO_4. Yields a phenyl-hydrazide [83°].

The corresponding sulphone $Ph.SO_2.CH_2Ac$ [58°] is formed from chloro-acetone and sodium benzene sulphinate (R. Otto, *B.* 19, 1642).

PHENYL-ACETOPHENONE [1:3]$C_6H_5.C_6H_4.CO.CH_3$. [121°]. (c. 326°). Formed from diphenyl, AcCl, and $AlCl_3$ (Adam, *A. Ch.* [6] 15, 255). Prisms, reduced by sodium amalgam to the carbinol [86°].

DI-PHENYL-ACETOXIM (so-called) *v. Oxim* of Benzophenone.

PHENYL-ACETURIC ACID $CH_2Ph.CO.NH.CH_2.CO_2H$.[142°]. S. ·73 at 12°. Occurs in horses' urine, and is also found in urine after a dose of phenyl-acetic acid (Salkowski, *B.* 17, 3010; *H.* 7, 162). Formed by the action of the chloride or anhydride of phenyl-acetic acid on glycocoll (Hotter, *B.* 20, 81; *J. pr.* [2] 38, 98). Small trimetric crystals (from alcohol); $a:b:c = ·890:1:2·374$. V. sl. sol. ether, v. sol. hot water and alcohol.—CaA'_2 2aq. S. 3·16 at 11·2°.—CuA'_2 aq.—PbA'_2 aq: prisms.—ZnA'_2: plates, v. sol. hot water.—AgA': amorphous.

Methyl ether MeA'. [86°]. Needles.

Ethyl ether EtA'. [79°]. Prisms.

Propyl ether PrA'. [31°]. Plates.

Amide $CH_2Ph.CO.NH.CH_2.CONH_2$. [174°]. Pearly hexagonal plates, v. sol. hot water. With HgO it yields $Hg(C_{10}H_{11}N_2O_2)_2$.

PHENYL-ACETYL-ACETONE $C_{11}H_{12}O_2$ *i.e.* $C_6H_5.CH_2.CO.CH_2.CO.CH_3$. *Benzyl-methyl-methylene-di-ketone.* (266°–269° at 748 mm.). Has weak acid properties.

Formation.—Phenyl-acetyl-acetoacetic ether, formed by the action of phenyl-acetyl chloride upon sodio-aceto-acetic ether, is boiled with water for 6 hours.

Properties.—Colourless oil. Sol. alcohol, ether, benzene, hot water, strong acids, and dilute alkalis, sl. sol. cold water. With phenyl-hydrazine it condenses to phenyl-benzyl-methyl-pyrazole.

Salts.—A'Ag: white pp.—A'Na^{x}: crystalline solid (Fischer a. Bülow, *B.* 18, 2136).

PHENYL-ACETYLENE C_8H_6 *i.e.* $C_6H_5.C:CH$. *Acetenyl-benzene.* (141·6° cor.). S.G. $\frac{20}{4}$ ·9295. $\mu_a = 1·542$ (Brühl, *A.* 235, 13). S.V. 125·8.

Formation.—1. By distilling phenyl-propiolic acid with dry $Ba(OH)_2$ (Weger, *A.* 221, 70).—2. By boiling styrene dibromide with alcoholic potash, and heating the resulting bromo-styrene with alcoholic potash (Glaser, *Z.* [2] 5, 97; *A.* 154, 155; Hollemann, *B.* 20, 3080).—3. From

acetophenone by treatment with PCl_5, the resulting $C_6H_5.CCl_2.CH_3$ being heated with conc. alcoholic potash at 120° (Friedel, *Z.* [2] 5, 123). 4. By the passage through a red-hot tube of a mixture of styrene and hydrogen, or of benzene and ethylene (Berthelot, *C. R.* 67, 952).

Properties.—Liquid with peculiar odour. Its alcoholic solution forms a yellow pp. $Cu_2(C_8H_5)_2O$ with ammoniacal cuprous chloride and a white pp. $Ag_4(C_8H_5)_2O$ with ammoniacal $AgNO_3$. These pps. are explosive. Sodium added to its ethereal solution ppts. CPh:CNa as a white powder, which takes fire in the air, and is reconverted by water into phenyl-acetylene.

Reactions.—1. Unites with *bromine.*—2. *Sodium* and CO_2 give sodium phenyl-propiolate, (Paternò, *G.* 2, 553).—3. *Sodium* and EtI give PhC:CEt (202°) (Morgan, *C. J.* 29, 162).—4. H_2SO_4, followed by water, yields acetophenone (Friedel a. Balsohn, *Bl.* [2] 35, 54).—5. Boiling HOAc and *zinc-dust* reduce it to styrene (Aronstein a. Hollemann, *B.* 22, 1181).

Di-phenyl-acetylene $C_{14}H_{10}$ *i.e.* CPh:CPh. *Tolane.* [71°] (Béhal). Formed by boiling CPhHBr.CPhHBr or the corresponding di-chloro-di-phenyl-ethane, with alcoholic potash (Limpricht a. Schwanert, *A.* 145, 347; Fittig, *A.* 168, 74). Formed also by the action of sodium-amalgam on an alcoholic solution of $CPhCl_2.CPhCl_2$ (Liebermann a. Homeyer, *B.* 12, 1974). Large crystals (from ether). May be distilled. Yields di-phenyl-ethylene (stilbene) when heated with HIAq and P at 180° (Barbier, *J.* 1876, 366). Yields benzoic acid on oxidation. Conc. H_2SO_4 gives a green colour, and on warming to 60°, diluting with water and distilling with steam, phenyl benzyl ketone (deoxybenzoïn) [55°] is produced (Béhal, *Bl.* [2] 49, 337).

Chlorides v. Di-chloro-di-phenyl-ethylene and Tetra-chloro-di-phenyl-ethane.

Dibromide v. Di-bromo-di-phenyl-ethylene.

Di-phenyl-di-acetylene $C_{16}H_{10}$ *i.e.* CPh:C.C:CPh. [97°] (G.); [88°] (H.). Formed by shaking the cuprous compound of phenyl-acetylene with alcoholic NH_3 and air, or, better, with alkaline K_3FeCy_6 (Glaser, *A.* 154, 159; Baeyer a. Landsberg, *B.* 15, 57). Long needles (from dilute alcohol), v. sol. ether. Hot H_2SO_4 carbonises it. In ethereal solution Br forms $C_{16}H_{10}Br_4$ [173°] and $C_{32}H_{20}Br_6$ [149°–153°] (Hollemann, *B.* 20, 3081).

Picric acid compound $C_{16}H_{10}C_6H_3N_3O_7$. [108°]. Yellow crystals (from alcohol).

References.—Amido-, Iodo-, and Nitro-phenyl-acetylene.

TRI-PHENYL-ACETYLENE-TRIAMINE $C_{20}H_{19}N_3$ *i.e.* $N_3H_2(C_2H_2)Ph_3$. [190°]. Formed from acetylene tetrabromide, aniline, and alcoholic potash (Sabancjeff, *A.* 178, 125). Needles, v. sl. sol. cold alcohol.—Salts: $B'_2H_2PtCl_6$.—$B'_4H_4Hg_3Cl_{10}$: amorphous pp.

DI-PHENYL-ACETYLENE-DI-THIO-DI-UREA $CS<\begin{matrix}NH.CPh.NH\\NH.CPh.NH\end{matrix}>CS$. Formed from benzil and thio-urea at 145° (Anschütz a. Geldermann, *A.* 261, 134). Crystals, decomposing at 300°; v. sl. sol. alcohol.

DI-PHENYL-ACETYLENE-DI-UREA $CO<\begin{matrix}NH.CPh.NH\\NH.CPh.NH\end{matrix}>CO$. *Tolane-urea.* Formed by heating benzil with urea at 175° (Anschütz a. Geldermann, *A.* 261, 133; Angeli, *B.* 24, 606; *G.* 19, 563). Crystals, not decomposed at 315°; v. sl. sol. alcohol and ether. Reduces ammoniacal $AgNO_3$.

Di-acetyl derivative $C_{15}H_{12}Ac_2N_4O_2$. [266°].

PHENYL-ACETYL-SUCCINIC ACID *v.* Acetyl-phenyl-succinic acid. The mono-ethyl-ether of this acid yields on treatment with alcoholic NH_3 a compound $C_{12}H_{12}N_2O_2$ [264°], which forms, on saponification, a compound $C_{12}H_{11}NO_3$ [148°], crystallising in small needles (Weltner, *B.* 18, 793).

PHENYL-ACRIDINE $C_{19}H_{13}N$ *i.e.* $C_6H_4<\begin{matrix}CPh\\N\end{matrix}>C_6H_4$. [181°]. (c. 404°). V.D. 129·7 [H=1].

Formation.—(Bernthsen, *B.* 15, 3011; 16, 1809; 19, 425; 20, 1552; *A.* 192, 19; 224, 12.) 1. By heating benzoyl-diphenylamine (30 g.) with $ZnCl_2$ (30 g.) at 210°–280°.—2. From benzotrichloride, diphenylamine, and $ZnCl_2$.—3. By heating benzonitrile with diphenylamine hydrochloride at 240°.—4. By heating di-phenyl-benzamidine hydrochloride to 250°.—5. In small quantity by heating di-phenyl-amine with cinnamic acid and $ZnCl_2$.—6. By diazotising chrysaniline (di-amido-phenyl-acridine) and boiling the product with alcohol (Fischer a. Körner, *B.* 17, 206; *A.* 226, 184).

Preparation.—By heating benzoic acid (50 g.) diphenylamine (70 g.) and $ZnCl_2$ (150 g.) at 260° for 10 hours. The yield of crude base (50 g.) is good.

Properties.—Colourless thin prisms (from alcohol), thick yellowish prisms (containing C_6H_6) or tables (from benzene). V. sol. benzene, m. sol. ether, sl. sol. alcohol, insol. water. Solutions of its salts exhibit green fluorescence. Not affected by boiling dilute HNO_3, by fuming HCl at 260°, by AcCl, by Ac_2O at 190°, by Bz_2O at 160°, by potash-fusion, by heating with H_2SO_4 (3 vols.) diluted with water (1 vol.), or by distillation with soda-lime.

Reactions.—1. CrO_3 in HOAc gives benzoic acid and CO_2.—2. On oxidation with $KMnO_4$ it gives phenyl-quinoline carboxylic acid. On the other hand, its alkyl-halogen addition products give rise to phenyl-amido-benzoic acid $C_6H_4(NHPh)CO_2H$ on oxidation with $KMnO_4$ (Claus a. Nicolaysen, *B.* 18, 2706).—3. Yields on nitration with H_2SO_4 and fuming HNO_3 di-nitro-phenyl-acridine $C_{19}H_{11}(NO_2)_2N$, which is sol. aqueous or alcoholic HCl but sl. sol. alcohol, and tri-nitro-phenyl-acridine, which crystallises from toluene and alcohol in minute yellow needles, hardly sol. alcoholic HCl, and converted by hot $SnCl_2$ into a red dye (? tri-amido-phenyl-acridine), which becomes colourless on further reduction.

Salts.—Partially decomposed by water.—B'HCl: orange needles or prisms, sl. sol. cold water, sol. alcohol. Its solution exhibits dark-green fluorescence.—B'HCl 3aq: red crystals.— — $B'_2H_2PtCl_6$. — Nitrate. [188°]. Yellow needles, sl. sol. HNO_3.—Sulphate: yellowish-red trimetric crystals, v. sol. hot water.—Picrate: Hair-like crystals (from alcohol). Phenyl-acridine does not appear to form an acetate.

Methylo-chloride B'MeCl: soluble needles.—$B'_2Me_2PtCl_6$: decomposes below 70°.

Methylo-nitrate $B'MeNO_3$. Sparingly sol. yellow needles.

Methylo-iodide B'MeI. Black monoclinic prisms (from alcohol), insol. ether. Converted by KOHAq, by NH_3Aq, or by moist Ag_2O, into B'MeOH [108°], which is also got by oxidising $C_6H_4<\begin{smallmatrix}CHPh\\NMe\end{smallmatrix}>C_6H_4$, a body to which it is reduced by tin and HClAq.

Hydride $C_6H_4<\begin{smallmatrix}CHPh\\NH\end{smallmatrix}>C_6H_4$. [164°]. Formed by reducing phenyl-acridine hydrochloride in aqueous solution with zinc-dust or by adding sodium-amalgam to an alcoholic solution. Colourless needles, with no basic properties; sol. alcohol and ether. Alcoholic $AgNO_3$ oxidises it to phenyl-acridine, a change which is slowly effected even by air. It yields an acetyl derivative $C_{19}H_{14}AcN$ [128°], and is converted by MeI at 140° into $C_{19}H_{14}MeN$ [104°], whence HCl and $NaNO_2$ produce the methylo-hydroxide of phenyl-acridine (*v. supra*).

Di-sulphonic acid. Got by heating phenyl-acridine (10 g.), H_2SO_4 (15 g.), and $H_2S_2O_7$ (15 g.) for 12 hours at 150°. Its dilute solutions exhibit green fluorescence. The salt $C_{19}H_{11}N(SO_3Na)_2$ is insol. absolute alcohol, and in very dilute solutions exhibits blue fluorescence. The Ba and mercurous salts are nearly insol. Aq.

References. — AMIDO- and OXY-PHENYL-ACRIDINE.

PHENYL-ACRIDINE CARBOXYLIC ACID $C_6H_4<\begin{smallmatrix}C(C_6H_4.CO_2H)\\N\end{smallmatrix}>C_6H_4$. *Acridyl-benzoic acid.* Formed by heating phthalic anhydride (30 g.) with diphenylamine (45 g.) and $ZnCl_2$ (75 g.) for 12 hours at 190° (Bernthsen a. Traube, *B.* 17, 1510; *A.* 224, 45). Yellow crystalline powder, sol. acids and alkalis, insol. water, sl. sol. boiling alcohol. Its solutions in dilute acids have a green fluorescence, in alkalis a blue fluorescence. Split up by heat into CO_2 and phenyl-acridine. Yields a hydride [160°–165°].

Salts.—NaA'aq: colourless pearly plates or long needles.—HA'HCl. [163°]. Yellow crystals (from hot dilute HCl), sl. sol. hot water.

An isomeric acid $C_6H_4<\begin{smallmatrix}CPh\\N\end{smallmatrix}>C_6H_3.CO_2H$, [252°–255°], formed by oxidation of phenyl-methyl-acridine with chromic acid mixture, is sl. sol. alcohol, and gives sparingly soluble BaA'_2 (Bonna, *A.* 239, 62).

PHENYL-ACRYLIC ACID *v.* CINNAMIC ACID and ATROPIC ACID.

Di-phenyl-acrylic acid *v.* PHENYL-CINNAMIC ACID.

PHENYL-ALANINE *v.* α-AMIDO-PHENYL-PROPIONIC ACID and PHENYL-AMIDO-PROPIONIC ACID.

PHENYL ALDEHYDE *v.* PHENYL-ACETIC ALDEHYDE.

PHENYL ALDEHYDO-BENZYL KETONE Ph.CO.CHPh.CHO. [110°]. Formed from deoxybenzoïn, formic ether, and NaOEt in ether (Claisen a. Meyerowitz, *B.* 22, 3279). Yellowish-white crystals. $FeCl_3$ gives a dark-violet colour.

PHENYL ALDEHYDO-ETHYL KETONE PhCO.CHMe.CHO. [119°]. Formed from phenyl ethyl ketone, formic ether, and NaOEt in Et_2O (Claisen a. Meyerowitz, *B.* 22, 3276). White needles, v. sol. alcohol and water. $FeCl_3$ colours its alcoholic solution dark-violet. Gives an anilide [132°] crystallising in needles.

PHENYL ALDEHYDO-PROPYL KETONE Ph.CO.CHEt.CHO. [87°]. Formed from phenyl *n*-propyl ketone, formic ether, and NaOEt in ether (Claisen a. Meyerowitz, *B.* 22, 3278). White plates. $FeCl_3$ gives a dark-violet colour. The anilide [120°] crystallises in white needles.

TETRA-PHENYL-ALDINE *v.* TETRA-PHENYL-PYRAZINE.

PHENYL-ALLENYL-AMIDOXIM *v.* CINNAMIDOXIM.

PHENYL-ALLOPHANIC ACID. *Ethyl ether* $C_6H_5NH.CO.NH.CO_2Et$. [120°]. Formed from phenyl-urea and chloro-glyoxylic ether $COCl.CO_2Et$ (Stojentin, *J. pr.* [2] 32, 18). Needles, v. sol. alkalis and conc. HClAq.

Phenyl ether $NHPh.CO.NH.CO_2Ph$. Formed from phenol and cyanic acid vapour (Tuttle, *J.* 1857, 451). Crystals (from alcohol), insol. cold water. Decomposes at 150° into phenol and cyanuric acid.

Benzyl ether $NHPh.CO.NH.CO_2C_7H_7$. [158°]. Formed by heating phenyl cyanate with benzyl carbamate at 150° under pressure (Traube, *B.* 22, 1574). V. sl. sol. water, m. sol. alcohol.

Di-phenyl-allophanic acid $NHPh.CO.NPh.CO_2H$.

Methyl ether MeA'. [231°].

Ethyl ether EtA'. [98°]. Formed from di-phenyl di-isocyanate $Ph_2N_2C_2O_2$ and alcohol (Hofmann, *B.* 4, 246), and by the action of HgO and alcoholic NH_3 on $NHPh.CS.NPh.CO_2Et$ (Seidel, *J. pr.* [2] 32, 266). Needles, sl. sol. ether. Yields $(C_{16}H_{16}N_2O_3)_23HgO$ [129°], crystallising in prisms (from alcohol).

Isoamyl ether $C_5H_{11}A'$. [58°].

Reference. — DI-BROMO-DI-PHENYL-ALLOPHANIC ACID.

PHENYL ALLYL-BENZYL KETONE $C_6H_5.CO.CHPh.C_3H_5$. (337°). Formed from deoxybenzoïn, NaOEt, and allyl iodide (Budde-berg, *B.* 23, 2067). Oil, v. sol. alcohol.

PHENYL-ALLYL-CYANAMIDE $C_{10}H_{10}N_2$ *i.e.* $C_6H_5N:C:NC_3H_5$. *Carboallylphenylimide.* [105°]. Formed from phenyl-allyl-thio-urea and $Pb(OH)_2$ (Bizio, *J.* 1861, 497). Silky needles (from dilute alcohol).—$B'HgCl_2$: amorphous.—$B'_2H_2PtCl_6$.

PHENYL-ALLYLENE $C_6H_5.C:C.CH_3$. (185°). Formed by the action of alcoholic potash on the bromo-propenyl-benzene, which is got by boiling $CHPhBr:CMe.CO_2H$ with water (Körner, *B.* 21, 276). Yellowish liquid, with unpleasant odour. Yields a liquid dibromide (c. 253°) and a solid tetrabromide [75°]. Aqueous $HgCl_2$ forms white amorphous $(C_9H_8)_2Hg_6Cl_6O_3$, which on heating with HCl yields phenyl ethyl ketone.

u-**PHENYL-ALLYL-HYDRAZINE** $C_3H_5.NPh.NH_2$. (198° at 184 mm.). Formed by reducing the nitrosamine derived from allyl-aniline (Michaelis a. Claessen, *B.* 22, 2233). Got also from allyl-bromide and phenyl-hydrazine. Oil, v. sol. dilute HCl. Reduces Fehling's solution on warming. Oxidised by aqueous $FeCl_3$ to the tetrazone $C_3H_5NPh.N:N.NPh.C_3H_5$ [86°]. Benzoic aldehyde yields $C_3H_5NPh.N:CHPh$ [52°].—B'HCl. [137°]. Silky needles.

Benzoyl derivative $C_9H_{11}AcN_2$. [139°].

s-**Phenyl-allyl-hydrazine** $C_9H_{12}N_2$ *i.e.* $Ph.NH.NH.C_3H_5$. (172° at 60 mm.). Got from phenyl-hydrazine and allyl bromide (Fischer a. Knoevenagel, *A.* 239, 203). Oil; sol. dilute acids. Reduces cold Fehling's solution. Oxidises by HgO to benzene-azo-propylene $Ph.N_2.C_3H_5$, an oil, (95°–100° at 27 mm.).

DI-PHENYL-DI-ALLYLIDENE-DIAMINE $C_{18}H_{18}N_2$ *i.e.* $N_2Ph_2(C_3H_4)_2$. Formed from aniline and acroleïn below 0° (Schiff, *A. Suppl.* 3, 358). Yellow resin.—$B'_2H_2PtCl_6$.

DI-PHENYL-DI-ALLYLIDENE-ETHYLENE DIAMINE $C_2H_4(N:CH.CH:CH.C_6H_5)_2$. [110°]. Formed by mixing ethylene-diamine (1 mol.) with cinnamic aldehyde (2 mols.) (Mason, *B.* 20, 271). Large colourless tables (from ether). V. sol. alcohol and benzene, m. sol. ether. Decomposed into its constituents by acids.

PHENYL ALLYL OXIDE $C_6H_5.O.C_3H_5$. (194°). Formed from allyl bromide and NaOPh (Henry, *B.* 5, 455). Liquid.

PHENYL ALLYL SULPHIDE $C_6H_5.S.C_3H_5$. (c. 208°). Formed by distilling the acid $CH_2:C(SPh).CH_2.CO_2H$ (Escales a. Baumann, *B.* 19, 1792). Liquid, forming a blue solution in H_2SO_4.

PHENYL - ALLYL - THIOSEMICARBAZIDE $C_6H_5NH.NH.CS.NHC_3H_5$. [119°]. Formed from phenyl-hydrazine and allyl thiocarbimide dissolved in benzene (A. E. Dixon, *C. J.* 57, 263; Avenarius, *B.* 24, 268). Silvery needles, insol. water, v. sol. alcohol and ether. Gives a mahogany colour with $FeCl_3$.

Di-phenyl-allyl-thiosemicarbazide $C_6H_5N(C_3H_5).NH.CS.NHPh$. [103°]. Formed from phenyl-allyl-hydrazine and phenyl-thiocarbimide (Michaelis a. Claessen, *B.* 22, 2237). Needles (from hot alcohol).

PHENYL-ALLYL-THIO-UREA $C_{10}H_{12}N_2S$ *i.e.* $NHPh.CS.NHC_3H_5$. *Phenyl-thiosinamine.* [98°]. S. (alcohol) 70 at 16°. Formed by the action of aniline on oil of mustard (Zinin, *A.* 84, 348) and of allylamine on phenyl thiocarbimide (Weith, *B.* 8, 1529). Monoclinic crystals, insol. water. Cyanogen passed into its alcoholic solution forms $C_{12}H_{12}N_4S$, which crystallises from alcohol in stellate forms, and is converted by dilute H_2SO_4 into $CS<\substack{N(C_6H_5).CO \\ N(C_3H_5).CO}$ [161°], whence alcoholic silver nitrate forms $CO<\substack{N(C_6H_5).CO \\ N(C_3H_5).CO}$ [108°], which is resolved by baryta-water into oxalic acid and phenyl-allyl-urea (Maly, *Z.* [2] 5, 258).

PHENYL-ALLYL-THIO-UREA CARBOXYLIC ACID *v.* ALLYL-THIO-URAMIDO-BENZOIC ACID.

PHENYL-ALLYL-UREA $NHPh.CO.NHC_3H_5$. [97°]. Formed as described under phenyl-allyl-thio-urea. Shining white needles.

PHENYL-AMENYL-AMIDINE $C_{11}H_{16}N_2$ *i.e.* $CMe_3.C(NH_2)(NPh)$. The oxalate $B'H_2C_2O_4$ [192°] is formed by heating the corresponding valeronitrile with aniline hydrochloride at 170° (Freund a. Lenze, *B.* 24, 2155).

PHENYL-AMIDO-ACETIC ACID $C_8H_9NO_2$ *i.e.* $CH_2(NHPh).CO_2H$. *Phenyl-glycocoll. Anilido-acetic acid.* [127°]. Formed by the action of aniline on bromo-acetic acid and on chloro-acetic acid (Michaelson a. Lippmann, *Z.* 1866, 15; Schwebel, *B.* 10, 2046). Prepared by boiling aniline (45 g.) dissolved in a little ether with chloro-acetic acid (25 g.) and water (1500 c.c.) for half an hour, and rapidly evaporating to crystallisation (Rebuffat, *G.* 17, 233). By-products are $C_{10}H_{11}NO_4$ [99°] (Meyer, *B.* 14, 1325) and $C_{16}H_{16}N_2O_3$ [213°], which is perhaps $CH_2(NHPh).CO.NPh.CH_2.CO_2H$, though this formula may also be assigned to an isomeric acid [130°] formed by the action of alcoholic potash on di-oxy-di-phenyl-pyrazine (Hausdörfer, *B.* 22, 1803; Abenius, *J. pr.* [2] 40, 432).

Properties.—Small crystals, m. sol. water, insol. ether. By fusion with potash at 260° it yields a mass which forms indigo on oxidation (Heumann, *B.* 23, 3043; *cf.* Lederer, *J. pr.* [2] 42, 383; Biedermann a. Lepetit, *B.* 23, 3289).

Salt.—CaA'_2 2aq. Needles (from dilute alcohol), m. sol. hot water, insol. alcohol. On distillation with calcium formate it yields indole (Mauthner a. Suida, *M.* 10, 251).

Methyl ether MeA'. [48°]. Formed by heating aniline with methyl chloro-acetate (Meyer, *B.* 8, 1157) and by the action of aniline on methyl diazo-acetate (Curtius, *J. pr.* [2] 38, 437). Rectangular plates (from ether) or needles (from alcohol).

Ethyl ether EtA'. [59°]. Formed in like manner. Colourless plates (from ether).

Formyl derivative $NPh(CHO).CH_2.CO_2H$. [124°]. Formed by saponification of its ether (290°–295°), which is the product of the action of chloro-acetic ether on sodium formanilide (Paal a. Otten, *B.* 23, 2593). Needles, v. sol. ether and hot water. Yields $C_9H_8NO_3Na$, a hygroscopic mass.

Acetyl derivative $NPhAc.CH_2.CO_2H$. [191°]. Formed from phenyl-amido-acetic acid, Ac_2O, and benzene (R.). Formed also by heating aniline with chloro-acetic acid and NaOAc at 110°–150° (Hausdörfer, *B.* 22, 1797), and by the action of boiling alcoholic potash on its ether (300°), which is got from sodium acetanilide and chloro-acetic ether (P. a. O.). Pearly plates (from water) or needles (from HOAc-ligroïn), v. sol. alcohol and hot water. Yields the salts NaA', $BaA'_2$3aq, and CuA'_2.

Chloro-acetyl derivative $CH_2Cl.CO.NPh.CH_2.CO_2H$. [133°]. Formed from phenyl-amido-acetic acid and chloro-acetyl chloride (Abenius, *J. pr.* [2] 40, 429, 499). Plates or prisms, v. sol. alcohol. On boiling with aqueous sodium carbonate it yields $CH_2(OH).CO.NPh.CH_2.CO_2H$ [128°], which crystallises in plates, forms the salts $CaA'_2$6aq and BaA'_2, the anhydride $PhN<\substack{CO.CH_2 \\ CH_2.CO}>O$ [169°], and the amide $CH_2(OH).CO.NPh.CH_2.CONH_2$ [129°].

Bromo-acetyl derivative. Plates, decomposing at 153° (Hausdörfer, *B.* 22, 1803).

Benzoyl derivative $CH_2(NPhBz).CO_2H$. [63°]. Amorphous pp. (Rebuffat).

Nitrosamine $NPh(NO).CH_2.CO_2H$. [105°]. Yellow needles (Schwebel, *B.* 11, 1132), v. sol. warm water.

Anhydride C_8H_7NO. [263°]. Got by heating the acid at 150° (Meyer, *B.* 10, 1967). Needles (from alcohol), insol. water.

Amide $CH_2(NHPh).CONH_2$. [133°]. Formed by heating chloro-acetamide with aniline and

NaOAc at 130° (Bischoff, *B.* 22, 1809; *cf.* Meyer, *B.* 8, 1154). Minute needles (from water).

Anilide $CH_2(NHPh).CO.NHPh$. [112°]. Formed by boiling chloro-acetic ether or $CH_2Cl.CO.NHPh$ with aniline (Wilm a. Wischin, *Z.* 1868, 74; Meyer, *B.* 8, 1156; Hausdörfer, *B.* 22, 1796). Formed also by heating aniline with alcohol and the compound of glyoxal with $NaHSO_3$ (Hinsberg, *B.* 21, 110). Needles (from alcohol), sl. sol. cold water.

p-Toluide $CH_2(NHPh).CO.NHC_6H_4Me$. [165°]. Formed by heating aniline with fused NaOAc and $CH_2Cl.CO.NHC_6H_4Me$ at 150° (Bischoff, *B.* 23, 2000; *cf.* Meyer, *B.* 8, 1158).

Nitrile $CH_2(NHPh).CN$. Formed from chloro-acetonitrile and aniline in ether at 90° (Engler, *B.* 6, 1004). Thick oil, forming a crystalline hydrochloride, decomposed by water.

Reference. — BROMO-PHENYL-AMIDO-ACETIC ACID.

Isomeride.—AMIDO-PHENYL-ACETIC ACID.

Di-phenyl-di-amido-acetic acid $C_{14}H_{14}N_2O_2$ *i.e.* $CH(NHPh)_2.CO_2H$. Formed as a yellow crystalline powder by adding aniline to an aqueous solution of glyoxylic acid (Böttinger, *B.* 11, 1559). Decomposed by hot water.

ω-PHENYL-AMIDO-ACETOPHENONE $C_{14}H_{13}ON$ *i.e.* $C_6H_5.CO.CH_2.NHPh$. *Aceto-phenone-anilide.* [93°]. Prepared by the action of aniline on ω-bromo-acetophenone (Möhlau, *B.* 14, 171; 15, 2467). Prisms or fine needles. Sol. alcohol, ether, chloroform, benzene, and CS_2. On boiling with aniline it gives phenyl-indole. Nitrous acid forms a nitrosamine $C_6H_5.CO.CH_2.NPh(NO)$ [73°].—B′HCl: prisms, decomposed by water.—B′HBr.

Acetyl derivative $C_{16}H_{15}NO_2$. [127°].

Benzoyl derivative. [145°]. Prisms.

PHENYL-AMIDO-ACRIDINE $C_6H_4\left<\begin{matrix}N—C.CH:C.NHPh\\CH.C.CH:CH\end{matrix}\right.$. [176°]. Formed by heating di-phenyl-*m*-phenylene-diamine (5 g.) with $ZnCl_2$ (10 g.) and formic acid (5 g. of 90 p.c.) for 5 hours at 250° (Besthorn a. Curtman, *B.* 24, 2042). Flat brownish-red needles, m. sol. alcohol, sl. sol. ether.

PHENYL-AMIDO-ACRIDYL-BENZOIC ACID $C_6H_4\left<\begin{matrix}N——————C.CH:C.NHPh\\C(C_6H_4.CO_2H).C.CH:CH\end{matrix}\right.$. [above 300°]. Formed by heating di-phenyl-*m*-phenyl-ene-diamine (5 g.) with phthalic anhydride (10 g.) at 250° (Besthorn a. Curtman, *B.* 24, 2047). Small red crystals, sol. HOAc.

PHENYL-AMIDO-ACRYLIC ACID $CH(NHPh):CH.CO_2H$. [194°]. Formed from the product of the action of aniline on di-bromo-succinic acid by boiling with potash (Reissert, *B.* 20, 3105). Insol. water, v. sol. alcohol.—$NaA'2\frac{1}{2}aq$: silky plates.

Ethyl ether EtA′. [144°].

PHENYL-AMIDO-AZOBENZENE *v.* *Benz-ene-*AZO-*diphenylamine.*

DI-PHENYL-AMIDO-BENZAMIDINE $C_{19}H_{17}N_3$ *i.e.* $C_6H_4(NH_2).C(NPh).NHPh$. *Carbo-triphenyltriamine.* [198°]. Prepared by heating *p*-nitro-benzoic acid with aniline and PCl_3 for two hours at 180° and reducing the product with tin and HCl (Weith, *B.* 12, 101). Formed also by the action of CCl_4, of CBr_4, and of $CCl_3.SO_2Cl$ on aniline (Hofmann, *Pr.* 9, 284; Bolas a. Groves, *A.* 160, 173; Michler a. Walder, *B.* 14, 2174). Four-sided tables. Split up by heating with HCl at 160° into aniline and *p*-amido-benzoic acid. Decomposed on distillation.—B′HCl. [282°].—$B'_2H_2PtCl_6$.

PHENYL-DIAMIDOBENZENE *v.* AMIDO-DIPHENYLAMINE.

TRI-PHENYL-TRI-AMIDO-BENZENE $C_6H_3(NHPh)_3$. [193°]. Made by heating phloro-glucin with aniline at 210° (Minunni, *B.* 21, 1984). Needles (from alcohol).—B′HCl: yellow powder, melting below 100°, decomposed by warm water.—$B'_2H_2PtCl_6$. [c. 250°].

Tri-acetyl derivative. [173°]. Needles.

Tri-benzoyl derivative. [above 300°].

PHENYL-AMIDO-BENZOIC ACID $C_6H_4(NHPh)CO_2H$. [222° uncor.]. Formed by oxidation of the methylo-iodide of phenyl-acridine with $MMnO_4$ (Claus a. Nicolaysen, *B.* 18, 2709). Small colourless needles. V. sol. ether and chloroform, insol. water.

Salts.—A′Na 4aq: easily-soluble colourless plates. — A'_2Ba 5aq: small sparingly-soluble colourless plates.—A′Ag^{x}: very sparingly-soluble white curdy pp.

PHENYL AMIDO-BENZYL KETONE $C_6H_5.CO.CH(NH_2).C_6H_5$. [60°–70°]. Formed by reducing the mono-oxim of benzil with HCl and $SnCl_2$ (Braun, *B.* 22, 556) and by heating desyl-phthalamic acid with HCl (Neumann, *B.* 23, 996). White crystalline mass, becoming brown in air.—B′HCl. [210°]. White needles.—$B'_2H_2PtCl_6$. [193°].—Picrate $B'C_6H_3N_3O_7$.

Carboxy-benzoyl derivative $C_6H_5.CO.CHPh.NH.CO.C_6H_4.CO_2H$. [168°]. Got by warming desyl-phthalimide with NaOHAq.—$AgC_{22}H_{16}NO_4$: crystalline.

Phenyl *p*-amido-benzyl ketone $C_6H_5.CO.CH_2.C_6H_4NH_2$. [95°]. S. ·33 at 100°. Formed by reducing nitro-benzil or nitro-deoxy-benzoïn with tin and HCl (Golubeff, *J. R.* 6, 114; 11, 101; *Bn.* 3, 109). Thin needles (from dilute alcohol).—B′HCl. Tables (from alcohol). S. ·25 in the cold.—$B'_2H_2PtCl_6$.—$B'_2H_2SO_4$.

Oxim $C_6H_5.C(NOH).CH_2.C_6H_4NH_2$. [141°]. Crystallises from alcohol (Ney, *B.* 21, 2449).

PHENYL-α-AMIDO-BUTYRIC ACID $C_{10}H_{13}NO_2$ *i.e.* $CH_3.CH_2.CH(NHPh).CO_2H$. [140°]. Prepared by heating α-bromo-butyric acid with an ethereal solution of aniline at 100° (Duvillier, *A. Ch.* [5] 20, 205; Nastvogel, *B.* 22, 1792. Feebly acid.—B′HCl.—EtA′. (278°).

Phenyl-β-amido-butyric acid $CH_3.CH(NHPh).CH_2.CO_2H$. [128°]. Formed by the action of baryta on the neutral isomeride (? betaïne) which is obtained, together with the anilide, by boiling β-chloro-butyric ether with aniline (Balbiano, *G.* 10, 144; *B.* 13, 312). Tufts of needles, sl. sol. water.—BaA'_2 (dried at 100°). Scales.—B′HCl.—$B'H_2C_2O_4$. [139°].

Anilide $CHMe(NHPh).CH_2.CO.NHPh$. The hydrochloride B′HCl [207°] crystallises in colourless plates, sl. sol. hot water.

Phenyl-α-amido-isobutyric acid $CMe_2(NHPh).CO_2H$. [185°]. Formed by saponi-fication of the nitrile or the ether (Tiemann, *B.* 15, 2042; Bischoff, *B.* 24, 1044). Concentric needles, m. sol. water. May be sublimed.

Ethyl ether EtA′. [30°]. (271°). Formed by heating aniline (2 mols.) with bromo-iso-butyric acid (1 mol.). Thick prisms.

Amide $CMe_2(NHPh).CONH_2$. [137°]. Needles, sol. alcohol and HClAq.

Nitrile $CMe_2(NHPh).CN$. [94°]. Made by heating acetone cyanhydrin with aniline. Long white prisms, sl. sol. hot water.

Di-phenyl-di-γ-amido-butyric acid. *Nitrile* $CH(NHPh)_2.CH_2.CH_2.CN$. [103°]. Formed by heating $CHO.CH_2.CH_2.CN$ with aniline at 350° (Chautard, *A. Ch.* [6] 16, 185). Scales, sol. water and alcohol.

PHENYL-AMIDO-CHLORO- *v.* CHLORO-PHENYL-AMIDO-.

PHENYL-β-AMIDO-CINNAMIC ACID $C_6H_5.C(NHPh):CH.CO_2H$.

Methyl ether MeA'. [93°]. Formed from methyl benzoyl-acetate and aniline (Knorr, *A.* 245, 372). Prisms.

Ethyl ether EtA'. Formed in like manner (Conrad a. Limpach, *B.* 21, 521). Oil, v. sol. alcohol. At 250° it yields (*Py.* 1,3)-oxy-phenyl-quinoline and alcohol.

Anilide $C_6H_5.C(NHPh):CH.CO.NHPh$. [133°]. Needles (from alcohol), almost insol. Aq.

PHENYL-AMIDO-CITRACONIC PHENYL-IMIDE? $\begin{matrix}C(NHPh).CO\\C(CH_3)-CO\end{matrix}>NPh$. [160°]. Formed by heating methyl-oxalacetic ether with aniline at 180° (Wislicenus a. Spiro, *B.* 22, 3351). Golden plates, v. sol. hot alcohol.

PHENYL-AMIDO-CRESOL $C_{13}H_{13}NO$ *i.e.* $NHPh.C_6H_3Me.OH$ [1:3:5]. [79°]. (345°). Formed by heating orcin (1 pt.), aniline (2 pts.), and $CaCl_2$ (1 pt.) at 260°–270° (Zega a. Buch, *J. pr.* [2] 33, 538). Thick needles (from alcohol). Reduced by distilling over zinc-dust to phenyl-*m*-tolyl-amine.

Salt.—B'HCl: crystalline powder, decomposed by water.

Isomeride: OXY-BENZYL-ANILINE.

PHENYL-AMIDO-CROTONIC ACID. *Methyl ether* $CH_3.C(NHPh):CH.CO_2Me$. [51°]. Formed by mixing aniline with methyl acetoacetate (Conrad a. Limpach, *B.* 21, 1965). Prisms (from MeOH). Yields (*Py.* 1,3)-oxy-methyl-quinoline when heated to 240°.

Ethyl ether $C_{12}H_{15}NO_2$ *i.e.* $CH_3.C(NHPh):CH.CO_2Et$. Formed by allowing a mixture of aniline (1 mol.) and acetoacetic ether (1 mol.) to stand for some days in the cold, drying with K_2CO_3, and filtering (Knorr, *B.* 20, 1397; *cf.* Conrad a. Limpach, *B.* 20, 944; 22, 83). Strongly refracting oil, split up by acids and alkalis into its components. At 200° it forms (*Py.* 1,3)-oxy-methyl-quinoline and a smaller quantity of oxy-phenyl-di-methyl-pyridine carboxylic ether.

The anilide of acetoacetic acid (vol. i. p. 19) $CH_3CO.CH_2.CONHPh$ [85°], which is isomeric with phenyl-amido-crotonic acid, is completely decomposed by heat, but yields the same oxy-methyl-quinoline on treatment with conc. HClAq.

PHENYL AMIDO-ψ-CUMYL KETONE $C_6H_5.CO.C_6HMe_3(NH_2)$ [5:1:3:4:6]. *Benzocumide.* [130°]. (c. 360°). Formed by saponification of its phthalyl derivative (Froehlich, *B.* 17, 1804, 2674). Long yellow needles or plates, v. sol. alcohol and ether, not volatile with steam.—$B'_2H_2PtCl_6$: orange needles. MeI forms $C_6HMe_3Bz.NMe_3I$ [187°], crystallising from water in prisms (containing aq). $ClCO_2Et$ gives $C_6HMe_3Bz.NH.CO_2Et$ [105°], crystallising in needles.

Acetyl derivative. [170°]. Needles.

Benzoyl derivative. [227°]. Needles.

Phthalyl derivative $C_6HMe_3Bz.N<\begin{matrix}CO\\CO\end{matrix}>C_6H_4$. [181°]. Formed by heating the phthalyl derivative of ψ-cumidine with BzCl and a little $ZnCl_2$ at 180°. Small rhombohedra, v. sol. hot water. On saponification by alcoholic potash it yields the acid $C_6HMe_3Bz.NH.CO.C_6H_4.CO_2H$ [195°], which crystallises in minute needles (containing aq).

PHENYL-AMIDO-CYANURIC ACID *v. Cyanuric acid* in the article CYANIC ACID.

PHENYL-AMIDO-ETHANE SULPHONIC ACID $C_6H_5NH.CH_2.CH_2.SO_3H$. *Phenyl-taurine.* [c. 280°].

Formation.—1. By heating the anilide with HCl.—2. By heating chloro-isethionic acid with an ethereal solution of aniline at 130° (Leymann, *B.* 18, 871; James, *C. J.* 47, 369; *J. pr.* [2] 31, 415).—3. By the oxidation of phenyl-thiohydantoïn with $KClO_3$ and HCl there is formed diphenyltaurocarbamic anhydride $C_{15}H_{14}N_2SO_3$ [186°], which is split up by boiling baryta-water into aniline, CO_2, and phenyl-taurine (Andreasch, *M.* 4, 137).

Properties.—Colourless leaflets, insol. alcohol and ether, sol. water forming an acid solution. Aqueous cyanamide at 110° forms phenyltaurocyamine $NH_2.C(NH).NPh.C_2H_4.SO_3H$, which crystallises from water in plates melting above 300°.—BaA'_2 3aq: leaflets, m. sol. water.

Anilide $NHPh.C_2H_4.SO_2NHPh$. [74°]. Formed, together with the anhydride $C_8H_9NSO_2$ [69°], by the action of an ethereal solution of aniline (3 mols.) on $CH_2Cl.CH_2SO_2Cl$ (1 mol.).—B'HCl. [169°]. Colourless crystals.

DI-PHENYL-AMIDO-ETHYL-AMIDO-ACETIC ACID $NHPh.CH_2.CH_2.NPh.CH_2.CO_2H$. [116°]. Formed from oxy-di-phenyl-pyrazine hexahydride and alcoholic potash (Bischoff, *B.* 23, 2026). Prisms, sol. ether. Converted into the parent substance by boiling with water or alcohol.

PHENYL AMIDO-ETHYL KETONE $C_6H_5.CO.C_2H_4NH_2$. Formed by the action of boiling HClAq on $C_2H_4Bz.N:C_2O_2:C_6H_4$ [85°], which is got from $C_6H_5.CO.C_2H_4Br$ and potassium phthalimide (Schmidt, *B.* 22, 3251).—B'HCl: crystalline, v. e. sol. water and alcohol.—$B'_2H_2PtCl_6$.—$B'C_6H_3N_3O_7$. [160°]. Needles.

PHENYL-AMIDO-ETHYL-PHTHALIMIDE $C_6H_4:C_2O_2:N.CH_2.CH_2.NHPh$. [100°]. Formed by heating bromo-ethyl-phthalimide with aniline at 150° (Gabriel, *B.* 22, 2224). Lemon-yellow needles, v. sol. dilute HClAq. Converted by NaOHAq into $C_6H_4(CO_2H).CO.NH.C_2H_4.NHPh$ [120°–130°], a crystalline powder.

PHENYL-AMIDO-FUMARIC IMIDE $C(NHPh)<\begin{matrix}CO——\\CH.CO\end{matrix}>NH$? [202°]. Formed by heating bromo-fumarimide with aniline (Löscher, *B.* 21, 2718). Golden plates, sl. sol. hot water.

PHENYL-AMIDO-GLUTACONIC PHENYL-IMIDE $C_{17}H_{14}N_2O_2$ *i.e.* $C(NHPh)<\begin{matrix}CH_2.CO\\CH.CO\end{matrix}>NPh$. [275°]. Formed from acetone dicarboxylic ether and aniline (Emery, *B.* 23, 3764). Yellowish plates, v. sl. sol. alcohol.

PHENYL-AMIDIMIDO-ETHENYL-o-AMIDO-PHENYL-MERCAPTAN $C_{14}H_{11}N_3S$ probably $C_6H_4<\substack{N\\S}>C.C(NHPh):NH$. [118°]. Formed together with the di-phenyl derivative by heating amido-imido-ethenyl-*o*-amido-phenyl-mercaptan with aniline, ammonia being evolved (Hofmann, *B.* 20, 2254). Plates. Sol. alcohol and ether.

Salts.—$B'H_2Cl_2PtCl_4$: small needles, m. sol. water.—$B'HClAuCl_3$: soluble yellow plates.

Di-phenyl-amidimido-ethenyl-o-amido-phenyl-mercaptan $C_{20}H_{15}N_3S$ which is probably $C_6H_4<\substack{N\\S}>C.C(NHPh):NPh$. [129°]. Obtained as above. White silvery plates. V. sol. alcohol and ether.

Salts.—$B''H_2Cl_2PtCl_4$: dark-yellow sparingly-soluble plates.—$B''H_2Cl_2Au_2Cl_6$: yellow needles.

PHENYL-AMIDO-JUGLONE *v.* JUGLONE.

PHENYL-AMIDO-MALEÏC ACID. The phenylimide $NHPh.C_2H:C_2O_2:NPh$ [232°] is formed, together with the mono-anilide $NHPh.C_2H(CO_2H).CONHPh$ [176°], by boiling dibromo-succinic acid or chloro- or bromo-maleïc or fumaric acids with aniline and water (Reissert a. Tiemann, *B.* 19, 626; Michael, *B.* 19, 1377). The phenylimide is also formed by heating aniline with oxalacetic ether at 140° (Wislicenus a. Spiro, *B.* 22, 3350).

PHENYL-AMIDO-MALONIC ACID. *Anilide.* $CH(NHPh)(CO.NHPh)_2$. [162°]. Formed by boiling chloro-malonic acid with aniline (Conrad a. Bischoff, *A.* 209, 231). Prisms.

PHENYL-AMIDO-METHENYL-AMIDO-NAPHTHOL $C_{10}H_6<\substack{O\\N}>C.NHPh$. [168°]. Formed from benzene-azo-(β)-naphthol by heating with CS_2 at 250° (Jacobson, *B.* 21, 419). Small needles, v. e. sol. cold alcohol. With HClAq at 190° it yields amido-(β)-naphthol, aniline, and CO_2.—Picrate [210°]. Acetate [120°–130°].

PHENYL-AMIDO-METHENYL-AMIDO-PHENYL MERCAPTAN $C_6H_4<\substack{N\\S}>C.NHPh$. [159°]. Formed from C_6H_4:NS:CCl and aniline (Hofmann, *B.* 12, 1130). Formed also by heating phenyl thiocarbimide with azobenzene at 270° (Jacobson a. Frankenbacher, *B.* 24, 1410). Needles, sol. alcohol, insol. water. Decomposed by alcoholic potash at 200° into aniline and amido-phenyl mercaptan.—B'HCl.—$B'HAuCl_4$.—$B'_2H_2PtCl_6$.—$B'C_6H_3N_3O_7$. [222°].

Acetyl derivative. [167°]. Needles.

PHENYL-AMIDO-METHENYL-AMIDO-PHENOL $C_6H_4<\substack{N\\O}>C.NHPh$. [173°]. Formed by boiling $C_6H_4<\substack{N\\O}>C.SH$ with aniline (Kalckhoff, *B.* 16, 1826). Needles, sol. alcohol, ether, and HOAc. May be distilled. Weak base.—$B'H_2PtCl_6$.

PHENYL-AMIDO-METHENYL-AMIDO-PHENYL-MERCAPTAN $C_{13}H_{10}N_2S$ *i.e.* $C_6H_4<\substack{N\\S}>C(NHPh)$. [159°]. Formed by heating chloro-phenyl-thiocarbimide with aniline (Hofmann, *B.* 12, 1129; 13, 12). Needles.

PHENYL-AMIDO-METHENYL-BENZ-AMIDESULPHIM $C_6H_5C<\substack{N.S\\N}>C.NHPh$. [174°]. Formed by boiling benzamidoxim (1 mol.) with phenyl thiocarbimide (2 mols.) for 10 hours (Koch, *B.* 24, 394). White plates, insol. water, sol. alcohol, ether, and conc. HClAq, insol. water and alkalis. Conc. HClAq at 150° decomposes it into S, H_2S, aniline, HOBz, and NH_3. Bromine forms $CPh:N_2S:CNH.C_6H_4Br$[1:4]. Yields a nitrosamine [119°] and an acetyl derivative [196°], both being crystalline.

PHENYL-AMIDO-METHYL-ACRIDINE $C_6H_4<\substack{N—C.CH:CNHPh\\CMe.C.CH:CH}$. [216°]. Formed by heating the di-acetyl derivative of *m*-phenylene-di-phenyl-diamine (1 pt.) with $ZnCl_2$ (2 pts.) for 6 hours at 250° (Besthorn a. Curtman, *B.* 24, 2044). Brownish-red needles, v. sol. alcohol. sl. sol. ether. Split up by HClAq at 250° into aniline and oxy-methyl-acridine.

DI-PHENYL-DI-AMIDO-METHYLENE-o-PHENYLENE-DIAMINE $C_6H_4<\substack{NH\\NH}>C(NHPh)_2$. [160°]. Formed from di-phenyl-cyanamide $C(NPh)_2$ and *o*-phenylene-diamine at 135° (Moore, *B.* 22, 1635; 3190). Needles (from benzene-ligroïn), insol. ligroïn, v. sol. alcohol. Yields with nitrous acid a nitrosamine $C_6H_4:N_2(NO)_2:C(NPhNO)_2$[138°]. Salts.—$B''_2H_3Cl_3$: needles, v. sol. water.—$B''H_2SO_4$: needles, sl. sol. hot water.—$B''_43H_2PtCl_6$ *x*aq.

Di-benzoyl derivative. [165°].

Tetra-benzoyl derivative. [148°].

TETRA-PHENYL-TETRA-AMIDO-DI-METHYLENE-o-PHENYLENE-DIAMINE $C_6H_4:N_2(C(NHPh)_2)_2$. [139°]. Formed by heating $C(NPh)_2$ with o-phenylene-diamine at 200° (Moore). Colourless prisms, v. sol. alcohol. Split up by heat into aniline and the preceding body.

Salts.—$B''_2H_3Cl_3$: needles, v. sol. hot water.—$B''_43H_2PtCl_6$.—$B''2H_2SO_4$: prisms, v. sol. hot water.

Tetra-acetyl derivative $C_6H_4:N_2(C(NPhAc)_2)_2$. [126°]. White prisms.

Tetra-benzoyl derivative. [182°].

DI-PHENYL-DI-AMIDO-METHYLENE-o-PHENYLENE-PHENYL-GUANIDINE $C_6H_4<\substack{N\\N}>C(NPh)>C(NHPh)_2$. [188°]. Formed from phenylene-phenyl-guanidine and $C(NPh)_2$ at 210° (Keller, *B.* 24, 2506). The homologous compound from o-tolylene-phenyl-guanidine melts at 200° while the corresponding body from o-tolylene-*p*-tolyl-guanidine melts at 176°. All three compounds crystallise from alcohol in white needles, sol. benzene.

PHENYL-AMIDO-METHYL-DI-ETHYL-PYRIMIDINE $N<\substack{CEt.CMe\\CEt{=}N}>C.NHPh$. [99°]. Formed from chloro-methyl-di-ethyl-pyrimidine (derived from cyanethine) by heating with aniline and alcohol at 220° (Von Meyer, *J. pr.* [2] 39, 274). Needles, v. sol. alcohol.—$B'_2H_2PtCl_6$: needles.

PHENYL-AMIDO-METHYL-MALONIC ACID. *Amic ether* $CO_2Et.CMe(NHPh).CONH_2$. [86°]. Formed by dissolving the nitrile in cold conc. H_2SO_4 and

pouring into water (Gersen, *B.* 19, 2965). The nitrile $CO_2Et.CMe(NHPh).CN$ [102°] is formed by heating $CO_2Et.CMe(OH).CN$ with an alcoholic solution of aniline for 24 hours at 80°. The amic ether crystallises in white needles, sol. hot water, and is converted by boiling aqueous NaOH into $CH_3.CH(NHPh).CO_2H$.

PHENYL-(α)-AMIDO-METHYL-NAPHTHO-PHENAZINE $C_6H_3Me{<}^{N}_{N}{>}C_{10}H_5NHPh$. [214°]. Formed by heating (1,3,4)-tolylene-diamine with benzene-azo-phenyl-(α)-naphthylamine hydrochloride and alcohol at 140° (Eicker, *B.* 23, 3806). Brass-yellow needles, forming yellowish-red solutions with yellowish-green fluorescence.—$B'_2H_2PtCl_6$: minute dark-red needles.

PHENYL-AMIDO-DI-METHYL-PYRIDINE $N{<}^{CMe:CH}_{CMe.CH}{>}C.NHPh$. *Phenyl-amido-lutidine.* [150°] (C. a. E.); [144°] (G. a. M.). (235°–238°). Obtained by heating chloro-di-methyl-pyridine with aniline at 185° (Conrad a. Epstein, *B.* 20, 165). Formed also by heating the corresponding oxy-di-methyl-pyridine (1 mol.) with phenyl cyanate (1 mol.) and benzene at 100°, CO_2 being evolved (Goldschmidt a. Meissler, *B.* 23, 274). White crystalline solid. V. sol. alcohol, ether, and dilute acids. With H_2SO_4 and a trace of HNO_3 it gives a blood-red colouration.—$^{\times}B'_2H_2Cl_2PtCl_4$: [209°] (C. a. E.); [204°] (G. a. M.), microscopic yellow needles.

PHENYL-AMIDO-DI-METHYL-PYRROLE $NHPh.N{<}^{CMe:CH}_{CMe:CH}$. [92°]. (c. 270°). Formed by heating its dicarboxylic acid, and also by the action of phenyl-hydrazine on acetonyl-acetone (Knorr, *B.* 18, 1568; 22, 170). Crystalline mass, volatile with steam. Insol. water and alkalis, sol. conc. HClAq. Reddens pine-wood moistened with HClAq.

PHENYL-AMIDO-DI-METHYL-PYRROLE-DICARBOXYLIC ACID $NHPh.N{<}^{CMe:C.CO_2H}_{CMe:C.CO_2H}$. Needles. Got from its ether Et_2A'' [127°], which is formed by mixing solutions of di-acetyl-succinic ether and phenyl-hydrazine in HOAc (Knorr, *B.* 18, 304, 1568).

PHENYL-(*Py.* 1)-AMIDO-(*Py.* 3)-METHYL QUINOLINE $C_6H_4{<}^{C(NHPh):CH}_{N\!=\!=\!=\!=\!CMe}$. [151°]. Formed by heating chloro-methyl-quinoline with aniline at 190° (Conrad a. Limpach, *B.* 20, 953). Prisms, sl. sol. ether, v. sol. alcohol.

Phenyl-(*Py.* 3)-amido-(*Py.* 1)-methyl-quinoline $C_{16}H_{14}N_2$. [130°]. Formed by heating (*Py.* 3,1)-chloro-methyl quinoline with aniline (Knorr, *A.* 236, 102). Shining plates. — $B'_2 2H_2PtCl_6$. [235°]. Yellow needles, insol. Aq.

Phenyl-(*Py.* 1)-amido-tri-methyl-quinoline $C_6H_2Me_2{<}^{C(NHPh):CH}_{N\!=\!=\!=\!=\!CMe}$. [150°]. Formed by heating the corresponding chloro-tri-methyl-quinoline with aniline at 185° (Conrad a. Limpach, *B.* 21, 528). Prisms (from dilute alcohol).

PHENYL-AMIDO-METHYL-THIAZOLE ${}^{CMe.N}_{CH\;.S}{>}C.NHPh$. [117°]. Formed by heating oxy-methyl-thiazole with aniline (Hantzsch a. Weber, *B.* 20, 3130), and by the action of chloro-acetone on phenyl-thio-urea (Traumann, *A.* 249, 47). Small white needles (from alcohol). Yields aniline when heated with HClAq at 240°.

PHENYL-AMIDO-NAPHTHALENE *v.* PHENYL-NAPHTHYL-AMINE.

Di-phenyl-di-amido-naphthalene *v.* DI-PHENYL-NAPHTHYLENE-DIAMINE.

Tri-phenyl-tri-amido-naphthalene $C_6H_4{<}^{C(NHPh):CH}_{C(NHPh):C.NHPh}$. [148°]. One of the products formed by heating benzene-azo-(α)-naphthylamine with aniline at 160° (Fischer a. Hepp, *A.* 256, 251). Needles, v. sol. alcohol. Yields phenyl-rosinduline and a yellow substance [140°] on oxidation.

Tetra-phenyl-tetra-amido-naphthalene $C_{10}H_4(NHPh)_4$. [191°]. Accompanies the preceding body. On oxidation it yields phenyl-amido-phenyl-rosinduline, di-phenyl-di-amido-naphthoquinone, and a body melting at 169°.

PHENYL-AMIDO-(α)-NAPHTHOQUINONE $C_{16}H_{11}NO_2$ *i.e.* $C_6H_4{<}^{CO.C.NHPh}_{CO.CH}$. [191°]. Formed by heating (α)-naphthoquinone with an alcoholic solution of aniline (Zincke, *B.* 12, 1645), by boiling phenyl-amido-(β)-naphthoquinone with HCl, and by the action of aniline and HOAc on oxy-(α)-naphthoquinone (Liebermann, *B.* 14, 1665). Long red needles, v. sol. hot alcohol and ether, insol. cold alkalis. Alcoholic potash forms a purple solution. Boiling dilute NaOH splits it up into aniline and oxy-(α)-naphthoquinone.

Anilide $C_6H_4{<}^{CO\text{——}CNPhH}_{C(NPh).CH}$. *Di-phenyl di-imidonaphthol.* [180°].

Formation.—1. By heating each of the naphthoquinone oxims with aniline and HOAc at 100° (Fuchs, *B.* 8, 1023; Brömme, *B.* 21, 393).—2. By heating di-imido-(α)-naphthol hydrochloride with aniline at 120° (Goës, *B.* 13, 124).—3. By boiling (β)-naphthoquinone with an alcoholic solution of aniline (Zincke, *B.* 15, 481).—4. By heating di-bromo-(α)-naphthol with aniline (Meldola, *C. J.* 45, 157).—5. By the action of aniline and aniline hydrochloride at 100° on benzene-azo-(α)-naphthol, on benzene-azo-(α)-naphthylamine, and on similar bodies (Fischer a. Hepp, *B.* 21, 679).

Properties.—Orange-red needles (from alcohol), forming orange solutions in benzene, acetone, and $CHCl_3$. Weak base. Its solution in HOAc is orange when hot, but crimson when cold. Hot HClAq forms a red solution. Insol. alkalis. Not attacked by boiling with alkalis, or by Ac_2O, AcCl, and MeI. H_2SO_4 at 120° yields oxy-naphthoquinone and aniline. Zinc-dust and HOAc reduce it to aniline and naphthalene. Alcoholic HCl or EtBr at 150° yields aniline and phenyl-amido-(α)-naphthoquinone. HNO_3 forms a di-nitro-derivative [143°].

S a l t s.—B'HCl: golden-green plates, forming a violet solution in alcohol. Decomposed by water. — $B'_2H_2PtCl_6$: bronze needles. — $B'_2H_2ZnCl_4$: bronze-green plates.—B'HI: black needles.—$B'_2H_2SO_4$.—$B'HNO_3$: plates.

Di-anilide $C_{10}H_5(NPh)_2(NHPh)$. [159°]. A product of the action of benzene-azo-(α)-naphthylamine on aniline (Fischer a. Hepp, *A.* 262, 246). Orange-yellow prisms.

Phenyl-amido-(β)-naphthoquinone $C_{10}H_5O_2(NHPh)$ or $C_6H_4<\begin{matrix}CO - COH \\ C(NPh).CH\end{matrix}$. *Oxy-(α)-naphthoquinone anilide.* '*(β)-Naphthoquinone anilide.*' [245°–250°]. Prepared by adding aniline to an alcoholic solution of (β)-naphthoquinone (Zincke, *B.* 14, 1494; 15, 279; Liebermann, *B.* 14, 1664). Red needles, sl. sol. alcohol. Weak acid. Readily converted by boiling with HOAc into the isomeric phenyl-amido-(α)-naphthoquinone. Boiling HClAq splits it up into aniline and oxy-(α)-naphthoquinone. Nitrous acid passed into a solution in alcohol and HOAc forms a nitroso- derivative $C_{16}H_{10}N_2O_3$, crystallising in red needles, and converted by NaOHAq into a yellow body [217°].

S a l t s.—BaA'_2: red needles, sl. sol. water.—PbA'_2: brown pp.—ZnA'_2.—HgA'_2.—AgA': red pp.

Methyl ether MeA'. [151°]. Formed from the Ag salt and MeI. Yellow needles, sol. alcohol and ether.

Ethyl ether EtA'. [104°]. Prisms.

n-Propyl ether PrA'. [104°]. Prisms.

Isopropyl ether PrA' [100°].

Di-phenyl-amido-(α)-naphthoquinone $C_{10}H_5O_2(NPh_2)$. [164°]. Formed by boiling (α)-naphthoquinone (5 g.) with diphenylamine (6 g.), alcohol, and conc. HClAq (10 c.c.) for twenty minutes, and ppg. with water (Plimpton, *C. J.* 37, 644). Needles (from alcohol).

Acetyl derivative $C_{22}H_{14}AcNO_2$. [173°].

PHENYL-AMIDO-NAPHTHYL-UREA $NHPh.CO.NH.C_{10}H_6.NH_2$. Formed from (1,2)-naphthylene-diamine and phenyl cyanate (Schieffelin, *B.* 22, 1377; *cf.* Goldschmidt, *B.* 23, 502). Granules (from alcohol); not fused at 335°.

DI-PHENYL-DI-AMIDO-OIAZTHIOLE $S<\begin{matrix}C(NHPh):N \\ C(NHPh):N\end{matrix}$. [181°]. Formed by adding hydrogen peroxide solution (3 p.c.) to phenyl-thio-urea dissolved in dilute alcohol, acidulated with HCl (Hector, *B.* 22, 1176). Needles, insol. water, v. sl. sol. cold alcohol. Nitrous acid forms $C_{14}H_{11}(NO)N_4S$, a green insoluble powder, exploding at 179°. Cyanogen passed into the warm alcoholic solution ppts. $C_{16}H_{12}N_6S$, crystallising in needles. — $B'HNO_3$. — $B'_2H_2PtCl_6$. — $B'AgNO_3$ aq: granules, v. sl. sol. hot alcohol.

Acetyl derivative $C_{14}H_{11}AcN_4S$. [233°].

Benzoyl derivative $C_{14}H_{11}BzN_4S$. [238°].

PHENYL-AMIDO-PALMITIC ACID $C_{16}H_{31}(NHPh)O_2$. [142°]. Formed by boiling α-bromo-palmitic acid with aniline (Hell a. Jordanoff, *B.* 24, 942). Sol. ether and benzene.

PHENYL-AMIDO-PHENOL *v.* OXY-DI-PHENYL-AMINE.

Di-phenyl-di-amido-phenol. *Hydrochloride* $(C_6H_3(NHPh)_2OH)HCl$. [192°]. Formed from azophenin, Sn, and HCl in presence of AcOH (Fischer a. Hepp, *A.* 256, 260). Plates.

PHENYLAMIDO-PHENYL-ACETIC ACID $C_{14}H_{13}NO_2$ *i.e.* $C_6H_5.CH(NHPh).CO_2H$. [164°–168°] (S.). Formed by saponification of the nitrile (Tiemann a. Piest, *B.* 15, 2030), and also by boiling bromo-phenyl-acetic acid with aniline and alcohol (Stöckenius, *J.* 1878, 779). Plates, subliming at 175° as slender white needles (T. a. P.). V. sl. sol. water, sol. alcohol.—HA'HCl: nodules, decomposed by water.—$HA'HNO_3$: thin needles.—BaA'_2: radiating mass.

Ethyl ether EtA'. [84°]. Needles.

Amide $C_6H_5.CH(NHPh).CONH_2$. Silky plates, v. sol. alcohol, nearly insol. ligroïn.

Nitrile $C_6H_5.CH(NHPh).CN$. [85°]. Formed by heating an alcoholic solution of the cyanhydrin of benzoic aldehyde with aniline at 100°. Formed also by the action of KCy and HCl on benzylidene-aniline (Cech, *B.* 11, 246). Needles or prisms, sol. ether and hot alcohol.

Phenyl-amido-di-phenyl-acetic acid $CPh_2(NHPh).CO_2H$. [168°]. Formed by passing HCl into an alcoholic solution of benzilic acid and treating the resulting $CPh_2Cl.CO_2Et$ with aniline (Klinger a. Standke, *B.* 22, 1212). Needles, v. sl. sol. water. Conc. H_2SO_4 forms a yellow solution, becoming crimson on warming.

Methyl ether MeA'. [107°]. Monoclinic.

Ethyl ether EtA'. [115°].

PHENYL-AMIDO-PHENYL-ACRIDINE $C_6H_4<\begin{matrix}N - C.CH:C.NHPh \\ CPh.C.CH:CH\end{matrix}$. [197°]. Formed by heating the di-benzoyl derivative of *m*-phenylene-di-phenyl-di-amine (10 g.) with $ZnCl_2$ (25 g.) at 250° (Besthorn a. Curtman, *B.* 24, 2045). Brownish-red needles, m. sol. alcohol, ether, and benzene. The dilute ethereal solution exhibits a greenish fluorescence. The h y d r o c h l o r i d e is v. sl. sol. water, and forms a red solution in alcohol.

DI-PHENYL-DI-AMIDO-TRI-PHENYL-CARBINOL $C_{31}H_{26}N_2O$ *i.e.* $CPh(OH)(C_6H_4.NHPh)_2$. Formed by heating diphenylamine with benzyl chloride and oxidising the product with arsenic acid. Formed also by heating diphenylamine with $ZnCl_2$ and benzoyl chloride or benzotrichloride, the resulting chloride $C_{31}H_{25}N_2Cl$ being decomposed by alcoholic NH_3 (Meldola, *C. J.* 41, 187). Amorphous, v. sol. ether, sol. hot alcohol and acetone. The c h l o r i d e $C_{31}H_{25}N_2Cl$, called 'diphenylamine green,' forms bronzed granules, and, in alcoholic solution, dyes wool bluish-green, and gives a dark-green pp. with H_2PtCl_6. Hot H_2SO_4 converts the chloride into the sulphonic acid $C_{31}H_{24}N_2SO_3$, ppd. by water in dark-green flakes.

Tri-phenyl-tri-amido-tri-phenyl-carbinol. The c h l o r i d e $CCl(C_6H_4NHPh)_3$, or 'diphenylamine blue,' is obtained by heating diphenylamine (1 pt.) with oxalic acid (2 pts.) (Willm a. Girard, *D. P. J.* 221, 192; Hausdörfer, *B.* 23, 1963). Formed also by heating pararosaniline with aniline. Brownish-red powder, v. sol. hot aniline and nitro-benzene, sl. sol. cold alcohol.

Hexa-phenyl-tri-amido-tri-phenyl-carbinol $C(OH)(C_6H_4.NPh_2)_3$. Formed by the action of alcoholic NH_3 on the chloride $C(C_6H_4.NPh_2)_3Cl$, which is got by heating triphenylamine with $COCl_2$ at 190° (Heydrich, *B.* 19, 758). White amorphous pp., forming a bluish-violet solution in H_2SO_4, turned blue by addition of alcohol.

PHENYLAMIDO-PHENYL-ISOCROTONIC ACID $C_6H_5.CH:CH.CH(NHPh).CO_2H$. [154°]. Formed by saponification of the nitrile (Peine, *B.* 17, 2116). Minute needles, v. sol. alcohol and ether.

Amide. [171°]. Thin plates.

Nitrile $C_8H_8(NHPh).CN$. [130°]. Formed by heating CHPh:CH.CH(OH).CN with aniline in alcoholic solution. Crystalline solid, sol. hot alcohol.

PHENYLAMIDO-PHENYL-ETHYL-KETONE $C_2H_4(NHPh).CO.C_6H_5$. *Homophenacylanilide.*

[38°]. Formed from phenyl bromo-ethyl ketone and aniline in alcoholic solution (Pampel a. Schmidt, *B.* 19, 2897). Yellow crystals. Yields an acetyl derivative [103°].

PHENYL - AMIDOPHENYL - HYDRAZINE. *Acetyl derivative* $C_6H_5.N_2H_2.C_6H_4.NHAc$. [146°]. Got by reduction of $C_6H_5.N_2.C_6H_4.NHAc$ with alcoholic ammonium sulphide (Schultz, *B.* 17, 463). Glistening plates, v. sol. alcohol and ether. $SnCl_2$ reduces it to aniline and *p*-phenylene-diamine. Conc. HClAq forms a blue compound.

PHENYLAMIDO - DI - PHENYL - METHANE $CH_2Ph.C_6H_4NHPh$. [c. 89°]. Formed by heating diphenylamine with benzyl chloride and $ZnCl_2$ at 100° (Meldola, *C. J.* 41, 198). White powder, v. sol. benzene, insol. alcohol.

Di-phenyl-di-amido-tri-phenyl-methane $C_{31}H_{26}N_2$ *i.e.* $CHPh(C_6H_4.NHPh)_2$. [c. 170°]. Formed by heating diphenylamine with benzylidene chloride, and also from diphenylamine, benzoic aldehyde, and $ZnCl_2$ (Meldola, *C. J.* 41, 192). White granules, v. sol. ether, yielding diphenylamine green on oxidation.

Reference. — CHLORO - DIPHENYLDIAMIDOTRIPHENYLMETHANE.

PHENYLAMIDO-PHENYL-METHYL-PYRIMIDINE $CPh\begin{smallmatrix}\diagup N{:}CMe\text{——}\diagdown\\ \diagdown N.C(NHPh)\diagup\end{smallmatrix}CH$. [150°-153°]. Formed from chloro-phenyl-methyl-pyrimidine and aniline (Pinner, *B.* 18, 2852).—$B'HNO_3$ [87°].—$B'HCl$. [240°]. Long slender needles.

PHENYLAMIDO - PHENYL - PROPIONIC ACID. *Nitrile* $CH_3.CPh(NHPh).CN$. [152°]. Formed by digesting an ethereal solution of acetophenone cyanhydrin and aniline at 50° (Jacoby, *B.* 19, 1515). White prisms (from alcohol). With alcoholic hydroxylamine it yields the oxim of acetophenone. Alcoholic HCl gives *s*-tri-phenyl-benzene.

Amide $CH_3.CPh(NHPh).CO.NH_2$. [119°]. Formed from the nitrile by heating with H_2SO_4 at 100° and pouring into water. Insol. water.

PHENYL-AMIDO- TRI-PHENYL-PYRROLE $\begin{smallmatrix}CH:CPh\\ CPh:CPh\end{smallmatrix}\!\!>\!N.NHPh$. [232°]. Formed from anhydracetophenone-benzil (1 mol.) and phenylhydrazine (2 mols.) in alcoholic solution at 100° (Japp, *B.* 21, 551; 22, 2885). Yellow needles.

PHENYL - AMIDO - TRI-PHENYL-QUINOXALINE DIHYDRIDE $\left[\begin{smallmatrix}3\\1\,4\end{smallmatrix}\right]C_6H_3(NHPh)\begin{smallmatrix}\diagup NPh.CHPh\\ \diagdown N{=\!=}CPh\end{smallmatrix}$. [223°]. Formed by heating di-phenyl-(1,3,4)-tri-amido-benzene with benzoïn at 160° (Fischer, *B.* 24, 722). Yellow plates, sl. sol. alcohol, forming a yellow solution with green fluorescence.

PHENYLAMIDO - PHENYL-ROSINDULINE $\left[\begin{smallmatrix}1\\4\,2\end{smallmatrix}\right]C_6H_3(NPh)\begin{smallmatrix}\diagup N - C\text{————————}\diagdown\\ \diagdown NPh.C.CH:C(NHPh)\diagup\end{smallmatrix}C_6H_4$. [192°]. Formed by heating benzene-azo-(α)-naphthyl-amine with aniline and benzene (Fischer a. Hepp, *A.* 262, 237). Formed also by oxidation of (1,2,3,4)-tetra-phenyl-tetra-amido-naphthalene (Fischer a. Hepp, *A.* 256, 252). Bronzed plates, forming a dark-green solution in conc. H_2SO_4, becoming reddish-violet on dilution. —$B'HCl$: bronzed plates.

TRI - PHENYL - TRI - AMIDO - DI-PHENYL-TOLYL-CARBINOL $C(OH)(C_6H_4.NHPh)_2(C_7H_6.NHPh)$. *Aniline blue. Lyons blue. Triphenylrosaniline.* Formed, together with mono- and di-phenyl-rosaniline by heating rosaniline acetate or benzoate with aniline (Girard a. De Laire, *D. P. J.* 162, 297; Hofmann, *Pr.* 12, 578; 13, 9). Prepared by heating rosaniline (1 pt.) with aniline (10 pts.) and a little benzoic acid, dissolving in alcoholic NH_3, and pouring into water. White pp., insol. water, v. sol. alcohol, m. sol. ether. Yields di-phenyl-amine on distillation. Reduced by zinc and HCl to tri-phenyl-tri-amido-di-phenyl-tolyl-methane or tri-phenyl-leucaniline (Hofmann, *C. R.* 57, 25).—$C_{38}H_{32}N_3Cl$. *Spirit soluble blue. Opal blue.* Small brassy crystals, insol. water and ether, sl. sol. alcohol. Becomes brown at 100°. Left with coppery lustre on evaporation of the alcoholic solution. Blue dye.—$(C_{38}H_{32}N_3)_2SO_4$: v. sl. sol. alcohol. The salts of mono-phenyl-rosaniline dye violet, those of di-phenyl-rosaniline a bluish-violet. Tri-phenyl-rosaniline yields mono-, di-, tri-, and tetra- sulphonic acids, the Na salts of which are v. sol. water and dye wool blue (Nicholson; Bulk, *B.* 5, 417).

The mono- and di- sulphonic acids are known as *Nicholson's* or *Alkali blue*, the tri-sulphonic acid as *Soluble blue.*

Reference.—TRI-CHLORO-TRI-PHENYL-ROSANILINE.

TRI-PHENYL-AMIDO-PHOSPHIDE OXIDE $PO(NHPh)_3$. [208°]. Formed from $POCl_3$ and aniline (Michaelis a. Soden, *A.* 229, 334). Six-sided plates, insol. water, sl. sol. ether and alcohol, v. sol. HOAc. Yields $PO(NHC_6H_3Br_2)_3$ crystallising in needles [253°]. The compound $HO.PO(NHPh)_2$ [197°] may be got by treating aniline with ether and $POCl_3$, followed by water.

TRI - PHENYL - TRI - AMIDO - PHOSPHINE SULPHIDE $PS(NHPh)_3$. [153°]. Formed from aniline and P_2S_5 below 150° (Knop, *B.* 20, 3352). Monoclinic crystals.

PHENYLAMIDO-PROPIONIC ACID $C_9H_{11}NO_2$ *i.e.* $CH_3.CH(NHPh).CO_2H$. [162°]. Formed by saponification of the nitrile or of the ether (Tiemann a. Stephan, *B.* 15, 2036; Nastvogel, *B.* 22, 1792; 23, 2010). Plates (from hot water), sol. alcohol. May be sublimed. Yields a hydrochloride decomposed by water, and a white silver salt.

Ethyl ether EtA'. (272°). S.G. $\frac{19.5}{19.5}$ 1·060. Formed by heating α-bromo-propionic ether with aniline on the water-bath. Oil.

Formyl derivative $CH_3.CH(NPh.CHO).CO_2H$. Prepared from NaNPh(CHO) and α-bromo-propionic ether (Paal a. Otten, *B.* 23, 2597). Large prisms, sol. alcohol and ether.—BaA'_2 aq: white powder.

Acetyl derivative $CH_3.CH(NAcPh).CO_2H$. [143°]. Plates (from hot benzene), sl. sol. cold water.—$NaC_{11}H_{12}NO_3$ 3aq. plates.—EtA'. (294°-298°). Oil, formed from sodium acetanilide and α-bromo-propionic ether.

Amide $CH_3.CH(NHPh).CONH_2$. [141°]. Plates, sol. alcohol and hot water.

Anilide $CH_3.CH(NHPh).CO.NHPh$. [126°]. Needles, v. sol. hot water.

Nitrile $CH_3.CH(NHPh).CN$. [92°]. Formed by heating the cyanhydrin of acetic aldehyde with aniline (T. a. S.). White plates, sol. alcohol and ether. Weak base.—$B'HCl$. [86°].

Isomerides *v.* AMIDO-PHENYL-PROPIONIC ACID.

Di-phenyl-di-amido-propionic acid. *Nitrile.* $CH(NHPh)_2.CH_2CN$. [113°]. Formed by heating $CHO.CH_2CN$ with aniline for 20 hours at 310° (Chautard, *A. Ch.* [6] 16, 180). Needles, v. sol. water and benzene.—$B'HCl$.—$B'_2H_2PtCl_6$: small yellow needles, v. sol. water.

Reference.—TRI-BROMO-PHENYL-AMIDO-PROPIONITRILE.

PHENYL-β-AMIDO-PROPYL-PHTHALIMIDE $C_6H_4:C_2O_2:N.CH_2.CHMe.NHPh$. [93°]. Formed from β-bromo-propyl-phthalimide and aniline (Seitz, *B.* 24, 2631). Yellow needles. Decomposed by HCl at 190° into phthalic acid and propylene-diamine.

Phenyl-γ-amido-propyl-phthalimide $C_6H_4:C_2O_2:N.CH_2.CH_2.CH_2.NHPh$. [89°]. Formed by heating γ-bromo-propyl-phthalimide (54 g.) with aniline (37 g.) at 150° (Goldenring, *B.* 23, 1168). Yellow crystals (from boiling ligroïn). Split up by heating with HCl, yielding phenyl-trimethylene-diamine.

PHENYLAMIDO-PROPYL-UREA $NHPh.C_3H_6.NH.CO.NH_2$. [98°]. Formed by warming $C_3H_6(NH_3Cl).NHPh$ with potassium cyanate at 100° (Goldenring, *B.* 23, 1173). Rose-coloured needles, v. sol. alcohol. Decomposes at 120° in NH_3 and phenyl-trimethylene-urea.

PHENYLAMIDO-PYROTARTARIC ACID $CO_2H.CH_2.CMe(NHPh).CO_2H$. *Anilido-methyl-succinic acid.* [102°]. Obtained by saponification of its ether (Schiller-Wechler, *B.* 18, 1037). White needles (containing aq.), v. sol. hot water and alcohol, nearly insol. ether. Its solution in KOHAq is colourless. NH_3Aq forms a violet solution.—CuA″ aq.—CuA″NH_3: green pp.—$H_2A''HCl$ aq: white crystalline solid.

Ethyl ether of the mono-amide $CO_2Et.CH_2.CMe(NHPh).CONH_2$. [125°]. Formed by digesting $CO_2Et.CH_2.CMe(OH).CN$ with aniline in ether, dissolving the resulting compound $CO_2Et.CH_2.CMe(NHPh).CN$ in H_2SO_4, and pouring into water. Plates, sol. hot water. Converted into the imide by heating with water, alcohol, acids, or alkalis.

Imide $\begin{matrix}CH_2.CO\\NHPh.CMe.CO\end{matrix}\!\!>\!NH$. [150°]. Formed as above. White prisms, sol. alcohol and hot water. Yields a nitrosamine $C_{11}H_{11}(NO)N_2O_2$ [173°], an acetyl derivative [235°], and a benzoyl derivative [190°].

Methylimide $\begin{matrix}CH_2.CO\\NHPh.CMe.CO\end{matrix}\!\!>\!NMe$. [103°]. Formed from the imide, MeI, MeOH, and KOH. Prisms. Yields a nitrosamine $C_{12}H_{13}N_3O_3$ crystallising in needles [147°]. Forms also $C_{12}H_{13}MeN_2O_2Me_2PtCl_6$, which is sl. sol. Aq.

Phenylimide $\begin{matrix}CH_2.CO\\NHPh.CMe.CO\end{matrix}\!\!>\!NPh$. So-called '*n-Phenyl-α-keto-γ-oxy-β-α$_1$-dimethyl-β-anilido-α$_1$-tetra-hydropyridine carboxylic lactone.*' [131°]. A product of the action of heat on phenylamido-pyrotartaric acid (Reissert, *B.* 21, 1385; Anschütz, *A.* 261, 140). Prisms (from alcohol). Its acetyl derivative [169°] forms tabular crystals.

Mono-anilide $C_3H_5(NHPh)(CO_2H)(CONHPh)$. [150°]. Got by boiling the phenylimide with NaOHAq. Forms with nitrous acid a compound melting at 204°.

Acetyl derivative of the anhydride $\begin{matrix}CH_2.CO\\NAcPh.CMe.CO\end{matrix}\!\!>\!O$. [136°]. Got by boiling the acid with AcCl (Anschütz). Tables, v. sol. chloroform, sl. sol. ether.

Acetyl derivative of the anilide $C_3H_5(NAcPh)(CO_2H)(CONHPh)$. [141°]. Formed from the preceding body by the action of aniline on its ethereal solution. Prisms.

PHENYL-(*Py.* 3)-AMIDO-QUINOLINE $C_6H_4\!\!<\!\begin{matrix}CH:CH\\N\ :C.NHPh\end{matrix}$. *Phenyl-quinolinamine.* [98°]. (above 360°). Formed by heating (*Py.* 3)-chloro-quinoline with aniline (Friedländer a. Weinberg, *B.* 18, 1532). White plates.

Reference.—BROMO-PHENYL-AMIDO-QUINOLINE.

PHENYL-AMIDO-QUINOLINEQUINONE-ANILIDE $\begin{matrix}CH:C(NHPh).C.CH:CH\\C(NPh).CO\ \ .C.\ N\ :CH\end{matrix}$. [222°]. Formed by adding excess of aniline to an alcoholic solution of $\begin{matrix}CH\ :CCl\\CCl_2.CO\end{matrix}\!\!>\!C_5H_3N$ (Hebebrand, *B.* 21, 2986). Long needles (from alcohol and HOAc), forms a deep-blue solution in dilute HClAq. — $B'HCl$: dark-golden needles. — *Acetate.* [199°]. Bronzed needles, decomposed by water.—$B'C_6H_3N_3O_2$. Coppery needles.

PHENYLAMIDO-QUINONE. *Dianilide* $C_6H_3(NPh)_2(NHPh)$[1:4:2]. [230°]. Formed from azophenine and HCl at 160° (Fischer a. Hepp, *A.* 256, 261). Reddish-brown needles, forming a blue solution in conc. H_2SO_4.

Di-phenyl-di-amido-quinone $C_6H_2O_2(NHPh)_2$[1:4:2:5]. *Quinone dianilide.* Formed, together with hydroquinone, by boiling quinone with an alcoholic solution of aniline (Hofmann, *Pr.* 13, 4; Wichelhaus, *B.* 5, 851; Zincke, *B.* 16. 1556; Knapp a. Schultz, *A.* 210, 178). Formed also by heating chloro-quinone with aniline and HOAc (Niemeyer, *A.* 228, 332) and by strongly heating aniline with di-oxy-quinone (Nietzki a. Schmidt, *B.* 22, 1655). Small violet plates, sol. HOAc and aniline, nearly insol. alcohol. May be sublimed. Conc. H_2SO_4 forms a reddish-violet solution.

Anilide $C_6H_2(NHPh)_2\!\!<\!\begin{matrix}O\\NPh\end{matrix}$. [203°]. A product of the action of aniline on quinone in HOAc (Zincke a. Hagen, *B.* 18, 785), on o-nitro-phenol (Fischer a. Hepp, *A.* 262, 247), and on quinone phenylimide (Bandrowski, *M.* 9, 415). Reddish-brown needles, forming a blood-red solution in H_2SO_4. On warming with alcoholic H_2SO_4 it yields $C_6H_2(NHPh)(OEt)\!\!<\!\begin{matrix}O\\NPh\end{matrix}$. Alcoholic potash forms $C_{18}H_{14}N_2O_3$ crystallising in red needles [192°], v. sol. alcohol, and forming a green solution in H_2SO_4.

Di-anilide $C_6H_2(NHPh)_2(NPh)_2$ is AZOPHENINE.

DI-PHENYL-DI-*p*-AMIDO-QUINONE DI-CARBOXYLIC ETHER $C_6(NHPh)_2O_2(CO_2Et)_2$[1:4:2:5:3:6]. *Di-anilido-quinone di-carboxylic ether.* [246°]. Formed by the action of aniline in alcoholic solution upon *p*-di-chloro-quinone-di-carboxylic ether $C_6Cl_2O_2(CO_2Et)_2$ (Hantzsch a. Zeckendorf, *B.* 20, 1312). Glistening garnet-red crystals.

PHENYLAMIDO-SUCCINIC ACID $CO_2H.CH_2.CH(NHPh).CO_2H$. *Phenylaspartic acid.* [132°]. Formed by boiling bromo-succinic

acid with aniline, and by the decomposition of an aqueous solution of acid maleate of aniline (Anschütz a. Wirtz, *Am.* 9, 248; *A.* 239, 140). Small crystals.—$H_2A''HCl$: monoclinic prisms.

Phenylimide $C_2H_3(NHPh):C_2O_2:NPh$. [211°]. Formed by heating maleïc anhydride with aniline. Formed also, together with the *dianilide* $C_2H_3(NHPh)(CONHPh)_2$ [206°], by heating asparagine with aniline (Piutti, *G.* 14, 474). Small needles (from alcohol). Yields a nitrosamine [180°]. Alcoholic NH_3 forms the amide-anilide [200°]. The dianilide yields a nitrosamine [190°].

Imide. [158°]. Formed from bromo-succinimide and aniline (Kusseroff, *A.* 252, 158).

Ethyl ether $C_2H_3(NHPh)(CO_2Et)_2$. (214°). Oil, forming a crystalline sulphate.

Di-phenyl-di-amido-succinic acid $CO_2H.CH(NHPh).CH(NHPh).CO_2H$. [c. 190°]. Formed by saponifying its ether, which is formed by heating di-bromo-succinic ether with aniline in alcohol (Lopatine, *C. R.* 105, 230; Gorodetzky a. Hell, *B.* 21, 1796). Plates (from HOAc), nearly insol. water, m. sol. alcohol.

Ethyl ether Et_2A''. [150°]. Needles. Forms with Br a hexa-bromo- derivative [104°].

PHENYL-AMIDO-SULPHO-BENZOIC ACID $C_6H_3(NHPh)(SO_3H).CO_2H$ [1:2:4]. Formed from bromo-sulpho-benzoic acid and alcoholic aniline (Fischer, *B.* 24, 3802). Plates.—BaA'' 5aq.—$(NH_3Ph)HA''$: needles (from water).

PHENYL-AMIDO-THIAZOLE $C_9H_8N_2S$ *i.e.* $\begin{matrix}S.C(NHPh)\\CH{=\!=}CH\end{matrix}\!\!>\!N$. [126°]. Formed by the action of phenyl-thio-urea on di-chloro-di-ethyl ether (Hantzsch a. Traumann, *B.* 21, 940; *A.* 249, 47). Small white needles, sl. sol. water, v. sol. alcohol.

PHENYLAMIDO-TOLUQUINONE $C_{13}H_{11}NO_2$ *i.e.* $C_6H_2Me(NHPh)O_2$. [145°]. Formed in small quantity, together with di-phenyl-amido-toluquinone and its phenylimide, by the action of aniline in alcohol and HOAc on toluquinone (Hagen a. Zincke, *B.* 16, 1559). Red needles (from dilute alcohol).

Anilide $C_6H_2Me(NHPh)\!<^{NPh}_{O}$. [151°]. Formed by reducing the anilide of di-phenyl-di-amido-toluquinone with $SnCl_2$ and HOAc (Fischer a. Hepp, *A.* 256, 259). Red needles.

Di-phenyl-di-amido-toluquinone $C_6HMe(NHPh)_2O_2$. [233°]. Formed as above. Brown needles (from alcohol), forming a red solution in H_2SO_4.

Anilide $C_6HMe(NHPh)_2\!<^{NPh}_{O}$. [173°].

Toluquinone trianilide. Formed as above, and also by heating nitroso-o-cresol (tolu-quinone mono-oxim) (1 pt.) with aniline (4 pts.) and aniline hydrochloride (2 pts.) (O. Fischer a. Hepp, *B.* 21, 678). Brown plates with bluish lustre, sol. hot alcohol.—$B'HI$. Brownish needles.—$B'_2H_2PtCl_6$.—$B'HBr$: dark-green needles.

PHENYLAMIDO-TOLYL-ACETIC ACID $C_{15}H_{15}NO_2$ *i.e.* [1:3]$C_6H_4Me.CH(NHPh).CO_2H$. [139°]. Formed by saponifying its nitrile, which is made by heating $C_7H_7.CH(OH)CN$ with aniline in ether at 100° (Bornemann, *B.* 17, 1471). Silvery plates (from dilute alcohol), v. sol. hot Aq.

Amide $C_{14}H_{14}N(CO.NH_2)$. [128°]. Plates.

Nitrile $C_{14}H_{14}N.CN$. [95°]. Plates.

PHENYL AMIDO-TOLYL KETONE

Phthalyl derivative $C_6H_5.CO.C_6HMeN:C_2O_2:C_6H_4$. [202°]. Formed, together with an isomeride [160°], by heating the phthalyl derivative of *p*-toluidine with benzoyl chloride and $ZnCl_2$ (Fröhlich, *B.* 17 2679). Dimetric crystals, v. sol. hot HOAc.

DI-PHENYL-AMIDO-*p*-TOLYL-UREA [1:3:4] $C_6H_3Me(NH_2).NH.CO.NPh_2$. [137°]. Formed by reducing the nitro- compound in alcoholic solution with $SnCl_2$ and HCl (Lellmann a. Bonhöffer, *B.* 20, 2123). Needles, solidifying at 165°–170°, and melting a second time at 220°–260°, yielding diphenylene and tolylene-urea at 300°.

PHENYLAMIDO-ISOVALERIC ACID $CHMe_2.CH(NHPh).CO_2H$. S. ·7 at 100°. Formed from bromo-isovaleric acid and aniline (Duvillier, *A. Ch.* [5] 21, 446; *C. R.* 88, 425). Scales (from hot water), v. sol. alcohol and ether.—$B'HCl$: needles, decomposing at 100°–110°.

DI-PHENYL-ω-DI-AMIDO-o-XYLENE $C_6H_4(CH_2.NHPh)_2$. [172°]. Formed by boiling o-xylylene bromide with an alcoholic solution of aniline (Leser, *B.* 17, 1825). Small colourless plates. Weak base.

PHENYLAMINE *v.* Aniline.

Diphenylamine $C_{12}H_{11}N$ *i.e.* $NHPh_2$. Mol. w. 169. [54°]. (302°) (Graebe, *A.* 238, 362). S.V. 203·4 (Lossen, *A.* 254, 72); 203·8 (Ramsay).

Formation.—1. By the dry distillation of tri-phenyl-rosaniline (Hofmann, *A.* 132, 163).—2. By heating aniline (3 mols.) with aniline hydrochloride (2 mols.) for thirty hours at 210° (De Laire, Girard, a. Chapoteaut, *Bl.* [2] 7, 360 *C. R.* 74, 811, 1254; Merz a. Weith, *B.* 5, 263; 6, 1511).—3. By distilling *u*-di-phenyl-urea or tri-phenyl-urea (Michler, *B.* 9, 715).—4. By heating phenol with aniline-zinc-chloride to 250° (Merz a. Weith, *B.* 13, 1298).—5. By heating a mixture of aniline, phenol, and $SbCl_3$ at 150°–160° (Buch, *B.* 17, 2639).

Preparation.—By heating aniline with aniline hydrochloride at 230° and treating the warm product with HClAq followed by water.

Properties.—Monoclinic plates. Forms a colourless solution in H_2SO_4, changing on warming to blue, when a trace of nitrous or nitric acid is present (test for nitrous acid in H_2SO_4: Kopp, *B.* 5, 284; Piutti, *A.* 227, 181). A solution in conc. H_2SO_4 (5 c.c.) is coloured blue by shaking with a solution (1 c.c.) containing nitric acid (test for nitric acid: Muller, *Bl.* [3] 2, 670). With PbO_2 and alcoholic HOAc it gives a bright olive-green colour (Lauth, *C. R.* 111, 975). Picryl chloride forms dark-red needles of $NHPh_2 2C_6H_2(NO_2)_3Cl$ [66°] (Herz, *B.* 23, 2540).

Reactions.—1. When passed through a *red-hot tube* it yields carbazole, aniline, benzene, and NH_3 (Graebe, *A* 174, 177).—2. $COCl_2$ forms $NPh_2.COCl$ (Michler, *B.* 8, 1664).—3. $ClCO_2Et$ forms $NPh_2.CO_2Et$ [72°].—4. *Chlorine* in presence of I yields $NH(C_6H_3Cl_2)_2$ and finally C_6Cl_6 (Knoff, *B.* 9, 1483).—5. *Bromine* and I yield tetra-, hexa-, octo-, and deca- bromo-diphenylamines (Gessner, *B.* 9, 1505).—6. Alkaline $KMnO_4$ yields oxalic acid, a resin, and a substance $C_{18}H_{14}N_2$, crystallising in yellow needles [176°–180°], which yields quinone on oxidation by MnO_2 and conc. HNO_3, may be reduced to *p*-phenylene-di-phenyl-diamine [135°], and yields a (hexa?)-bromo-

derivative [243°] (Bandrowski, *M.* 7, 375; 8, 475; 9, 418).—7. Yields acridine on warming with $AlCl_3$ and chloroform. HOAc and $ZnCl_2$ give methyl-acridine, and other acids act in like manner.—8. PCl_3 and $ZnCl_2$ at 250° yield $C_{12}H_{10}NPO$, a white powder (Michaelis, *B.* 21, 1504; *A.* 260, 39).—9. *Acroleïn* in alcoholic solution forms $(C_{12}H_{10}N)_2C_3H_4$, an amorphous powder, sol. chloroform, capable of combining with Br (Leeds, *B.* 15, 1158; *A. C. J.* 4, 32).—10. Heated with oxalic acid it gives diphenylamine blue.—11. Heated with sulphur it gives imido-di-phenyl sulphide.—12. HNO_3 forms a hexa-nitro- derivative which decomposes carbonates.

Salts.—B'HCl: needles (from alcohol), decomposed by water.—$B'H_2SO_4$. [125°]. Insol. ether and benzene, decomposed by water.—Benzene sulphonate. [117°].—Toluene *p*-sulphonate. [64°] (Norton, *Am.* 10, 129, 140).

Formyl derivative $C_{13}H_{11}NO$ *i.e.* $NPh_2.CHO$. [74°]. Formed by heating diphenylamine with oxalic or formic acid (Willm a. Girard, *B.* 8, 1195). Insol. water, sol. benzene and alcohol. Yields acridine on heating with $ZnCl_2$.

Acetyl derivative NPh_2Ac. [103°]. Plates (from ligroïn), sol. hot water. Yields NPh_2Bz on heating with BzCl (Pictet, *B.* 23, 3013). PCl_5 followed by water forms an acid $C_{14}H_{15}ClNPO_3$ aq and an oil converted by alcoholic NH_3 into $C_{28}H_{30}N_4O$ [186°] (Claus, *B.* 14, 2367).

Thio-acetyl derivative $NPh_2.CS.CH_3$. [111°]. Formed by heating *u*-di-phenyl-acet-amidine with CS_2 at 100° (B.). Tables, sl. sol. water, v. e. sol. ether.

Benzoyl derivative NPh_2Bz. [177°]. Formed from diphenylamine and BzCl (Hofmann, *A.* 132, 166; Bernthsen, *A.* 192, 13; 224, 12; Wallach, *A.* 214, 235), and also by the action of $Ph_2N.COCl$ on benzene in presence of $AlCl_3$ (Lellmann a. Bonhöffer, *B.* 19, 3231). Trimetric needles; $a:b:c = \cdot950:1:\cdot324$. Sl. sol. ether and water, m. sol. hot alcohol.

p-Toluyl derivative. [155°].

Di-methyl-benzoyl derivative [4:3:1] $C_6H_3Me_2CONPh_2$. [136°]. Formed from *o*-xylene, $NPh_2.COCl$, and $AlCl_3$ (Lellmann, *B.* 20, 2119).

Nitrosamine $NPh_2.NO$. [66·5°]. Yellow four-sided tables (from benzene-alcohol) (Witt, *B.* 8, 855; Fischer, *A.* 190, 174). Yields azophenine when heated with aniline and aniline hydrochloride at 120°. Its hydrochloride heated with *p*-bromo-aniline at 80° yields tetra-bromo-azophenine $C_{36}H_{25}Br_4N_5$ [243°] (Ikuta, *A.* 243, 285). On heating with aniline it yields $PhN_2C_6H_4NH_2$, $PhN_2.NHPh$, and diphenylamine. By heating with alcoholic HCl it is converted into nitroso-diphenylamine.

Tri-phenyl-amine $C_{18}H_{15}N$ *i.e.* NPh_3. Mol. w. 245. [127°]. Formed by dissolving K or Na in aniline or diphenylamine and digesting the product with bromo-benzene (Merz a. Weith, *B.* 6, 1514; Heydrich, *B.* 18, 2156). Monoclinic crystals (from ether), $a:b:c = \cdot991:1:\cdot412$; $\beta = 88° 38'$. Sl. sol. hot alcohol, m. sol. benzene. Does not form salts. AcCl at 100° gives a greenish substance. Cold conc. H_2SO_4 gives a violet colour, changing to blue. Benzotrichloride and $ZnCl_2$ give a green colouring matter on heating. A solution in HOAc is coloured green by a little HNO_3. Chlorine and I yield $N(C_6Cl_5)_3$, and finally C_6Cl_6 (Ruoff, *B.* 9, 1483).

Isomeride of triphenylamine. $C_{18}H_{15}N$. Got by distilling the compound of cinnamic aldehyde with $(NH_4)HSO_3$ (Gössmann, *A.* 100, 57). Liquid, volatile in a current of H at 140°–150°, sl. sol. water, v. sol. alcohol and ether. Forms unstable salts, decomposed by water and alcohol. EtI yields B'EtI, whence moist Ag_2O yields oily B'EtOH, while platinic chloride forms $B'_2Et_2PtCl_6$.—$B'_2H_2PtCl_6$: monometric crystals.—B'_2PtCl_4.

References. — AMIDO-, DIBROMO-, BROMO-DI-NITRO-, CHLORO-, CHLORO-NITRO-, NITRO-, and OXY-, DIPHENYLAMINE.

DIPHENYLAMINE SULPHONIC ACID $C_{12}H_{11}NSO_3$ *i.e.* $NHPh.C_6H_4.SO_3H$. [200°]. Formed, together with the disulphonic acid, by heating diphenylamine with H_2SO_4 at 160° (Merz a. Weith, *B.* 5, 283; 6, 1512). Formed also by heating $NPh_2HSO_4H_2$ at 190° for 2 hours (Vignon, *C. R.* 107, 263). Crystalline mass, becoming blue in air.—KA': plates.—BaA'_2: plates, sl. sol. water.—PbA'_2: nodules, sl. sol. water.

Diphenylamine disulphonic acid $NH(C_6H_4SO_3H)_2$.—$BaA'_2$2aq: nodules, v. e. sol. water. Hydrolysed by HClAq at 200° (Girard, *Bl.* [2] 23, 2).

Diphenylamine disulphonic acid $C_6H_3(NHPh)(SO_3H)_2$[1:2:4]. Formed from bromo-benzene disulphonic acid and aniline in glycerin (Fischer, *B.* 24, 3807). V. e. sol. Aq.—BaA″3aq.

Anilide $C_6H_3(NHPh)(SO_2NHPh)_2$. [222°]. Yellowish crystals, insol. water.

Triphenylamine trisulphonic acid $N(C_6H_4.SO_3H)_3$. Formed by adding powdered triphenylamine to fuming H_2SO_4 at 60° (Herz, *B.* 23, 2541).—Na_3A''': crystalline powder (from 95 p.c. alcohol), v. e. sol. water, insol. alcohol.

PHENYL-AMMELINE *v. Cyanuric acid* in the article CYANIC ACID.

PHENYL-AMYL-AMINE *v.* AMYL-ANILINE.

Di-phenyl-isoamyl-amine $NPh_2C_5H_{11}$. (330°–340°). Formed from diphenylamine, amyl alcohol, and HCl (Girard, *Bl.* [2] 23, 2). Gives a blue colouring matter when heated with oxalic acid and H_2SO_4.

DIPHENYL-DI-ISOAMYL-TETRAZINE $NPh(C_5H_{11}).N_2.NPh(C_5H_{11})$. [86·5°]. Formed from phenyl-isoamyl-hydrazine in ether and HgO (Michaelis a. Philips, *A.* 252, 286). Yellowish crystals.

PHENYL-AMYLENE CHPh:CHPr. (210°–215°). Formed by passing bromine-vapour into amyl-benzene at 150° and distilling the product (Schramm, *A.* 218, 392). Yields a dibromide [54°].

Phenyl-isoamylene CHPh:CHPr. (201°) at 737 mm. S.G. $\frac{16}{}$ ·878. Made in like manner from isomyl-benzene (S.). Yields a dibromide [129°].

Phenyl-amylene $CHPhEt.CH:CH_2$. (173°). S.G. $\frac{23}{}$ ·816. Formed by boiling $CHPhEt.C_2H_4Br$ with water or alcoholic potash (Dafert, *M.* 4, 621). Liquid, readily converted into the polymeride $C_{22}H_{28}$, (208°–212°), S.G. $\frac{23}{}$ ·960; V.D. 10·2 (calc. 10·1).

DI-PHENYL-AMYLENE DIKETONE $(C_6H_5.CO.CH_2.CH_2)_2CH_2$. *aω-Di-benzoyl-pentane.* [68°]. Formed by the action of boiling KOH in

MeOH on $CH_2Bz.CH_2.CH_2.CH_2.CHBz.CO_2Et$, which is got from sodium benzoyl-acetic ether and phenyl bromo-butyl ketone (Kipping a. W. H. Perkin, jun., *C. J.* 55, 349). Long colourless needles, insol. water, m. sol. cold alcohol.

Di-oxim. [176°]. Small needles.

PHENYL-ISOAMYL-HYDRAZINE $NPh(C_5H_{11}).NH_2$. (260°). Formed from isoamyl bromide and sodium phenyl-hydrazine in benzene (Michaelis a. Philips, *A.* 252, 284). Reduces warm Fehling's solution. Ac_2O yields $NPh(C_5H_{11}).NHAc$ [125°] crystallising in scales.

DI-PHENYL-AMYLIDENE DISULPHONE $CEt_2(SO_2Ph)_2$. [131°]. Formed from NaOH, $CH_2(SO_2Ph)_2$, and EtI (Fromm, *A.* 253, 163). Crystalline, v. sl. sol. hot alcohol.

PHENYL AMYL KETONE $C_6H_5.CO.CHEt_2$. (230°) at 710 mm. Formed by boiling di-ethyl-benzoyl-acetic acid with dilute alcoholic potash (Baeyer a. Perkin, jun., *B.* 16, 2131; *C. J.* 45, 185). Thick oil.

Phenyl amyl ketone $C_6H_5.CO.CH_2Pr$. (240°) at 720 mm. Formed by heating isobutyl-benzoyl-acetic ether with dilute alcoholic potash (W. H. Perkin, jun., a. Calman, *C. J.* 49, 166). Oil, with aromatic odour.

PHENYL AMYL KETONE CARBOXYLIC ACID $C_6H_5.CO.CH_2.CH_2.CH_2.CH_2.CH_2.CO_2H$. [82°]. Formed by boiling the compound $CH_2Bz.CH_2.CH_2.CH_2.CHBz.CO_2Et$ with KOH in MeOH (Perkin a. Kipping, *C. J.* 55, 350). Plates (from light petroleum), or needles (from water). Yields an oxim [75°]. AgA′: amorphous pp.

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PHENYL ISOAMYL OXIDE $C_6H_5.O.C_5H_{11}$. (225°). Got from phenol (Cahours, *A.* 78, 227).

DI-PHENYL-ISOAMYL-PHOSPHINE OXIDE $P(C_6H_5)_2(C_5H_{11})O$. [97°]. Formed from $PPh_3C_5H_{11}I$ and Ag_2O (Michaelis a. Soden, *A.* 229, 317). Needles, sol. water and ether.

DI-PHENYL-ISOAMYL-THIO-SEMICARBAZIDE $C_5H_{11}.NPh.NH.CS.NHPh$. [160°]. Formed from phenyl-isoamyl-hydrazine and phenyl thiocarbimide (Michaelis a. Philips, *A.* 252, 285). Yellow needles.

PHENYL-AMYL-THIO-UREA $C_{12}H_{18}N_2S$ *i.e.* $NHPh.CO.NH.CH_2.CMe_3$. [136°]. Formed from the corresponding amylamine and phenyl-thiocarbimide (Freund a. Lenze, *B.* 23, 2868).

PHENYL-AMYL-UREA $C_{12}H_{18}N_2O$ *i.e.* $NHPh.CO.NH.CH_2CMe_3$. [155°]. Formed from phenyl cyanate and the corresponding amylamine in alcoholic solution (Freund a. Lenze, *B.* 23, 2867; 24, 2158). White needles.

PHENYL-ANGELIC ACID $C_{11}H_{12}O_2$ *i.e.* $CHPh:CHEt.CO_2H$. Mol. w. 176. [104°]. Formed by heating benzoic aldehyde with sodium butyrate and Ac_2O at 100° (Perkin, *C. J.* 31, 391; 32, 661; 35, 136; Slocum, *A.* 227, 53). Formed also by heating benzoic aldehyde with butyryl chloride at 125° (Fittig, *A.* 153, 364). Needles, v. sol. ligroïn (unlike cinnamic acid). Melts at 81° after having been fused.—BaA'_2: needles, m. sol. hot water.—CaA'_2.—AgA′: white pp.

Chloride $C_{10}H_{11}.COCl$. Oil.

Amide $C_{10}H_{11}.CONH_2$. [128°].

Phenyl-angelic acid $CHPh:CH.CH_2.CH_2.CO_2H$. Formed from $CHPh:CH.CH:CH.CO_2H$ by reduction with sodium-amalgam (Perkin; Baeyer a. Jackson, *B.* 13, 122). Liquid.—AgA′: white pp.

Phenyl-angelic acid $CHPh:CH.CHMe.CO_2H$. [110.5°]. Formed by boiling the dibasic acid $CHPhBr.CH(CO_2H).CHMe.CO_2H$ with water (Penfield, *A.* 216, 123), and by distilling $CHPh<\begin{smallmatrix}CH(CO_2H)\\O——CO\end{smallmatrix}>CHMe$ (Fittig a. Liebmann, *A.* 255, 262). Plates (from water).—BaA'_2 aq: needles, v. sol. water.

Phenyl-angelic acid $CHPh:CMe.CH_2.CO_2H$. [113°]. Formed by distilling the lactonic acid $CHPh<\begin{smallmatrix}CMe(CO_2H)\\O——CO\end{smallmatrix}>CH_2$ (F. a. L.). Thin tables, sl. sol. water.—BaA'_2: groups of needles, sol. water.

Phenyl-angelic acid. *Nitrile* $C_3H_5.CHPh.CN$. (c. 265°). Formed by heating phenyl-acetonitrile with NaOH and allyl iodide (Buddeberg, *B.* 23, 2068). Oil, converted by NaOEt and benzyl chloride into the benzyl derivative $C_3H_5.CPh(CH_2Ph).CN$ (c. 325°).

PHENYL-ANTHRACENE $C_{20}H_{14}$ *i.e.* $C_{14}H_9Ph$. [153°]. (417°). Formed by heating phenyl-anthranol with zinc-dust (Baeyer, *A.* 202, 61), and by the action of chloroform and $AlCl_3$ on benzene (Friedel, Crafts, a. Vincent, *Bl.* [2] 40, 97; *A. Ch.* [6] 1, 495). Leaflets (from alcohol), forming solutions with blue fluorescence. Reduced by P and HI to a crystalline *dihydride* [120°], which is oxidised by CrO_3 in HOAc to phenyl-oxanthranol.

PHENYL-ANTHRANOL $C_{20}H_{14}O$ *i.e.* $C_6H_4<\begin{smallmatrix}CPh\\C(OH)\end{smallmatrix}>C_6H_4$. [141°–144°]. Formed by dissolving tri-phenyl-methane *o*-carboxylic acid in H_2SO_4 and ppg. with water (Baeyer, *A.* 202, 57). Golden needles, sol. hot alcohol. Its ethereal solution shows greenish-yellow fluorescence.

Acetyl derivative. [166°]. Golden needles, turned red by conc. KOHAq.

Reference.—DI-CHLORO-PHENYL-ANTHRANOL.

PHENYL-ARSINE *v.* vol. i. p. 319. The sulphides PhAsS [152°] and $Ph_2As_2S_3$ [130°] have been prepared by Schulte (*B.* 15, 1956).

PHENYL-AZIMIDO-COMPOUNDS *v.* AZIMIDO-COMPOUNDS.

DI-PHENYL-TETRAZINE $C_{14}H_{12}N_4$ *i.e.* $NPh<\begin{smallmatrix}N:CH\\CH:N\end{smallmatrix}>NPh$. [180°]. Mol. w. 240 by Raoult's method (calc. 236). Formed by the action of chloroform and alcoholic potash on phenyl hydrazine (Ruhemann, *C. J.* 53, 850; 55, 243). White needles (from alcohol). HNO_3 yields $C_{14}H_{11}(NO_2)N_4$ [above 300°]. H_2SO_4 forms $C_{14}H_{11}(SO_3H)N_4$. Bromine gives $C_{14}H_{11}BrN_4$ [220°], $C_{14}H_{10}Br_2N_4$ [131°], and $C_{14}H_9Br_3N_4$, decomposing at 224°.

Salts.—B′HCl: needles.—$B'_2H_2PtCl_6$.—B′MeCl. [244°]. Needles.—$B'_2Me_2PtCl_6$.—B′MeI. [214°]. Yellow needles, v. sol. alcohol.

PHENYL-AZO-COMPOUNDS *v.* AZO-COMPOUNDS.

PHENYL-TETRAZOLE $CPhHN_4$ *i.e.* $N<\begin{smallmatrix}N.NPh\\N:CH\end{smallmatrix}$. Formed by heating its carboxylic acid [138°] at 155° (Bladin, *B.* 18, 2907). Heavy oil, v. sol. alcohol and ether. Explodes when strongly heated. Sol. acids, but reppd. on dilution.

PHENYL-TRIAZOLE CARBOXYLIC ACID $CH<\begin{smallmatrix}N.NPh\\N:C.CO_2H\end{smallmatrix}$. [184°]. Formed by boiling

phenyl-hydrazine dicyanide $NH_2NPh.CCy:NH$ with formic acid and heating the resulting formyl- derivative with alcoholic potash (Bladin, *B.* 23, 3788). Silvery plates (from water).

Methyl ether MeA′. [118°]. Prisms.

Phenyl-triazole dicarboxylic acid

$CO_2H.C{<}^{N.NPh}_{N:C.CO_2H}$. Formed by oxidising phenyl-methyl-triazole carboxylic acid with alkaline $KMnO_4$ (Bladin, *B.* 23, 3785). The free acid is unstable, readily changing to the preceding acid. The acid K and Na salts also readily give off CO_2.—CuA″ 4aq: blue needles.—Ag_2A'' ½aq? Bulky white pp.

Methyl ether Me_2A''. [167°]. Needles.

Ethyl ether Et_2A''. [82°]. Needles.

Di-phenyl-triazole carboxylic acid

$CPh{<}^{N.NPh}_{N:C.CO_2H}$. Formed by saponification of the nitrile (Bladin, *B.* 22, 797). Crystals (containing EtOH), decomposing at 172°–182°. V. sol. alcohol, m. sol. ether.—CuA'_2.—AgA′: white pp.

Methyl ether MeA′. [159°]. Needles.

Ethyl ether EtA′. [165°]. Needles.

Nitrile $C_2N_3Ph_2.CN$. [156·5°]. Formed from phenyl-hydrazine dicyanide, alcohol, and benzoic aldehyde. Needles, v. sol. benzene.

Amide $C_2N_3Ph_2.CO.NH_2$. [196°]. Formed from the nitrile by the action of dilute (3 p.c.) H_2O_2 and KOHAq. Plates (from alcohol) or needles (from water).

Amidoxim $C_2N_3Ph_2.C(NOH).NH_2$. [214°]. Formed from the nitrile and hydroxylamine (Bladin, *B.* 22, 1752). Prisms (from alcohol). Yields an acetyl derivative [177°] which yields $C_2N_3Ph_2C{<}^{N.O}_{N}{>}CMe$ [153°], and a benzoyl derivative [180°] which yields in like manner $C_2H_3Ph_2.C{<}^{N.O}_{N}{>}CPh$ [206°].—B′HCl: crystalline.

PHENYL-TETRAZOLE CARBOXYLIC ACID

$N{<}^{N.NPh}_{N:C.CO_2H}$. [138°]. Got by saponification of its nitrile, which is formed by the action of nitrous acid on phenyl-hydrazine dicyanide (Bladin, *B.* 18, 2907). Colourless needles, v. sol. alcohol.—KA′: plates, v. sol. water.—CuA'_2 2aq.—AgA′: colourless crystalline pp.

Methyl ether MeA′. [116°]. Plates.

Ethyl ether EtA′. [74°]. Needles.

Amide $CN_4Ph.CO.NH_2$. [168°]. Formed from the nitrile by treatment with hydrogen peroxide. Crystals, sl. sol. cold water.

Amidoxim $CN_4Ph.C(NOH).NH_2$. [177°]. Formed from the nitrile and hydroxylamine (Bladin, *B.* 22, 1755). Scales, v. sl. sol. water. Yields an acetyl derivative [203°] and a benzoyl derivative [206°], both crystallising in needles.

END OF THE THIRD VOLUME.

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